DYNAMIC SIMULATIONS OF MOLTEN-CARBONATE FUEL-CELL SYSTEMS
DYNAMIC SIMULATIONS OF MOLTEN-CARBONATE FUEL-CELL SYSTEMS

PROEFSCHRIFT

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SUMMARY

A molten-carbonate fuel cell (MCFC) power-generation system provides a new and promising option for the efficient conversion of fossil fuels into electricity. The two crucial components used in an MCFC system, the fuel-cell stack and the reformer, are new apparatus for power-generation systems. Moreover, to achieve high system efficiency, an MCFC system integrates the fuel-cell stacks and the reformer by recycling loops, which may cause dynamic interactions between them.

In order to introduce the fuel-cell stack and reformer into power-generation systems, first their operating characteristics with regard to load-following modes must be identified, and then the complete system must be investigated. The crucial obstacles to the operation of MCFC systems are formulated by four main questions. This thesis puts emphasis on answering these four questions, which form guidelines throughout the thesis:

i. What are the power-generation characteristics of a fuel-cell stack? Does a fuel-cell stack operate within its safety constraints?

ii. Can the reformer provide gases which satisfy the requirements of the fuel-cell stack (i.e. flow rate, concentration, temperature, and pressure)?

iii. What are the power-generation characteristics of a complete MCFC system?

iv. What are the dynamic interactions between the reformer and the fuel-cell stacks?

To answer these questions, this thesis examines four major aspects:

- System design
- Fuel-cell stack models
- Reformer model
- System model

System design
The system design part of this thesis defines the framework within which the four main questions have to be answered. The major results of the system design are as follows:

- The state-of-the-art 1 MW MCFC system is selected and adapted to the Dutch situation (e.g. different input fuel gas and equipment type).
- The qualitative analysis shows that the system is suitable for practical application and meets major safety and efficient operation criteria.
- The quantitative analysis of the system is implemented by using the program CYCLE-TEMPO developed at the author’s laboratory. The system at full load has a net electric efficiency of 45.8%.
- The geometry and physical properties of the fuel-cell stack, reformer, and heat exchangers are computed in order to establish their dynamic models.

Fuel-cell stack models
Two types of fuel-cell stack models have been developed. A three-dimensional (3D) dynamic stack model attempts to answer the first main question and a lumped stack model has been developed for integration into the system model.
The 3D-stack model presents the internal behavior of the stack. It includes all the processes that contribute to the stack power-generation behavior with regard to load-following modes. More precisely, it describes:

- The gas transport, chemical reactions, and heat transfer at cell level
- The heat and gas transport at stack level
- The current and heat generations due to the electrochemical reactions at the electrodes

The 3D-stack model has been implemented by using a computational-fluid-dynamics (CFD) program PHOENICS. The 3D-stack model has two advantages over most dynamic stack models in lumped form presented in the literature:

- **Improvement in predicting power-generation behavior.** The 3D-stack model predicts the current density distribution from the temperature and gas concentration distributions. The 3D stack simulation results show the two dimensional distributions of the current density in each cell (cross-flow). A calculated case shows that the variations in the current density reach around 1000 A/m² in a cell reaction area of 1 m². It is difficult for a stack model in lumped or one-dimensional form to adequately represent such current output characteristics, which are crucial for an accurate power-output prediction.

- **New functions identifying stack safety operation.** The 3D-stack model has new functions indicating whether operating limits are violated for a certain power generation. For example, in order to identify safe stack operation, the 3D-stack model provides the temperature distributions that cannot be obtained from a stack model in lumped form.

The performance of the 3D-stack model has been evaluated under steady-state conditions. The predicted temperature profiles from the model presented agree qualitatively with the simulated profiles given in the literature. Furthermore, the variations between the isothermal lines computed with the proposed model and most of the measured data given in the literature are less than 10 K (i.e. less than 2%).

To answer the first main question, the fuel-cell stack power-generation characteristics and the safe stack operation are demonstrated:

- The dynamic behavior of the stack was illustrated by the simulated responses of the current density and temperature to a +10% voltage-change step. The response of the stack output power consists of: i) an immediate response due to the electrode power-generation behavior, ii) a fast response (time order of 0.1 to 1 second) due to the gas concentration variation (gas transport), and iii) a slow response (time order of 10 to 10² seconds) due to temperature variation (heat storage).

- The simulation results of the 1 MW stack have shown that the temperature distribution under transient conditions is within the safety constraints (i.e. a maximum temperature lower than 750°C and a maximum temperature gradient smaller than 10 K/min).

The 3D-stack simulation results are used in developing the lumped stack model for integration into the system. This study explored two different approaches to achieve the lumped stack model:

- Represent the response characteristics of the 3D-stack model by using simple approximation equations.
- Establish a stack model by using lumped parameters based on physical laws, and then remedy the accuracy loss by using the results from the 3D-stack model.
In the first approach, a methodology used for simplifying the 3D-SOFC stack model from the literature is adapted to simplify the 3D-MCFC stack model. The second approach reflects the physical nature of the main processes and fits the 3D-simulation results. The stack model from the second approach is integrated into the system model.

In the first approach, a methodology used for simplifying the 3D-SOFC stack model from the literature is adapted to simplify the 3D-MCFC stack model. The second approach uses a combination of modeling based on physical laws and identifying model parameters based on 3D-simulation results. It reflects the physical nature of the main processes and uses the results of 3D-simulations for improvement. The stack model from the second approach is integrated into the system model.

Reformer model
The reformer apparatus is adapted from the processing plants. First, the reformer operation in a power-generation system is essentially different from that in processing plants, where continuous full-load operation is the rule. The reformer in a fuel-cell system is required to operate in such a manner that the production of the gases entering to the fuel-cell stack always follows the changes in the power demand. Secondly, the heat exchange reformer (HER) from Haldor Topsoe is used. The HER-operation is different from the operation of a conventional reformer. The conventional reformer uses one catalyst bed with an inter-connected or separated burner. In the HER, the process-gas conversion is carried out in two catalyst beds at two different temperatures. Therefore, in the development of the reformer model much attention has been paid to two aspects: i) the HER capability with regard to load-following operation modes, and ii) the representation of the HER working principle.

To answer the second main question, the reformer operating characteristics are demonstrated by the following cases:
- In the stationary case, the processed gas from the reformer has a temperature of 607°C, a pressure of 3.2 bar, and a concentration of H\textsubscript{2} of 47%. Hence, the processed gas suits the feeding gas requirement to the fuel-cell anode. The flue-gas from the reformer has a temperature of 633°C, a pressure of 3.3 bar, and a substantial amount of CO\textsubscript{2} of 40%. The flue-gas will be cooled down to about 550°C after the air heater, and it also suits the feeding gas requirement to the fuel-cell cathode.
- Four cases show the reformer responses to a frequently occurring load-following mode and three disturbances respectively. Manipulation of the input process gas is effective in controlling the feeding gas to the fuel-cell anode, though it leads to two side effects: fluctuations of the hydrogen concentration and temperature. The reformer shows a low sensitivity to disturbances of the input-gas temperature to the burner and the ratio of steam/natural gas, but a high sensitivity to the process operating pressure.

System model
The system model is obtained by integrating the fuel-cell stack model, reformer model, and the other component models constituting parts of the system. The system model has been implemented in a recent dynamic simulation program SPEEDUP. The system model comprises a connected network of operational units, which emulates the system flow diagram. Each operational unit refers to one type of component model and is individually parameterized with design and operating data. The system model has been evaluated by the 100 kW test data given in the literature. The simulated utilization of H\textsubscript{2} at the fuel-cell anode and CO\textsubscript{2} at the cathode under
load-ramp change is qualitatively consistent with the H₂ and CO₂ profiles derived from the literature.

To answer the third main question, the system power-generation characteristics are simulated. The results are:

- **System efficiency.** The system electric efficiency of the system is in a range of 40 - 50% throughout the load range. The system reaches its highest efficiency at partial load instead of at full load. This is caused by the fact that the fuel-cell stack has a higher efficiency at a lower power output, but most other components in the system still have lower efficiency at a lower power output.

- **System load-following capability with regard to current change.** The manipulation of the current results in a fast change in the power output, but a large voltage drop. For a +5% step current change, the power output increases 2.5% within a time order of 10 seconds, but the voltage drops 23 V (3.3%) at high fuel utilization (80%). The manipulation of the current is more effective at low gas utilization. For the same +5% step current change, the power output increases 4% within a time order of 10 seconds with a voltage drop of 14 V (1.8%) at low fuel utilization (40%).

- **System load-following capability with regard to both current and fuel changes.** With both +5% step current and fuel changes, the output power increases 4.2%. The side effect of the voltage drop (4 V) is much smaller than the 23 V or 14 V that occurred in the above cases with the single current manipulation.

To answer the fourth main question, the interactions between the fuel-cell stacks and reformer are predicted. The results are:

- **Excessive hydrogen utilization in the stack under load-up mode.** High current output in the fuel-cell stack causes high fuel utilization, which results in low hydrogen concentration at the stack outlet. The lower hydrogen concentration causes less combustion heat to be released in the reformer. This reduces the effectiveness of the reforming processes and results in even higher gas utilization in the fuel-cell stack. During a load-up operation (a +5% step change in both fuel input and current output), the H₂ utilization in the stack increases from about 80% to 87.5%, and then falls back to 80% in a time order of 100 seconds. Hence, the H₂ utilization exceeds the limit of 85%.

- **High reformer-combustor temperature under load-down mode.** During a load-down operation, the fuel utilization in the stack decreases and the anode exhaust gas has higher H₂ concentration. This higher H₂ concentration results in a higher combustion temperature in the reformer burner, which increases the effectiveness of the reforming processes and results in even lower fuel utilization in the fuel-cell stack.

It has also been demonstrated that the proposed system model is useful for improving system operation and design. More specifically, the system model can be effectively used to access an alternative operation strategy to reduce the dynamic interactions, and to select a suitable location for a control valve.

In conclusion, this thesis has answered the proposed four main questions. Hence, it provides insight for introducing the fuel-cell stack and reformer into power-generation systems. The results of this study are interesting to a designer or an operator engaged in optimizing the design and operation of fuel-cell stacks and systems.
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1 INTRODUCTION

This chapter gives the motivation and background of this thesis, and formulates the thesis goals. It also presents the state-of-the-art development about the fuel-cell stack, reformer, and complete system. Finally, the thesis approach and organization are presented.

1.1 Motivation and Background

A fuel cell is an electrochemical device that converts the chemical energy of a reaction into electrical energy and heat without combustion as an intermediate step. A fuel-cell power-generation system provides a new and promising option for the efficient conversion of fossil fuels into electricity because of its high efficiency (which is not subject to the Carnot limitation imposed on heat engines) and low negative environmental impact. Besides the direct production of electricity, heat is also produced in fuel cells. Depending on the temperature, this heat can be utilized for the generation of additional electricity or for other purposes.

The low temperature phosphoric acid fuel cell (PAFC) uses mature technology. Several PAFC packages ranging from several hundred kW to several MW are already available. To date, the largest PAFC demonstration plant (11 MW) is in Japan (Yokota et al., 1992). However, the PAFC systems are at the low end of the efficiency goal (around 40-45%) for fuel-cell power plants. Moreover, the fuel has to be reformed externally to the cell, and carbon monoxide poisons the fuel-cell catalyst. These limitations have prompted the development of higher temperature cells, the molten carbonate fuel-cell (MCFC) and the solid oxide fuel cell (SOFC).

The MCFC is a second-generation fuel cell, whose entry into the power-generation market will follow that of the PAFC. An MCFC has advantages over the PAFC because of its higher electrical efficiency, the possibility of using natural gas without external reforming, and the high-grade heat generated (Selman, 1993). The MCFC also has advantages over the SOFC because of its relatively simple method of construction and sealing. There is increasing interest in developing and demonstrating MCFC technologies, and MCFC is rapidly approaching a commercialization phase (Baker and Maru, 1997).

Several MCFC demonstration plants have been set up recently. These plants include: one built in Japan, in 1993 with a capacity of 100 kW that is designed to test the operating capability of the system (Yoshida and Inoue, 1993); one in the USA in 1994 with 250 kW (Figueroa et al., 1996); one in the USA in 1997 with 2 MW (Skok et al., 1996); and one in Japan, scheduled in 1999, with 1 MW (Matsunaga et al., 1998). These projects have strengthened the belief of the
manufacturers in the MCFC, and indicate that the development of the MCFC is approaching towards commercial stage.

In the Netherlands, where the first MCFC was demonstrated by Broers and Ketelaar in the 1950s (Broers, 1958), two MCFC demonstration projects on the scale of 250 kW were scheduled for 1996 (Joon and Vaal, 1994). In order to realize these two demonstration projects, many MCFC activities were initiated. These activities can be classified into five main categories: (i) fundamental electrochemistry research; (ii) material development; (iii) stack technology; (iv) system analysis; and (v) commercialization. The research related to this thesis belongs to the category of the system analysis. Though the 250 kW demonstration projects have suffered from a delay and have been changed (Kortbeek and Machielse, 1996), this study was continued to provide numerical analysis tools for designing systems for future demonstration projects.

The success of a demonstration project for a fuel-cell system strongly depends on how the obstacles related to design, production, operation and maintenance have been overcome. This thesis puts the emphasis on operations. There have been many research projects focused on the power-generation performance of fuel-cell systems under stationary conditions (Uchijama and Segawa, 1991; Van der Laag and Verbruggen, 1994; De Groot and Woudstra, 1995; and Kivisaari, 1998). Few research projects have focused on the dynamic power-generation behavior of fuel-cell systems, especially with regard to load-following operation modes.

In order to successfully introduce fuel-cell systems into the power-generation market, it is also important to identify the power-generation behavior of fuel-cell systems under load-following operation modes. Therefore, this study is designed to investigate the power-generation performance of fuel-cell systems with regard to load-following operation modes. It is also worth considering that the results of this research also provide a basis for component selection, system efficiency analysis and cost evaluation.

1.2 Formulation of Thesis Goals

This section first reviews the fuel-cell working principle and the fuel-cell power-generation characteristics, and then it discusses the operational requirements of the fuel-cell system. A comparison between fuel-cell and thermal power-generation systems is presented. Finally, the four thesis goals are formulated.

1.2.1 Operating problems of fuel-cell systems

1.2.1.1 Working principle of a fuel-cell

Electricity generation. The working principle of fuel-cell electricity generation is shown in Figure 1.1. The MCFC involves the reduction of an oxidant and the oxidation of a fuel. The oxidant gas, containing oxygen and carbon dioxide, is supplied to the cathode. There oxygen reacts with carbon dioxide forming carbonate ions. These ions are transported towards the anode where they are involved in the oxidation reaction of hydrogen. Both hydrogen and carbon monoxide act as fuels and are supplied to the anode. In the anode reaction, water and
carbon dioxide are formed. These products are removed from the cell. The carbon dioxide gas can be reused at the cathode.

By adding the cathode and anode reactions shown in Figure 1.1, it is clear that the overall fuel cell reaction is

\[ H_2 + \frac{1}{2}O_2 + CO_2 (\text{cathode}) \Rightarrow H_2O + CO_2 (\text{anode}) \]  

(\(\Delta H^{\circ}_{298} = -242 \text{ kJ/mol}, \ \Delta S^{\circ}_{298} = -44 \text{ kJ/mol K}, \text{ referring to standard state conditions})

The anode reaction produces electrons, while at the cathode electrons are consumed. The electrons pass from the fuel electrode to the oxidant electrode via an external circuit, and the electrical circuit is completed by ionized particles crossing an electrolyte. The electrochemical conversion in an MCFC generates electricity and also produces heat.

**Reversible thermodynamics.** The maximum electrical work \(W_{el}\) obtainable from a fuel cell operating at constant temperature and pressure is given by a change in the Gibbs free energy \(\Delta G\) of the electrochemical reaction.

\[ W_{el} = \Delta G = -n \times F \times E \]  

(1.2)

where \(n\) is the number of electrons participating in the reaction (for an MCFC, \(n=2\)), \(F\) is Faraday’s constant \((96439 \text{ coulombs/g-mol electron})\), and \(E\) is the reversible cell potential or open cell voltage (V).

If we consider the case of all reactants and products being in the standard state, then

\[ \Delta G^\circ = -n \times F \times E^\circ \]  

(1.3)

At the operating temperature of 650°C, the standard open cell voltage \(E^\circ\) is 1.02 V.

The reversible cell potential \((E)\) also depends on the gas composition at the fuel electrode (partial pressures of \(H_2, H_2O,\) and \(CO_2\)) and at the cathode (partial pressures of \(O_2\) and \(CO_2\)):

\[ E = E^\circ + \frac{RT}{2F} \ln\{\frac{(pH_2 \cdot pO_2)^{1/2}}{pH_2O} \frac{pCO_{2,c}}{pCO_{2,a}}\} \]  

(1.4)

where the subscripts \(a\) and \(c\) refer to the anode and cathode gases, respectively, and \(R\) is the gas constant \((8.314 \text{ J/mol.K})\). When the partial pressure of \(CO_2\) in the cathode and anode gas is
identical, the reversible potential depends only on the partial pressure of the net reactants and products.

The maximum efficiency ($\eta_{\text{max}}$) of the electrochemical conversion reads:

$$\eta_{\text{max}} = \frac{\Delta G}{\Delta H} = 1 - \frac{T \times \Delta S}{\Delta H} = -\frac{n \times F \times E}{\Delta H}$$

(1.5)

where $\Delta H$ (kJ/mol) and $\Delta S$ (kJ/mol.K) stand for the change in enthalpy and in entropy. $T$ is the cell operating temperature in Kelvin.

The minimum heat ($Q$) generated in a fuel cell is the difference between the reaction enthalpy and the Gibbs free energy. Operating at constant temperature and pressure, a fuel cell produces minimum heat as follows

$$Q = T \times \Delta S = \Delta H - \Delta G$$

(1.6)

Table 1.1 shows the maximum efficiency $\eta_{\text{max}}$ of a fuel cell in comparison with the efficiency of the reversible Carnot cycle under several operating temperatures (Makkus, 1991). The fuel cell efficiency calculated in this table is based on hydrogen as the fuel and oxygen as the oxidant. The Gibbs free energy $\Delta G$ equals $\Delta H - T \times \Delta S$ (kJ/mol) and $\Delta H$ and $\Delta S$ stand for the values of the enthalpy and entropy. The sink temperature $T_L$ is 298 K for the Carnot cycle theoretic efficiency $\eta_{\text{Carnot}}$.

### Table 1.1 Comparison between the cell efficiency and Carnot efficiency

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$-\Delta G$ (kJ/mol)</th>
<th>$-\Delta H$ (kJ/mol)</th>
<th>$\eta_{\text{max}} = \frac{\Delta G}{\Delta H}$ (%)</th>
<th>$\eta_{\text{Carnot}} = 1 - \frac{T_L}{T}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>228.6</td>
<td>241.8</td>
<td>94</td>
<td>0</td>
</tr>
<tr>
<td>400</td>
<td>223.9</td>
<td>242.8</td>
<td>92</td>
<td>26</td>
</tr>
<tr>
<td>500</td>
<td>219.1</td>
<td>243.8</td>
<td>91</td>
<td>40</td>
</tr>
<tr>
<td>1000</td>
<td>192.6</td>
<td>247.7</td>
<td>78</td>
<td>70</td>
</tr>
<tr>
<td>2000</td>
<td>135.2</td>
<td>252.1</td>
<td>54</td>
<td>85</td>
</tr>
</tbody>
</table>

Table 1.1 confirms that below 1000 K, the efficiency $\eta_{\text{max}}$ of an electrochemical conversion in a fuel-cell apparatus is higher than the efficiency of a Carnot cycle. An MCFC usually operates around 650°C. The actual efficiencies of both the electrochemical conversion and the Carnot cycle are less than $\eta_{\text{max}}$ and $\eta_{\text{Carnot}}$ due to losses.

**Irreversible thermodynamics.** Electrical energy is supplied by a fuel cell only when a reasonably large current is drawn. The cell potential, however, is always less than the equilibrium potential of the reaction because of irreversible losses. These losses are due to ohmic polarization of the electrolyte: $\Delta V_{\text{ohmic}}$, and concentration and activation polarizations at both the anode and cathode: $\Delta V_{\text{anode}}$ and $\Delta V_{\text{cathode}}$ (Hirschenhofer et al., 1994). These losses result in a working voltage of an actual fuel cell $V_{\text{cell}}$ that is less than the reversible potential $E$ of the cell reaction.

$$V_{\text{cell}} = E - |\Delta V_{\text{ohmic}}| - |\Delta V_{\text{anode}}| - |\Delta V_{\text{cathode}}|$$

(1.7)
The total value of these three voltage losses is approximately 200 mV for a typical gas utilization of 80% (Selman, 1993). The actual cell operating voltages ($V_{cell}$) are typically between 0.6 and 0.8V.

The local current density $i_{local}$ at any point in the cell can be calculated by solving the local potential balance equation

$$i_{local} = \frac{E - V_{cell} - \Delta V_{anode} - \Delta V_{cathode}}{R_{ohmic}}$$  \hspace{1cm} (1.8)

where $R_{ohmic}$ is the local ohmic impedance of the cell.

### 1.2.1.2 Fuel-cell power-generation characteristics

The power-generation performance of a single fuel cell or a fuel-cell stack is characterized by its voltage and current behavior for specified conditions. These conditions include the temperature, pressure and the inlet compositions of the fuel and oxidant gases, and the utilization of the fuel gas and the oxidant gas. In addition, a fuel cell must operate within the safety constraints specified by the manufactures (e.g. maximum temperature and temperature gradient, pressure difference between anode gas and cathode gas, and gas utilization).

The actual cell voltage must be the same everywhere, since the separator plate is, by design, a good ohmic conductor. However, the local current density changes significantly across the thin electrode-electrolyte-electrode package. According to Eq. 1.8, the local current density depends on the thermodynamic driving forces, i.e., the reversible cell voltage $E$ and the local “resistance” (ohmic impedance $R_{ohmic}$ and polarization at anode and cathode: $\Delta V_{anode}$ and $\Delta V_{cathode}$). The driving force, i.e., the reversible cell voltage $E$, is different from point to point in the cell due to the increasing utilization of fuel gas and oxidant as both flow from inlet to exit.

The fuel utilization ($U_f$) refers to the fraction of the fuel gas that reacts electrochemically in the fuel cell. Since an MCFC is capable of utilizing H$_2$ and CO as fuel, H$_2$ and CO are both present in the definition of the fuel utilization.

$$U_f = \frac{N_{H_2, in} + N_{CO, in} - N_{H_2, out} - N_{CO, out}}{N_{H_2, in} + N_{CO, in}}$$ \hspace{1cm} (1.9)

where $N_{H_2, in}$, $N_{CO, in}$ and $N_{H_2, out}$, $N_{CO, out}$ are the molar fluxes of H$_2$ and CO at the inlet and outlet of the fuel cell, respectively.

The local current density is related to the change in the reactant flow rate, e.g. for hydrogen,

$$i_{local} = -n \times F \times \left( \frac{dN_{H_2}}{dx} \right) \times h_a$$ \hspace{1cm} (1.10)

where $N_{H_2}$ is the hydrogen molar gas flux, and $x$ is the cell length axial and $h_a$ is the height of the fuel gas channel (Selman, 1993).

The total DC (direct current) power output from a cell $P_{cell}$ is

$$P_{cell} = V_{cell} \times \int_{reaction-area} i_{local} \, dx \, dz$$ \hspace{1cm} (1.11)

where $x$ and $z$ are the cell length and width.
The magnitude of the AC (alternative current) output power also depends on the power factor. In this study the power factor is assumed to be 1. The AC power factor of an MFC system is expected to have similar value as that of a PAFC system. The AC power factors of PAFC systems change from 0.85 lagging to 0.95 leading, while the power output varies from 25 to 100% (Bowers et al. 1997).

When the gas utilization is significant, the cell performance depends strongly on the gas flow configuration. The operating temperature also plays an important role, since the reversible cell voltage and voltage losses are closely related to it. In order to quantify the polarizations at the anode and cathode, Yuh and Selman (1991) report

\[ \Delta V_{\text{anode}} = i_{\text{local}} \times 2.27 \times 10^{-5} (P_{H_2})^{-0.42} (P_{CO})^{-0.17} (P_{H,O})^{-0.1} \exp\left(\frac{53,500}{RT}\right) \]  \hspace{1cm} (1.12)

\[ \Delta V_{\text{cathode}} = i_{\text{local}} \times e^{-11.8} (P_{O_2})^{-0.43} (P_{CO})^{-0.09} \exp\left(\frac{77,300}{RT}\right) \]  \hspace{1cm} (1.13)

The use of a high operating temperature reduces the total voltage losses, because (i) the activation polarization is lower due to the larger activation energy of electrode kinetic reactions, (ii) the concentration polarization is lower due to the faster transport processes, and (iii) the Ohmic resistance is lower. Accordingly, the local current increases at a higher temperature. The local heat generation increases more than linearly with the current density, since the irreversible heat generation is proportional to the square of the current density (Ohmic law). Therefore, if heat is not conducted or convected away from a high current density area, the current density will be amplified, leading to a "hot spot".

In order to achieve a high power output for practical applications, a large number of cells are often connected in series (to achieve a high voltage) to form a stack. The additional problems related to a stack operation are the gas distribution among its cells and the heat transfer in the stack direction. The stack output voltage \( V_{\text{stack}} \) is the sum of each cell voltage \( V_{\text{cell}} \) (k). Considering the cells in stack are connected electrically in series, the same current must flow through each cell. The stack output current \( I_{\text{stack}} \) is the same at each cell \( I_{\text{cell}} \) (k). That is:

\[ V_{\text{stack}} = \sum_{k=1}^{N} V_{\text{cell}}(k) \]  \hspace{1cm} (1.14)

\[ I_{\text{stack}} = I_{\text{cell}}(k) \{ k = 1, 2, ..., N \} \]  \hspace{1cm} (1.15)

where \( N \) is the total cell number, \( k \) is cell number.

1.2.1.3 Operational requirements of fuel-cell power-generation systems

System integration is the key to the successful introduction of a high-efficiency fuel-cell apparatus into practical application. In order to use available natural resources (e.g. natural gas) and to satisfy the load demand of the consumer, as well as to achieve a high efficiency, a fuel-cell system requires chemical, thermal and electrical integration. Accordingly, a fuel-cell system often consists of the following four major sub-systems and is shown in Figure 1.2:

- Fuel processing (converting accessible fuel to appropriate inputs for fuel cell)
- Fuel-cell power-generation (producing DC power and heat)
- Power conversion (converting electricity from DC to required AC power)
- Heat recovery (utilizing the heat from fuel cell)
Figure 1.2 Working principle of an MCFC system using natural gas

The explanations of these four sub-systems are as follows:

- In the fuel processing sub-system, the reformer is the key component which converts the hydrocarbon in natural gas into the fuel gas with a high hydrogen and carbon monoxide concentration by using the steam-reforming reaction. Since the reforming process is strongly endothermic, a heat supply is required. This heat is provided by the combustion of the anode off-gas with air. The flue-gas resulting from the combustion reactions in the reformer with a significant carbon dioxide concentration is fed to the fuel-cell cathode.

- A fuel-cell stack is the key component in the fuel-cell power-generation subsystem. The gases from the fuel processing subsystem react electrochemically at the anode and cathode electrodes of the fuel-cell stack, which generates direct current (DC) power and heat.

- The power conversion subsystem consists of electronic devices and it converts the DC power from the fuel-cell stack into the required DC or AC power.

- In order to improve the overall system efficiency in the heat recovery subsystem, the high-temperature anode- and cathode-off gases are used to generate power and to heat the gas streams of the fuel processing and fuel-cell power-generation subsystems. The heat recovery subsystem usually consists of the components from conventional power-generation systems.

A fuel-cell system operates in isolated or interconnected operating modes. When a fuel-cell system is not connected to a power system and it feeds electricity directly to a load, the requirements are more or less directly imposed by the load. When a fuel-cell system is connected to an existing power system, the requirements evidently are imposed by the power system.

The major operational requirements for the power output from an MCFC system are that: (i) the system output power is equal to the demand of the consumer; (ii) the system output power rapidly and smoothly follows the consumer demand. With regard to these requirements, the operating characteristics of systems in load-following modes should be studied.

The system power output can be controlled by the fuel-cell current output or fuel and air inputs. In order to accommodate fast small load variations the current output of the fuel cell is controlled. When there are large variations in the load, the flow rates of fuel and air have to be adapted to maintain the fuel and oxidant utilization of the fuel cell within the allowable ranges. Therefore, the fuel processing sub-system is required to provide the appropriate gases to match the
operation of the fuel-cell power-generation subsystem. The power generated by the fuel cell (which is the major part) and by the heat recovery co-generation sub-system should vary to match the load demand. The power conversion subsystem consists of electronic devices and is expected to be fast.

1.2.2 Comparison between fuel-cell and thermal power-generation systems

Table 1.2 gives a comparison between fuel-cell power-generation systems and thermal power-generation systems, which is based on Takahira et al. (1994). The table indicates that the power-generation behavior of a fuel-cell system is significantly different from that of a thermal power-generation system. New numerical tools are required to identify the operating problems of fuel-cell systems.
<table>
<thead>
<tr>
<th>Items</th>
<th>Fuel-cell power-generation systems</th>
<th>Thermal power-generation systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power generation method</td>
<td>Electro-chemical reaction of hydrogen and oxygen</td>
<td>Electro-magnetic induction</td>
</tr>
<tr>
<td>Energy conversion</td>
<td>• Chemical energy (Fuel)</td>
<td>• Chemical energy (Fuel)</td>
</tr>
<tr>
<td></td>
<td>↓</td>
<td>• Thermal energy (Boiler)</td>
</tr>
<tr>
<td></td>
<td>• ii) Electric energy (Generator)</td>
<td>• Kinetic energy (Steam turbine)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Electric energy (Generator)</td>
</tr>
<tr>
<td>Generated power control</td>
<td>Inverter output power control</td>
<td>Turbine control valve</td>
</tr>
<tr>
<td>Plant shut-down mode</td>
<td>• No load of fuel cell (OCV)</td>
<td>• No load of generator</td>
</tr>
<tr>
<td></td>
<td>• Fuel cell isolation (Stop of H₂/O₂ feed)</td>
<td>• Steam turbine stop</td>
</tr>
<tr>
<td></td>
<td>• Plant shut down</td>
<td>• Boiler shut-down</td>
</tr>
<tr>
<td>Excessive energy discharge</td>
<td>Exhaust of excessive fuel (Hydrogen)</td>
<td>Exhaust of excessive steam</td>
</tr>
<tr>
<td>method</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Working fluid</td>
<td>Fuel gas/steam</td>
<td>Water/Steam (Heat exchange in boiler)</td>
</tr>
<tr>
<td>High priority safety</td>
<td>• Cathode/anode differential pressure</td>
<td>• Pressure of water/steam</td>
</tr>
<tr>
<td>constraints</td>
<td>• High temperature creep</td>
<td>• High temperature creep</td>
</tr>
<tr>
<td></td>
<td>• (Subject to electrolyte and metal strength)</td>
<td>• (Subject to metallurgical strength)</td>
</tr>
<tr>
<td>Fuel type</td>
<td>• LNG: Hydrogen conversion by reformer</td>
<td>• LNG: Direct combustion</td>
</tr>
<tr>
<td></td>
<td>• Coal: Hydrogen conversion by gasification</td>
<td>• Coal: Pulverized combustion</td>
</tr>
<tr>
<td></td>
<td>• Naphtha: Hydrogen conversion by reformer</td>
<td>• Oil: Direct combustion</td>
</tr>
<tr>
<td>System efficiency</td>
<td>• High efficiency under partial load conditions</td>
<td>• Significant lower efficiency under partial load than under full load conditions</td>
</tr>
<tr>
<td>under partial load</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Environmental impact</td>
<td>• NOₓ reduction by low temperature combustion in catalyst combustor</td>
<td>• NOₓ: high temperature oxidation of air nitrogen due to combustion adding to oxidation of fuel nitrogen</td>
</tr>
<tr>
<td></td>
<td>• SO₂ removal of fuel sulfur to avoid catalyst poison for reformer</td>
<td>• SO₂: generated by oxidation of fuel sulfur</td>
</tr>
<tr>
<td></td>
<td>• CO₂ reaction by high system efficiency</td>
<td>• CO₂: generated by oxidation of fuel carbon</td>
</tr>
</tbody>
</table>

### 1.2.3 Statement of thesis goals

This thesis puts the emphasis on operations. Basically, the problem is to predict a "what would happen if" situation for an MCFC power-generation system with regard to load-following modes, before control systems are implemented. The crucial obstacles of MCFC system operation have to be addressed.
Since the fuel-cell stack is a new apparatus in the power system, it is important to fully understand its power-generation characteristics and its safe operation.

The fuel processing sub-system employs a reformer from the process industry where continuous full-load operation is the rule. Thus, it is necessary to evaluate its capability to provide appropriate gases to the fuel-cell stacks under load-following modes.

The prediction of the power output characteristics from a complete MCFC system is not straightforward. The power output depends not only on the stack characteristics, but also on the gases from the fuel processing sub-system and from the heat recovery sub-system.

The anode-off gas from the fuel-cell stack is recycled to the reformer inlet. There may be dynamic interactions between the stack and reformer under load-following modes.

The above obstacles related to MCFC system operation are formulated by four main questions. This thesis puts emphasis on answering these four questions, which form guidelines throughout the thesis:

i. What are the power-generation characteristics of a fuel-cell stack? Does a fuel-cell stack operate within its safety constraints?
ii. Can the reformer provide gases which satisfy the requirements of the fuel-cell stack (i.e. flow rate, concentration, temperature, and pressure)?
iii. What are the power-generation characteristics of a complete MCFC system?
iv. What are the dynamic interactions between the reformer and fuel-cell stacks?

By answering the above four questions, this thesis provides insight required for introducing the fuel-cell stack and reformer into power-generation systems. The results of this study are interesting to a designer or an operator engaged in optimizing the design and operation of fuel-cell stacks and systems.

1.3 Methodology of the Research

The three main approaches to the problems stated in the preceding section are: experimental investigation, theoretical analysis and numerical simulation.

Experimental investigation. The most realistic information concerning the power generation of the fuel-cell stack, the capability of fuel processing by the reformer, and the responses of a complete system is, in principle, given by direct measurement.

An experimental investigation of a fuel-cell stack requires a full-scale cell, but may also use fewer cells connected in series. The basic experimental test is to measure the stack output voltage at standard current density output (1500 A/m²) under various inputs. It is possible to measure parameters such as the temperature at various locations in a stack and the gas composition at the inlet and outlet under steady-state conditions. However, under transient conditions it is difficult to measure the temperature at various locations in a stack. It is difficult to measure the local current density, even under steady-state conditions. An experimental investigation of a reformer should be carried out at full-scale, and tests are
usually conducted by manufacturers to verify the design aspects. An experimental investigation of a complete fuel-cell system can be carried out on a small scale, but only for a few design and operating conditions. Such an experimental approach to a stack, reformer and MCFC system is obviously expensive.

**Theoretical analysis.** An MCFC system features the integration of various components, some of them (e.g. fuel-cell stack and reformer) are non-standard components and involve many complex processes. Theoretical analysis is usually unable to provide a direct solution for such applications. However, theoretical analysis is possible for highly idealized models, and the analytical results are important in understanding the results obtained from numerical simulations and the empirical relations derived from experimental data.

**Numerical simulation.** Owing to the limitations of the approaches described above and to the development of numerical simulation tools for complex components and systems, numerical simulations have been used extensively in system analysis. Recent computational fluid dynamic (CFD) software packages have made significant progress in dealing with complex components (e.g. the capability of solving inter-related fluid-flow, heat-transfer and chemical-reaction in three-dimensional, time-dependent form). Recent system dynamic simulation tools can simultaneously solve implicit differential conservation equations (e.g. flow and energy) and algebraic equations (e.g. chemical reactions), initialize model variables, and access various data libraries (e.g. physical properties). These tools provide promising facilities to accomplish a dynamic simulation model for an MCFC system.

Numerical simulation of the components and complete MCFC systems can be carried out for various design alternatives and over a wide operational range. Numerical simulation of MCFC also provides useful information for establishing experimental investigation and predicts the non-measurable parameters under test conditions, and it is a cost effective way to understand the components and systems. In this study, a numerical simulation approach is used.

**1.4 State-of-the-Art**

In order to understand the position of the four proposed goals of this thesis (described in Section 1.2.5), the literature with regard to numerical approaches to the fuel-cell stack, reformer and complete systems is reviewed.

**1.4.1 Fuel-cell stack models**

The numerical modeling fuel cells can be appropriately divided into the electrode level (micro-modeling), the cell level and the stack level (macro-modeling). Micro-modeling aims at building better electrodes through study of microscopic processes (in dimension of μm). However, macro-modeling aims at optimal design and operation, provided that the electrochemical performance at micro-level of the given electrodes and electrolytes is known. In this study, fuel-cell modeling at stack level is emphasized.

As described in Section 1.2.2, the power-generation characteristics of a fuel-cell strongly depend on gas flow configurations and temperature distributions. For a large cell with
commercially realistic dimensions (about 1 m\(^2\)), the isothermal approximation is no longer appropriate, as a temperature difference of several hundred degrees Kelvin may be attained across the plane of a single cell operating at maximum load (Wolf and Wilemski, 1983). When evaluating stack power-generation performance, it is important to accurately predict the stack temperature distributions. The local current density (which essentially determines the output power) depends on the local temperature and the output current is the sum of the local current.

A stack model using lumped parameters based on physical laws cannot usually adequately represent stack performance, because the lumped stack model is not capable of dealing with the temperature gradients in a stack.

The most advanced models for an individual stack which are mainly based on physical laws are the two-dimensional (2D) model from Watanabe et al., (1991) and the 3D model from Fujimura et al. (1992). The 2D model extended the cell model of Wolf and Wilemski (1983) to transient conditions, but it assumed that each cell had the same performance. The experimental results reported by Takashima (1993) indicated a significant inhomogeneity (e.g. mass flow rate) along the direction of the stack, which increases with the stack height and operating pressure. The 3D model extended the cell model of Wolf and Wilemski to stack configuration, but it works only under steady-state conditions. Recently, Ding et al., (1997) developed a 3D, dynamic stack model by considering fluid flow, heat and mass transfer, and chemical and electrochemical reaction processes. The computed results under steady-state have been reported and compared with the experimental results. However, no detailed modeling procedures and results under transient conditions have been reported.

These previous works indicate that a stack model can be enhanced by considering the phenomena along the stack direction and extending its working scope to transient conditions. Consequently, the stack model must be in a 3D dynamic stack form. The 3D dynamic stack model may continue the work of Watanabe et al. (1991) by considering the stack effect. An extension of the 3D model of Fujimura et al. (1992) may also cover the transient conditions. Such a 3D-stack model often requires implementation by using a computational fluid dynamic (CFD) program and the simulation is time consuming. Thus, a 3D-stack model is not suitable for direct integration into system models.

1.4.2 Reformer model

In hydrogen processing plants, the use of a reformer is a well established practice. The research work is focused on maximizing the fuel conversion rate and optimizing reformer design. The previous work has provided the methodology for studying reformers in various processing plants. The overview paper of El-Nashaie et al. (1988) discussed the kinetic rate expressions for the chemical reactions in reformers and indicated that the developed reformer models are applicable for specific processes. Rostrup-Nielsen (1991) presented a structural design for reformers, and Wagner and Froment (1992) studied the optimal operation of reformers.

The reformer operation in a fuel-cell system is essentially different from that in processing plants, where continuous full-load operation is the rule. The reformer in a fuel-cell system is
required to operate in such a manner that the production of the gases to the fuel-cell stack always follows the changes in the power demand. It is therefore necessary to develop a reformer model to evaluate the reformer capability of providing gases for the fuel-cell stacks with regard to load-following modes.

1.4.3 System simulation

The simulation models of whole MCFC systems can be classified as stationary or dynamic system-performance models. The stationary MCFC system models compute the overall system parameters (e.g. flow, gas concentration, temperature and pressure) based on mass, energy and momentum balances. The simulation results provide a basis for component selection, system efficiency analysis and cost evaluation. The simulation models, e.g. Uchijama and Segawa (1991), Kivisaari (1992), Van der Laag and Verbruggen (1994) and De Groot and Woudstra (1995), have found applications in various MCFC systems for computing mass and energy balances at full load. However, these models have not provided insight into the system operational characteristics under transient conditions.

With regard to dynamic MCFC system models, frequent reference is made to the system model of Yamaguichi et al. (1990). The dynamic simulation model was developed for a 1 MW MCFC system based on the test results of a 100 kW MCFC system. The model can predict the responses of the major components and the overall system with regard to load-following operating modes. The system model employs component models of first-order, lumped form by using empirical correlation. However, the usability of the system model depends on the availability and the quality of experimental data. Furthermore, the uncertainty (statistical deviation or fitting error) must also be considered. The literature provides no indication that general dynamic MCFC system models with physically based component models are available.

In the field of PAFC system modeling, Alkasab and Lu (1985) developed a dynamic system model by using a combination of physical laws and experimental data. They established a two-dimensional PAFC stack model to provide the basis for a lumped PAFC stack model for integration into the system model. Their approach has the potential to provide component models with physical significance in a simple form (suitable for integration into system models). Although the simulated power-generation behavior derived from their models is not applicable to an MCFC stack, the modeling methods can be adapted.

These previous works indicate the need for a general dynamic model for MCFC systems with accurate component models. To be integrated into the system model, the component model must be a compromise between the accuracy and the complexity. An over-simplified model for new component based on physical laws often loses valuable information. Therefore, the first priority for a new and complicated component (e.g. fuel-cell stack) is to establish a detailed stand-alone model. The second objective is to derive a simple model for integration into the system model.
1.5 Thesis Approach and Organization

In order to solve the four problems proposed in this thesis (described in Section 1.2.3), simulation tools for a fuel-cell stack, a reformer, and a complete fuel-cell system must be provided. Technically seen, this thesis focuses on the modeling of the fuel-cell stack and reformer, as they are the new and crucial apparatus in the power-generation systems.

The thesis approach is shown in Figure 1.3 and consists of four major aspects.

- **System design.** The system design part of this thesis defines the framework within which the four thesis goals have to be realized. The system power-generation performance in stationary conditions must be acceptable. Then the system operating conditions and the component design are determined for developing dynamic component models.

- **Fuel-cell stack models.** A stand-alone fuel-cell stack model and a simple stack model suited for integration into the system model must be developed. The stand-alone fuel-cell stack aims at: i) accurately predicting stack power-generation behavior, ii) evaluating whether a stack operates within its safety constraints, and iii) providing insight for developing the simple stack model. The two requirements for the simple stack model are: i) accurate prediction of the stack power-generation characteristics with regard to load-following modes, and ii) suitability for integration into the system model.

- **Reformer model.** The reformer model is used to evaluate whether the reformer output gases satisfy the concentration, temperature, pressure, and flow-rate with regard to the fuel-cell stack load-following operating modes.

- **System model.** The system model comprises all component models. It aims at predicting the system power-generation characteristics and identifying the dynamic interactions between the reformer and fuel-cell stack under load-following operation modes.

This study is confined to the normal load-following operating conditions. The methodology of this study is also applicable to abnormal conditions, such as startup, shutdown and accident, though the system flow diagram often has to be accommodated.

The remainder of this thesis is organized as shown in Figure 1.3. Chapter 2 gives a system design. It includes a system selection, a qualitative estimate of the system operating capability, and a quantitative evaluation of the system performance at full load. It also provides component data needed for developing dynamic component models. Chapter 3 develops a stand-alone fuel-cell stack model and a stack model suited for integration into the system. Chapter 4 investigates the reformer capability with regard to its providing gases for the fuel-cell stack. The modeling of other components in the system is described in Appendix B. Chapter 5 presents a complete system model to demonstrate the power-generation characteristics of the system, and to predict the potential dynamic interactions between the reformer and fuel-cell stack with regard to load-following operation modes. The effectiveness of the system model for operation and design is also illustrated. Finally, Chapter 6 submits the conclusions and recommendations.
1.6 References


Laag, V.D.P. and Verbruggen, T.W., 1994, "Conceptual designs of first-generation 250 kW MCFC demonstration plants", presented at Fuel Cell Seminar, November 28-December 1, San Diego, California, USA, pp. 152-155


Technology for Environmentally Safe Reactors and Products, Aug. 25- Sept. 5, Ontario, Canada.


2 SYSTEM DESIGN

This chapter provides a system design to obtain the operating conditions and component design data needed for developing dynamic component models. The system design includes the following aspects:

- Selection of the system
- Qualitative evaluation of the system
- Computation of system parameters
- Evaluation of the system performance at full load
- Modeling decisions at system level
- Estimation of the component geometry and physical properties

2.1 Selection of the System

The system selection is based on the following four criteria:

i. Suitability for realization of the four thesis goals (described in Section 1.2.3).
ii. Availability of the experimental data about the components and system.
iii. Presentation of the state-of-the-art MCFC system development.
iv. Provision of valuable information for the preparation of the Dutch MCFC projects.

The system selected for this study is the 1 MW Japanese MCFC system with adaptation to the Dutch situation. This system satisfies the above four criteria as follows.

i. Fuel-cell systems at the research stage often aim at a high efficiency, but result in a high complexity. On the other hand, fuel-cell systems at the demonstration stage are usually much simpler, have a moderate efficiency, and are cost-effective. This thesis is an initial effort to numerically identify the operating problems of a fuel-cell stack, a reformer, and a complete fuel-cell system. The possible interactions between the fuel-cell stack and reformer should also be identified. Therefore, three systems used in recent demonstration plants have been studied. These demonstration plants include: a 250 kW system built in the USA in 1994 (Figueroa et al., 1996), a 2 MW system built in the USA in 1997 (Skok et al., 1996), and a 1 MW system scheduled in Japan in 1999 (Matsunaga at al., 1998). The 250 kW system in the USA has no integration between the reformer and fuel-cell stack and the 2 MW system in the USA uses an internal reformer. Therefore, these two American systems are not suitable to illustrate the dynamic interactions between the fuel-cell stack and the reformer (which is one of the four thesis goals). In the Japanese 1 MW system, the fuel-cell anode-off gas is recycled to the reformer. Hence, this Japanese 1 MW system is suitable to realize the four thesis goals.

ii. The Japanese 1 MW system concept has been verified by a 100 kW test facility and the major components have been tested by manufacturers (MCFC, 1995). The system diagram
and the system performance under full load are known from the literature. There are experimental data available from literature for evaluation of simulation results.

iii. The Japanese 1 MW MCFC pilot plant that is scheduled to operate in May 1999 presents the state-of-the-art MCFC system development (FCS, 1996). A view of the plant is shown in Appendix A.1. The system has a net electric efficiency of 45% at full load (Uchijama and Segawa, 1991).

iv. In order to achieve applicable results for the Dutch MCFC projects, the Japanese 1 MW system has been modified to the Dutch situation. In the Netherlands, different criteria are imposed with regard to the operating conditions and component selection than those applied in Japan. In this study, the two adaptations are: i) input of Dutch natural gas (Nederlandse Gasunie, 1989), and ii) selection of Haldor Topsøe HER reformer (Stahl and Laursen, 1992). The HER type of reformer was considered for the proposed Dutch 50 kW and 250 kW MCFC projects (Laag and Vergruggen, 1994).

### 2.2 Qualitative Evaluation of the System

The system flow diagram that has been developed is shown in Figure 2.1. This is an adaptation of the Japanese 1 MW system flow diagram (Uchijama and Segawa, 1991). A gas blower has been added to raise the pressure of the natural gas at the input. The Japanese system uses LNG from a pressure vessel of 6 bar. However, our system uses Dutch natural gas which is assumed to be at a lower pressure of 3 bar.

![System flow diagram of 1 MW system](image)

**Figure 2.1 System flow diagram of 1 MW system**

The complete system includes four subsystems: fuel processing, fuel-cell power-generation, power conversion, and heat recovery subsystems. The major functions of the apparatus in the flow diagram are as follows:
- **Reformer.** The reformer converts hydrocarbons (the major composition of natural gas) into \( \text{H}_2 \) and \( \text{CO} \) by using steam reforming reactions. However, the steam reforming reactions are strongly endothermic. The heat required for the steam reforming reactions is provided by burning combustible gases in anode exhaust gas (i.e. \( \text{CH}_4, \text{H}_2 \), and \( \text{CO} \)) with air. The reformer then provides the fuel-cell anode with the processed gas of appropriate temperature, pressure and high concentration of \( \text{H}_2 \) and \( \text{CO} \). The reformer also provides the fuel-cell cathode with flue-gas from the combustion with a significant \( \text{CO}_2 \) concentration.

- **Fuel-cell stack.** The fuel gas (the processed gas from the reformer) and the oxidant gas (the flue-gas from the reformer mixed with air) are fed to the fuel-cell anode and cathode respectively. The fuel-cell stack generates DC electricity by using electrochemical reactions and releases the exhaust gases.

- **DC/AC inverter.** The DC/AC inverter converts the DC electric power generated by the fuel-cell stack into the required AC power.

- **Steam generator.** The steam generator uses the heat of the cathode exhaust gas to generate the super-heated steam for the reformer. The steam generator is comprised of a preheater, an evaporator (a heater with a drum and a pump), and a superheater. The water is first heated to saturation, then evaporated, and heated further in the superheater, while the cathode-off gas is cooled down.

- **Water separator.** The water separator is used to separate water from the cooled anode-off gas. The allowed mol-fraction water in the outlet gas is determined by the partial pressure.

- **Mass-transport equipment.** The mass-transport equipment here includes a cathode gas recycling blower, an anode gas blower, a water pump, and a turbo-compressor (including expander and compressor). The blower, compressor, and pump increase the fluid pressure by consuming energy, while the expander decreases the gas pressure by generating energy.

- **Heat exchangers.** There are three gas/gas heat exchangers in the system: a fuel preheater, an air preheater, and an anode heat exchanger. The fuel preheater uses anode exhaust gas to heat the natural gas that is fed to the reformer. The air preheater uses flue-gas from the reformer to heat the air which is fed to the reformer. The anode heat exchanger further utilizes anode exhaust gas after the fuel preheater to heat recycled anode gas after the water separator.

In addition, the following apparatus should be mentioned:

- Many control valves (not shown in the Figure 2.1) are used in the system.
- An auxiliary combustor exists in the Japanese 1 MW system which is used if the temperature of the cathode-off gas is too low. Since the auxiliary combustor is not designed to operate under normal load-following modes, it is not considered in this study.
- To reduce the cost, the proposed Dutch system for a demonstration project eliminated the molten carbon (MC) scrubber (Laag and Verbruggen, 1994) which exists in the 1 MW Japanese system. This study did not include a MC scrubber.
- The simple components of splitters and mixers are also used to split one stream into multiple streams or to mix multiple streams into one stream.

The operating characteristics of the four subsystems are qualitatively analyzed. Table 2.1 shows that the system satisfies four major design criteria with regard to safe and efficient electricity generation. The system is able to: i) use inputs of natural gas, water, and air, ii) maintain the stack operating temperature, iii) convert the DC power generated by the fuel-cell stack into AC power, and iv) use the heat and combustible exhaust gases from the fuel-cell stack.
Table 2.1 Design criteria and approaches of the system flow diagram

<table>
<thead>
<tr>
<th>Subsystems</th>
<th>Design criteria</th>
<th>Approaches</th>
</tr>
</thead>
</table>
| fuel processing  | convert accessible resources to the useable gases for fuel-cell stack          | • inputs are natural gas, steam, and air.  
• processed gas from the reformer rich with hydrogen is supplied to the fuel-cell anode.  
• air and flue-gas from the reformer with carbon dioxide is supplied to the fuel-cell cathode.  
• recycling the anode exhaust gas to the inlet of the fuel-cell cathode enhances the concentration of carbon dioxide at the inlet of the cathode. |
| fuel-cell        | maintain the stack operating temperature                                       | Use cathode-gas recycling and manipulate the flow ratio to maintain the stack temperature within its constraints.                             |
| power generation |                                                                                 |                                                                                                                                              |
| power conversion | output AC power                                                                  | Use DC/AC inverter                                                                                                                           |
| heat recovery    | use the heat and combustible exhaust gases from the fuel-cell stack             | • the energy of the cathode exhaust gas is recovered by the turbo-compressor and then provides heat for the steam generator.  
• the heat of the anode exhaust gas is used to heat the natural gas for reformer.  
• the water in the anode exhaust gas is separated and supplied to the steam generator.  
• the unreacted fuel gas in the anode exhaust is combusted in the reformer which supplies heat for the reforming process. |

2.3 Principle of Computing System Parameters

In order to evaluate the system performance quantitatively under stationary conditions, the system parameters (e.g., flow, concentration, temperature, and pressure at each stream) must be computed. The approach to the system parameters consists of the following four major steps:

- Specification of the system feed streams;
- Decisions on the system operating conditions by first considering the fuel-cell stack, secondly the reformer, and then the other components;
- Determination of the system parameters by component models, e.g., calculate the changes between the successive streams;
- Computation of the mass flow of all streams on the basis of mass and energy conservation.

2.3.1 Specification of the system feed streams

The feed streams for the system are: natural gas (Nederlandse Gasunie, 1989), air, and water. The specifications of the feed streams are listed in Appendix A.2.
2.3.2 Decisions on system operating conditions

The system operating conditions are related to the requirements of the individual component, the inter-connection between the components, and the required system output. The decisions on system operating conditions take account of first the requirements of the fuel-cell stack, then the reformer, and the other components in the system. This section presents the decisions on one of the most influential variable of the reformer (i.e. steam-to-carbon ratio) and four variables of the fuel-cell stack (i.e. pressure, temperature, average current density, and fuel gas utilization).

The proposed decision involves three main steps:
- Qualitative evaluation of the impact resulting from the selection
- Quantitative computation of the workable range (e.g. minimum steam-to-carbon ratio of the reformer)
- Adaptation of the available design value to this study

Steam-to-carbon ratio. A lower ratio of steam-to-carbon results in a higher hydrogen content at the anode inlet and a higher cell performance. However, a low ratio of steam-to-carbon may cause carbon deposits in the reformer. In order to avoid carbon deposits, the feasible steam-to-carbon ratio should be higher than the lower limit. Appendix A.3 presents the computation of the minimum steam-to-carbon ratio. The results show that the minimum ratio first increases and then decreases in the temperature range of 450°C to 800°C. The maximum value occurs between 600°C and 650°C. The calculated minimum ratios vary from 0.5 to 1.5 in the temperature range of 450°C to 800°C and pressure range of 1 bar to 5 bar. The ratio recommended by the manufacture is from 2.5 to 3.5 (Stahl and Lausen, 1992). The Japanese 1 MW system uses a ratio of 3, which is a feasible (higher than the calculated minimum ratio) and conservative decision. This value is adopted in this study.

Operating pressure. An increase in operating pressure has several beneficial effects on the fuel-cell performance, because the reactant partial pressure, gas solubility, and mass transfer rates increase. Differentiating the theoretical voltage of the fuel-cell (E) with respect to the pressure yields (Hirschenhofer, et al., 1994):

$$\left( \frac{\partial E}{\partial P} \right)_T = -\frac{\Delta V}{nF}$$  \hspace{1cm} (2.1)

where E is the theoretical cell voltage, P is the operating pressure, ΔV is the gas volume change of the cell reaction, n is the number of electrons participating in the reaction, and F is the Faraday constant.

Since the gas volume (ΔV) decreases in the cell reaction (Eq. 1.1), the theoretical cell voltage E increases with an increase in pressure. One should notice however, that a high operating pressure often reduces the fuel-cell life.

A high operating pressure results in the decrease of the fuel reforming reaction rate. Moreover, it results in more power consumption for fluid compression and for fluid transfer. The overall net electric efficiency normally increases in the low operating pressure region and decreases when the pressure exceeds a certain value. The maximum operating pressure of a state-of-the-art stack reaches 0.7 MPa, e.g., for the ECN stack, the operating pressure range is between 0.1 and 0.7 MPa (Klerks, et. al, 1994). For the Japanese 1 MW system, the stack operating pressure used is around 0.3 MPa which seems feasible. That value is used in this study.
**Operating temperature.** An increase in the operating temperature is beneficial for the fuel-cell performance because of the increase in the reaction rate, the higher mass transfer rate, and usually the lower cell resistance. Differentiating the theoretical voltage of the fuel-cell (E) with respect to the temperature yields (Hirschenhofer et al., 1994):

\[
\left. \frac{\partial E}{\partial T} \right|_p = \frac{\Delta S}{nF}
\]

(2.2)

Where \( \Delta S \) is the change in entropy of the cell reaction.

Since the entropy change (\( \Delta S \)) of the cell reaction (Eq. 1.1) is negative, the theoretical cell voltage \( E \) decreases with an increase in temperature. However, the achievable actual cell voltage often increases with the temperature in the temperature range of 550°C to 750°C (Hirschenhofer et al., 1994), because the cell losses decrease with an increase in temperature. However, a high operating temperature will reduce the cell life because the problems related to corrosion (electrode degradation and electrolyte loss by evaporation) accelerated at higher temperatures.

The design stack-operating temperature is around 650°C. The temperature increases of the fuel and oxidant gases between the inlet and outlet are often around 100°C (Kinoshita, 1988). The heat generated within the fuel-cell is removed by the oxidant gas. Thus, the inlet temperatures of 600°C and 550°C for fuel and oxidant gases are used in the Japanese 1 MW system. These values appear feasible and have been adopted.

**Average current density.** The higher the average current density in the fuel-cell, the lower the fuel-cell stack cost (the smaller fuel-cell reaction area is required). However, a high average current density usually accelerates the deterioration of the fuel-cell performance, and results in a lower efficiency (the loss due to the electrical resistance becomes larger). The current density of 1500 A/m² for full load used in the Japanese 1 MW system is adopted. In the following discussion, the full load operating conditions refer to an average current density of 1500 A/m² instead of the electric power output of 1 MW.

**Fuel gas utilization.** The higher the fuel utilization in the fuel-cell, the lower the amount of natural gas is required by the reformer. However, a too high fuel utilization may reduce the stack voltage as the hydrogen content at each anode exit decreases. Therefore, the fuel gas utilization should be limited. A maximum fuel utilization limit for an individual stack is usually 90% (IEA, 1993). In addition, the fuel-cell exhaust gas is combusted in the reformer burner to supply heat for the reforming process. The maximum fuel utilization limit is 85% (IEA, 1993). A fuel utilization of 80% has been selected for operating condition under full load.

Appendix A.4 gives the determination of the temperature parameters in the heat recovery subsystem.

2.3.3 Determination of system parameters by component models

The changes in the mass concentration, temperature, and pressure between the successive stream flows are determined by the characteristics of the components. The relations between the concentration, temperature, and pressure of the input and output stream flows for each component
are provided by the component model, which also depend on the mass flow of input and output stream flows.

Though each component involves very different processes, the models related to the components can be classified as a set of conservation equations for mass, energy, and momentum balances. Each component also has a set of auxiliary equations to solve the variables in the conservation equations. The auxiliary equations often include the computation of reaction rates, heat-transfer coefficient, and physical properties.

![Diagram of Apparatus](image)

**Figure 2.2 Mass streams of an apparatus**

Figure 2.2 shows the mass stream flows of a component. The stationary mass balance of a component reads:

\[
\sum_{j=1}^{n_{in}} F_{in}(j) \cdot \bar{y}_{in}(j) - \sum_{i=1}^{n_{out}} F_{out}(i) \cdot \bar{y}_{out}(i) = \vec{b}
\]  
(2.3)

The vector \(\vec{b}\) (mass source and loss) includes the mass generation resulting from the chemical reaction and mass loss.

The energy balance of an apparatus reads:

\[
\sum_{j=1}^{n_{in}} F_{in}(j) \cdot h_{in}(j) - \sum_{i=1}^{n_{out}} F_{out}(i) \cdot h_{out}(i) = B
\]

(2.4)

The parameter B (energy source and output) includes the reaction heat, the heat exchange with its surrounding, and its power output.

A realistic computation of the momentum balance requires extensive computational fluid dynamics techniques in the distributed model. A simple equation using the pressure drop to express the pressure of the input and output streams uses:

\[
P_{in}(j) \{j = 1, 2, ..., n_{in}\} = P_{out}(i) \{i = 1, 2, ..., n_{out}\} + \Delta P(k) \{k = 1, 2, ..., k\}
\]

(2.5)

The pressure drop \(\Delta P\) uses an empirical equation related to the mass flow (Woudstra and Verschoor, 1995).
2.3.4 Computation of the mass flow

To solve the mass flow of a system consisting of interconnected components, a system matrix $\vec{A}$ is introduced. The vector of mass flow of all streams is $\vec{F}$, and the vector of mass and energy output is $\vec{E}$. The equation for calculation the mass flow of all streams reads.

$$\vec{A} \cdot \vec{F} = \vec{E}$$  \hspace{1cm} (2.6)

In the system coefficient matrix $\vec{A}$, the coefficients for mass flow balance are either 1 for the flow into the stream or -1 for the flow out of the stream, and therefore these coefficients are independent of the mass flow rates; the coefficients for energy balances are specific enthalpy values and these values are often dependent on mass flow rates. When the system coefficient matrix $\vec{A}$ and the mass and energy output vector $\vec{E}$ are known (or in the function of mass flow), the vector of mass flow of all streams $\vec{F}$ can be solved by Eq. 2.6. A detailed description of solving the mass flow by using the system matrix is given by Woudstra and Verschoor (1995).

In addition, for a system with the open-loop flow diagram, the size of the mass flow vector $\vec{F}$ is the number of all streams. For a system with a closed-loop flow diagram, the number of the independent equations for the mass flow $\vec{F}$ is one less than the number of all streams.

2.4 Computation of System Parameters by Using CYCLE-TEMPO

2.4.1 Selection of CYCLE-TEMPO

In order to compute the system behavior under stationary conditions, a computer simulation package is needed. The software package CYCLE-TEMPO, developed at the Laboratory of Thermal Power Engineering, Delft University of Technology, is a tool for thermodynamic analysis and optimization of electricity and heat production systems (Woudstra and Verschoor, 1995). The primary function of CYCLE-TEMPO (TEMPO: Thermodynamic Energy systems, Mass flow computations for POwer processes) is to compute the quantity of all relevant mass and energy flows in the system. CYCLE-TEMPO has 29 components, including 15 components for conventional steam and gas-turbine cycles, and three fuel-cell related components (stack, reformer, and fuel gas condenser). CYCLE-TEMPO covers most of the components in our system depicted in Figure 2.1 and it requires few input data. Therefore, CYCLE-TEMPO is selected.

2.4.2 Principal of CYCLE-TEMPO

Figure 2.3 shows the principle of calculating the system behavior using CYCLE-TEMPO. The input file contains input data related to the system flow diagram, including the input conditions, imposed output (e.g. required output power) and the decisions of the essential variables associated with the system operating conditions. The unknown quantities (e.g. concentration, temperature, specific enthalpy, and pressure) of all streams are computed by the component
models. Then the system coefficient matrix $\tilde{A}$ can be calculated, and the mass flow of all streams can be computed. The termination criteria are that the composition ($y$) and mass ($F$) differences of all streams between two successive iteration steps are sufficiently small (Woudstra and Verschoor, 1995) as follows.

$$|\hat{y}_i(k) - \hat{y}_i(k-1)| < \varepsilon_1$$  \hspace{1cm} (i = 1, 2, ..., n)  \hspace{1cm} (2.7)

and  $$\frac{F_i(k) - F_i(k-1)}{F_i(k)} < \varepsilon_2$$  \hspace{1cm} (i = 1, 2, ..., n)  \hspace{1cm} (2.8)

where $i$ is the stream, $n$ is the total stream number, $k$ is the iteration step, and $\varepsilon_1, \varepsilon_2$ are allowed different values (e.g. around $10^{-3}$).

After termination of the iterative procedure, the parameters of all streams are once more determined according to the final mass flow rates.

![System flow diagram](image)

**Figure 2.3 Computation of system behavior by using CYCLE-TEMPO**

### 2.4.3 Program implementation by using CYCLE-TEMPO

When computation of the system behavior is carried using CYCLE-TEMPO, the component representation is first considered. The components shown in Figure 2.1, such as, fuel-cell, water separator, mass-transport equipment (e.g. blower, compressor, expander and pump), heat exchanger, splitter, and mixer, can be covered by CYCLE-TEMPO component models (Woudstra and Verschoor, 1995). However, the other components need attention as follows:
• **Reformer.** The reformer model in CYCLE-TEMPO does not include combustion, thus the reformer is represented by a combination of two models: an external combustion burner model and a reformer model.

• **Steam generator.** The steam generator is represented by a combination of three models: a preheater model, an evaporator model (a heater with a drum and pump), and a superheater model.

• **DC/AC inverter.** There is no separate DC/AC inverter model in CYCLE-TEMPO. The impact of the DC/AC inverter is treated as a fixed power conversion efficiency and is lumped together with the fuel-cell model.

• **Water treatment.** The water treatment is represented by a water input and output stream.

An input or output of the system is represented by a stream coming from or going to a source. Appendix A.5 gives the implementation of the system computation by using CYCLE-TEMPO.

### 2.4.4 Input file of CYCLE-TEMPO

The input data file of CYCLE-TEMPO for computing the system parameters at full load contains three main aspects:

• Representation of the system flow diagram

• Specifications of the system feed streams

• Input data for each component

The first two aspects have been discussed in the previous sections. This section deals with the input data for each component, which includes the component design data and operating conditions. The component design data are mainly derived from the system design results of the Japanese 1 MW system (Uchijama and Segawa, 1991) and from the design results of the component manufactures (Fujimura, et al., 1992, Stahl and Laursen, 1992). The component operating conditions are based on the decisions on system operating conditions described in Section 2.3.2. Table 2.2 lists the input data for the fuel-cell stack and reformer. Appendix A.5 lists the input data for the other components in the system.
Table 2.2 Input data for fuel-cell and reformer

<table>
<thead>
<tr>
<th>Component models</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel-cell</td>
<td>Operating conditions:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Pressure (bar)</td>
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<tr>
<td></td>
<td>• Temperature (°C)</td>
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<tr>
<td></td>
<td>• Temperature of anode output (°C)</td>
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</tr>
<tr>
<td></td>
<td>• Fuel utilization (mol/mol)</td>
<td>80</td>
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<tr>
<td></td>
<td>• Current density (A/m²)</td>
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<td>Design features:</td>
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<tr>
<td></td>
<td>• Anode pressure drop (bar)</td>
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<tr>
<td></td>
<td>• Cathode pressure drop (bar)</td>
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<tr>
<td></td>
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<td>• Temperature of anode output (°C)</td>
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<tr>
<td></td>
<td>• Cell reaction area (m²)</td>
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<tr>
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<td>• Lumped electric resistance (Ωcm²)</td>
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<td>• DC/AC power conversion efficiency</td>
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<td>Reformer</td>
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</tr>
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<td>• Steam-to-carbon ratio</td>
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<tr>
<td></td>
<td>• Reforming temperature (°C)</td>
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<td>• Reforming pressure (bar)</td>
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<td>• Excess air ratio of combustion (%)</td>
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<tr>
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</tr>
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<td></td>
<td>• Pressure drop of process gas (bar)</td>
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</tr>
<tr>
<td></td>
<td>• Pressure drop of flue gas (bar)</td>
<td></td>
</tr>
</tbody>
</table>

2.5 System Performance under Full Load

The system quantities (i.e. flow-rate, concentration, temperature, and pressure at each stream) are computed by using CYCLE-TEMPO. The main features are as follows.

- Natural gas of 140 kg/h is provided, and is preheated in the fuel preheater. The preheated natural gas and super-heated steam are then fed into the reformer. The Natural gas with methane (81%) and higher hydrocarbons reacts with steam to produce gas with a H₂ concentration of 54%, which provides the anode inlet gas.
- The air flow of 3949 kg/h is compressed to 0.37 MPa (3.7 bar), and is fed to the combustion chamber of the reformer and fuel-cell cathode. The air flow to the reformer depends on the concentration of combustible gas in the recycled anode gas. Then the flue-gas from the reformer and the compressed air are supplied to the fuel-cell cathode.
- The system delivers 979 kW AC power from the fuel-cell stack. The cathode exhaust gas at 700°C is recovered by the turbo-compressor and steam generator. The steam generator provides steam of 481 kg/h at 450°C to the reformer.
• The anode-off gas is cooled down to 400°C by the fuel preheater and heat exchanger. In the water separator, the anode-off gas is cooled down to 85°C and is separated from water. The anode-off gas is then recycled to the reformer, where it is combusted to produce the heat needed for the endothermic reforming reaction.

The energy output and heat exchange within components are listed in Appendix A.7. The net electric efficiency $\eta_e$ reads:

$$\eta_e = \frac{P_{\text{net}}}{E_{\text{NG}}} = \frac{P_{\text{fuel-cell(AC)}} + P_{\text{Turbo-compressor}} - P_{\text{consumption}}}{E_{\text{NG}}} = \frac{979 + 50 - 91}{2048} = 45.8\% \quad (2.9)$$

where $P_{\text{net}}$, $P_{\text{fuel-cell(AC)}}$, $P_{\text{Turbo-compressor}}$, and $P_{\text{consumption}}$ stand for the system net power output, the AC power from the fuel-cell stack after conversion, the power generated by the turbo-compressor, and the total power consumption of the blower, compressor, and pump respectively. $E_{\text{NG}}$ is the natural gas energy input based on a low heat value.

The power outputs in Eq. 2.9 show that the magnitude of the fuel-cell power output is much larger than the power from the turbo-compressor minus the power consumption (e.g. blower, compressor, and pump). In addition, only the power output from the fuel-cell is connected to the DC/AC inverter to follow the load demands. In this study, the system load-following power output refers to the fuel-cell power output. That is: $P_{\text{load-following}} \approx P_{\text{fuel-cell(AC)}}$.

![Sankey diagram of the system energy flow](Figure 2.4)

Figure 2.4  Sankey diagram of the system energy flow

Figure 2.4 presents a Sankey diagram of the system energy flow at full load, in which all the energy streams are presented as a percentage of the fuel input energy. The net system efficiency $\eta_e$ reaches 45.8% and it is a little higher than the Japanese 1 MW design value of 45%. This results from the differences in both the input fuel gas and in the reformer type. This high system efficiency at full load motivated the following investigation on the system performance under load-following conditions.
2.6 Modeling Decisions at System Level

2.6.1 Component representation

The system consists of various components for fuel processing, fuel-cell power-generation, power conversion, and heat recovery co-generation. In order to reduce the number of component types required for modeling, the components within the system have been classified according to their working principles. Two examples are given as follows.

- **Heat exchanger.** The working principles of the fuel preheater, air preheater, and gas/gas heat exchanger are similar. However, the gas flow-rate, the temperature, and the required heat transfer flux for these three heat exchangers are different. Accordingly, these three heat exchangers are modeled as the same type of component, but with different operating inputs, geometry, and physical properties.

- **Mass-transport equipment.** The blower, compressor, and pump increase the fluid pressure by consuming energy, while the expander generates energy by decreasing the gas pressure. Though the structure of a blower, pump, compressor, and expander are very different (the blower and compressor are usually used for gases and the pump for liquid), their working principles are identical. Accordingly, these four components are considered to be of approximately the same type of component, but with different characteristic curves (or functions), geometry, and physical properties.

All components in the fuel-cell system are represented by nine types of component models: (1) the fuel-cell stack, (2) the reformer, (3) the steam generator, (4) the water separator, (5) the mass-transport equipment (e.g. blower, compressor, expander and pump), (6) the heat exchanger, (7) the DC/AC inverter, (8) the splitter, and (9) the mixer. Since the fuel-cell stack and reformer are new and vital components in the system, the approach to these two models will be discussed in detail. The other seven types of component models are discussed in Appendix B.

In addition, many pipes are employed in the plant. A change of the input flow in a pipe will not immediately result in a change of the output. There is a pressure drop and a time delay (e.g. gas composition, enthalpy, and temperature) due to the transport in the pipe. According to a general engineering approach (GPSA, 1998), the impact of the pipes is lumped to the related dynamic component, e.g., the weight and storage of the pipes are added to the dynamic component.

2.6.2 Modeling simplifications at system level

First, in view of the complexity of the system, the system performance resulting from the fuel-cell stacks and the reformer is focused. The dynamic impacts from the steam generator and water separator are not included in this study.

Secondly, the test facility of the 100 kW MCFC plant at Agika indicated that the system load-following capability is about 25% per minute (Yoshida and Innoue, 1993). The IHI experts predicted that the load-following capability of a 1 MW system should be about 10%/minute in order to satisfy the load-following requirements (IHI, 1995). Therefore, the time constant range of
an influential process in the system is considered from 10 to \(10^3\) seconds. Accordingly, if the time constant of a process is much faster than this time scale, it is assumed to reach its next steady state immediately, and then it can be modeled in a steady-state form. If the time constant of a process is much slower than this time scale, the impact of the process is neglected, and then it is not modeled. For example, the power conversion process in the DC/AC inverter is estimated to be very fast (time constant around \(10^3\) seconds), and is modeled in a steady-state form. The decay process of the fuel-cell electrodes due to corrosion is very slow (time constant around \(10^5\) seconds) and its impact is not considered. With regard to the time constant consideration, the following components involve fast processes and will be modeled in a steady-state form.

- Mass-transport equipment (including blower, compressor, expander, and pump)
- DC/AC inverter, splitter, and mixer

Finally, the fuel-cell stack, reformer, and heat exchangers are modeled in dynamic form. The modeling simplifications in this section will be further discussed in Chapter 5.

### 2.7 Estimation of Component Geometry and Physical Properties

In order to establish the dynamic models of the fuel-cell stack, reformer, and heat exchangers, more design data are required than the input data provided for computing the system performance at full-load implemented in CYCLE-TEMPO. Some design features have been provided by manufacturers, however, there are still many unknown factors due to the confidential policies of the companies concerned. It is therefore necessary to estimate the unknown parameters of the fuel-cell stack, reformer, and the heat exchangers. In this study, the estimates of the unknown design data are intended to provide input conditions for dynamic modeling, rather than discussing all the trade-offs for optimal designs.

From our literature study, it appeared that no general approach is available for such an estimation of the fuel-cell stack or reformer. Therefore, we proposed methods to estimate the fuel-cell stack and reformer as follows.

- **Estimation of the fuel-cell stack.** First a 1 MW stack was selected. Secondly, the available design data from manufacturers were compared against the required performance of the fuel-cell stack at full load. Thirdly, the stack power-generation characteristics were evaluated and the gas channel geometry was estimated.

- **Estimation of the reformer.** The available design data from manufacturers were compared against the required performance of the reformer at full load. Then, the gas channel geometry was estimated according to the gas flow rate at full load and the assumed average gas velocity. The Reynolds number was calculated and the gas flow pattern was determined.

Appendices A8-10 presents the calculation and the results of the geometry and physical properties of the fuel-cell stack, reformer, and heat exchangers.

### 2.8 Selection of Simulation Software Packages

The software package CYCLE-TEMPO has been selected to compute the system parameters at full load. CYCLE-TEMPO focuses on the performance under design conditions, rather than on the operating characteristics under various conditions. All component models in CYCLE-
TEMPO are in steady-state form. CYCLE-TEMPO has no facilities for simulation under transient conditions. Therefore, it is necessary to select other software packages to implement the simulation of the fuel-cell stack and the complete system with regard to load-following modes.

2.8.1 PHOENICS software package

The computational fluid dynamic (CFD) software package PHOENICS (CHAM, 1995) is the acronym for Parabolic, Hyperbolic, or Elliptic Numerical Integration Code Series. PHOENICS provides a solver for fluid-flow, heat-transfer, chemical-reactions, and related problems ranging in complexity from one-dimensional single-phase under steady-state conditions to 3D multi-phase under transient conditions.

PHOENICS can effectively deal with differential conservation equations for a fuel-cell stack with commercial realistic dimensions (e.g. cell reaction area 1 m$^2$). Hence, it is capable of computing the crucial parameter distributions in a fuel-cell stack under transient conditions. Therefore, PHOENICS has been selected to implement the 3D dynamic fuel-cell stack model. The 3D-stack model aims to accurately predict the performance of fuel-cell stacks, and to evaluate whether a stack operates within its safety constraints under load-following modes. The simulation of the 3D-stack by using PHOENICS is extremely time consuming, thus the 3D-stack model is not suitable for incorporation into the system model.

PHOENICS is not designed for dealing with systems that involve components interconnected by process streams. Therefore, it is necessary to select another software package to implement the complete system with regard to load-following modes.

2.8.2 SPEEDUP software package

The software package SPEEDUP (SPEEDUP, 1996) is a recent tool for the dynamic simulation of comprehensive processes and processes with a series of unit operations interconnected by process streams. SPEEDUP can simultaneously solve implicit differential conservation equations (e.g. flow and energy) and algebraic equations (e.g. chemical reactions), initialize model variables, and has access to various data libraries (e.g. chemical reactions). In addition, the SPEEDUP library provides a wide range of frequently used process models as well as procedures and functions. Therefore, SPEEDUP is a promising tool to simulate the dynamic behavior of inter-connected chemical, thermal, and electricity-generation processes in a fuel-cell system.

The advantages of SPEEDUP over other dynamic packages, such as ACSL(1995) are its capability to solve integrated implicit differential conservation equations and algebraic equations, to initialize model variables, and to access various data libraries (e.g. physical properties). SPEEDUP has been selected for the implementation of the fuel-cell system model. Consequently, the component models for integration into the system model should also be implemented in a SPEEDUP environment.
2.9 Conclusions

The main results of the system design are as follows.
- The state-of-the-art 1 MW MCFC system is selected and adapted to the Dutch situation (e.g. different input fuel gas and different reformer type).
- The qualitative analysis shows that the system is suitable for practical application (use natural gas, water, and air as system input). It also meets major safety and efficient operation criteria.
- The quantitative analysis of the system is implemented by using the program CYCLE-TEMPO developed at the author’s laboratory. The system at full load has a net electric efficiency of 45.8%.
- In order to reduce the number of component types required for modeling, the components in the system are classified according to their working principle. This yields the following nine types: fuel-cell stack, reformer, steam generator, water separator, mass-transport equipment (e.g. blower, compressor, expander, and pump), heat exchanger, DC/AC inverter, splitter, and mixer.
- The geometry and physical properties of the fuel-cell stack, reformer, and heat exchangers are computed to develop dynamic models.

Therefore, the system design has provided the operating conditions and component design data for further investigation with regard to load-following operation modes that are discussed in the following chapters.

2.10 References


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3 FUEL-CELL STACK MODELS

This chapter provides two types of fuel-cell stack models. More precisely, it develops a stand-alone 3D-stack model and a lumped-stack model suited for integration into the system model. The 3D-stack model is rather detailed in that it describes processes at electrode, cell and stack level. The 3D-stack model attempts to accurately predict power-generation characteristics and to verify whether the stack operates within its safety limits. The 3D-stack model also provides insight for developing the simple stack model.

In Section 3.1, the structure of the fuel-cell stack is presented. In Section 3.2, a literature survey is given to position the proposed stack models. In Section 3.3, the development of the 3D-stack model consists of the following four major steps:

- Representation of fuel-cell stacks
- Description of main processes
- Formulation of stack equations
- Solution method of stack equations

The 3D-stack is simulated under both stationary and transient conditions (Sections 3.4 and 3.5). The discussion of the 3D-stack model is presented in Section 3.6. In principle, the development of the lumped stack model follows the same steps presented above and it is described in Section 3.7.

3.1 Stack Structure

Four 250 kW fuel-cell stacks connected in parallel are used in the Japanese 1 MW MCFC plant. These four stacks are of two types: one with a Hitachi configuration and the other with an IHI configuration (Kahara et al., 1996). A single cell in the Hitachi stack has a larger reaction area than that in the IHI stack (each IHI cell consists of four sub-cells connected in parallel). The distribution problems (e.g., temperature and current density) in a single cell in the Hitachi stack are more crucial than those in the IHI stack. A Hitachi stack also has more design features available from literature than those of the IHI stack. However, there are still many unknown features about both the Hitachi and the IHI stacks due to the confidential policies of the companies concerned. This study focuses on one type of fuel-cell stack: the Hitachi stack.

The structure of a Hitachi stack is illustrated in Figure 3.1 (Fujimura et al., 1992). The fuel and oxidant gases are fed to the stack separately via the anode and cathode gas input manifolds. Then gases are distributed to each cell where electrochemical reactions take place. The gas-transport in each cell involves the diffusion of reactant and product gases through the porous electrodes and their flow along the cell channels. Finally, the exhaust gases from each cell are discharged through the gas output manifolds. The electricity and heat are generated in the reaction region of a cell, which consists of an electrolyte, an anode, and a cathode of about 1 m². A stack of 1 MW
contains many hundreds of cells. A stack normally operates in a temperature range of 550°C to 750°C and in a pressure range of 0.1 MPa (ambient atmosphere pressure) to 0.7 MPa.

![Structure of a Hitachi fuel-cell stack](image)

**Figure 3.1 Structure of a Hitachi fuel-cell stack**

The dimensions of each cell are about 1 m long, 1 m wide and about 10 mm high. The dimension of the pores in the electrodes is in the order of a μm. Hence, the phenomena in a stack can be identified appropriately at electrode level (micro-level), at cell level, and at stack level (macro-level) (IEA, 1992). Most studies about fuel cells are from a chemical engineer’s viewpoint and place the emphasis on building better electrodes and electrolytes through studying the processes at micro-level. However, this study is from a mechanical engineer’s viewpoint and emphasizes operating a stack through studying the cell and stack processes at macro-level. The electrochemical performance of the given electrode and electrolyte is assumed to be known (e.g. known empirical equation to calculate local electrical resistance). In addition, this chapter deals with an MCFC stack without internal reforming. The reforming process is studied separately in a reformer model.

### 3.2 Literature Overview

A literature survey is given with regard to numerical approaches to an individual MCFC stack, an MCFC stack for system analysis, and other types of fuel-cell stacks.

#### 3.2.1 Individual MCFC stack study

The fuel-cell stack power-generation performance depends on the phenomena at the electrode, cell, and stack levels. Therefore, the modeling of the fuel-cell stack is focused on these three levels as shown in Figure 3.2.
Chapter 3  Fuel-cell Stack Model

![Diagram: Stack, Cell, Electrode]

**Figure 3.2 Fuel cell modeling at different levels**

The related literature information on MCFC models at these three levels is given as follows:

**At electrode level.** Electrode models can be divided into two types. The first type of electrode model (e.g., Sampaethe et al., 1980, and Yuh and Selman, 1984) handled the fundamental microscopic processes at electrode level quantitatively. They described the processes in the electrode pores, the dimensions of which are in μm and require detailed data of the electrode characteristics (e.g. geometry and physical properties). Therefore, the first type of model is difficult to integrate into the stack model at macro-level. The second type of electrode model (e.g., Watanabe et al., 1991, Yuh and Selman, 1991 and Wilemski et al., 1985), used empirical correlation to represent the electrode performance by a local resistance. The local resistance is determined by coefficients of the cell characteristics and operating conditions (i.e. local gas compositions and temperature). These coefficients in the empirical equations can be derived from experimental results using similar test cells on small scale. The second type of electrode model (without dealing with the microscopic processes) is suitable for integration into the stack model.

**At cell level.** Frequent reference is made to the cell model of Wolf and Wilemski (1983). Their model deals with the cell processes in a two-dimensional, steady-state form. The cell model takes into account the gas stream utilization due to the electrochemical reaction, the conductive heat transfer by the bulk streams, and the inplane heat conduction through the cell hardware. Individual porous electrode models are used to predict the local dependence of the current density on the cell temperature and gas composition. The cell model of Wolf and Wilemski (1983) showed that the temperature difference within the cell could be several hundred degrees Kelvin at maximum load for a cell with a reaction area of 1 m². Therefore, the isothermal approximation is no longer appropriate for a realistic reaction area of about 1 m².

When evaluating the cell performance, it is important to predict the cell temperature distribution because the local current density depends on the temperature. A cell model in lumped form based on physical laws usually cannot adequately represent the performance of the stack with a cell reaction area about 1 m². A lumped stack model is not capable of including the temperature gradients that essentially determine the cell current output. Watanabe et al. (1991) extended the cell model of Wolf and Wilemski (1983) to transient conditions, and used their own empirical correlation equation for the local cell performance.

**At stack level.** For a fuel-cell stack without internal reforming, Fujimura et al. (1992) provided a model which describes a 3D steady-state temperature distribution across a stack without reforming. This model takes into account the heat transfer in the stacking direction and the heat transfer between the end-plates and the surroundings. Matsuyama et al. (1997) modified the model of Fujimura et al. (1992) by using a new electrode model and treated the effect of the boundary temperature.
For fuel-cell stacks with internal reforming, Shinoki et al. (1995) provided a two-dimensional steady-state model incorporating the reforming processes.

The above literature provides no indication that MCFC stack models are available that can be used for the computation of the distribution of certain stack parameters under transient conditions of MCFC stacks. Hence, a transient model must be developed to study the transients of MCFC stacks. Two approaches to such a stack model are as follows:

- Extension of the cell model of Watanabe et al. (1991) to a stack model. This can be done by taking into account the heat transfer (Matsuyama et al., 1992) and gas transport processes with regard to the stack configuration.
- Extension of the stack model of Matsuyama et al. to cover transient conditions.

### 3.2.2 MCFC stack study for system analysis

There are MCFC studies for system analysis under steady-state or transient conditions. Usually the stack model used for integration into system models is in a simple form (e.g. lumped or one-dimensional). The steady-state stack models used for integration into steady-state system models, e.g., the models of Uchijama and Segawa (1991), Kivisaari (1992), van der Laag and Verbruggen (1994), and De Groot and Woudstra (1995), compute the stack input or output parameters on the basis of mass and energy balances under design conditions. However, these MCFC stack models do not represent the stack operating characteristics during changes from full to partial loads.

The dynamic stack models used for integration into dynamic system models, e.g., the model of Yamaguchi et al. (1990), represent the stack operating characteristics. The stack model is a lumped model and derived from experimental data. The model performance depends on the availability and the quality of the experimental data.

The literature provides no indication that general dynamic MCFC stack models are available for system analysis.

### 3.2.3 Other types of fuel-cell studies

The work on the other types of fuel cell such as SOFC, PAFC, and PEM, may also provide useful information on fuel cell modeling to our study. The SOFC activities are most relevant to our MCFC simulation. Achenbach (1994 and 1995) provided the current and temperature distributions in a SOFC stack under both steady-state and transient conditions. However, his model is still based on the assumption of a uniform gas distribution along the stack direction. In the modeling of a PEM, Amphlett et al. (1995) developed a parametric model by using a combination of mechanistic and empirical modeling techniques, and gave the resulting empirical model a firmer theoretical basis.
3.3 Development of 3D Fuel-cell Stack Model

A stand-alone stack model is developed that accurately predicts the power generation behavior of a MCFC. The same model is also capable of predicting the internal distributed behavior of the stack. Since the internal behavior of the stack can be described, it is easy to determine whether its operating limits are violated for a certain power generation. To create such a model much effort is expended in developing a physically based 3D-stack model.

The proposed stack model extends the 2D cell model of Watanabe et al. (1991), to a stack model by taking into account the heat transfer in stack direction (Matsuyama et al., 1992) and gas transport processes with regard to the stack configuration. Consequently, the stack model must be in a 3D dynamic form. The development of the 3D-stack model consists of four major steps as follows:

- Representation of fuel-cell stacks
- Description of main processes
- Formulation of stack equations
- Solution method of stack equations

3.3.1 Representation of fuel-cell stacks

Two major simplifications are introduced to represent the complicated fuel-cell stack structure shown in Figure 3.1.

- **Known power-generation characteristics at electrode level.** The dimensions of the electrode structure are much smaller than the dimensions of the cell structure (the pore in an electrode is in the order of a μm, whereas the cell has a reaction area of 1 m² and a thickness of 10 mm). The detailed structure within the electrodes and electrolyte is not included, and the processes at electrode level are not treated in detail. The power-generation characteristics are assumed to be known. More specifically, the empirical equation of the local electrical resistance is used (further discussed in Section 3.3.2.2 and in Appendix C.1).

- **Simplified gas manifolds.** The gas manifolds are simplified as an equivalent rectangular channel. The across section area of the rectangular channel is equal to the total area of the cylindrical gas channels. The average gas velocity in the simplified rectangular channel maintains the same velocity as that in the cylindrical gas channels.

Figure 3.3 shows the proposed stack representation. The stack structure is represented by a series of repeated cells, stack walls, and gas manifolds. Each cell contains a cell unit (including electrolyte, anode, and cathode), two half-separators, a layer of fuel gas, and a layer of oxidant gas.

The stack representation in Figure 3.3 includes the heat and gas transport processes at stack level, the gas transport, the chemical reactions, and the heat transfer processes at cell level. It can also incorporate the impact of processes at electrode level (i.e. electrochemical reactions).
The simplified stack is assumed to have the following specifications:

- The stack has an internal gas manifold. The cell is with cross-flow (for examining the model performance, the co-flow and counter-flow cases are also calculated). The inputs and outlets of the fuel and oxidant gases are located at the bottom of the stack.
- The fuel and oxidant gases flow in narrow, smooth-walled channels of constant cross section.
- The stack wall is completely insulated. However, capabilities to permit heat transfer between the stack walls and atmospheric ambient gas, or to use stack walls of fixed temperature or fixed heat flux have been built into the model.

### 3.3.2 Description of main processes

The total power-generation performance of a stack depends directly on two local aspects: local electrochemical-reaction rates and power-generation characteristics at electrode level. However, these two local aspects are also closely related to both gas concentration and temperature. Therefore, the processes significant for the power-generation performance of a stack are classified into four aspects: i) electro- and chemical reactions, ii) power-generation characteristics, iii) gas-transport, and iv) heat generation and transfer. These four processes are modeled at macro-level. Though the relevant processes at electrode level are not modeled in detail, their impacts are incorporated.

In addition, it should be mentioned that the important processes (e.g., corrosion and electrode dissolution) relevant to the decay of the cell power-generation performance are not considered in this study. Cell decay is usually on a time scale of hundred hours; thus, it is not significant within the time scale of this study.

### 3.3.2.1 Electro- and chemical reactions

At the fuel-cell electrodes, the following electrochemical reactions occur:

At the anode:

\[
H_2(g) + CO_3^2-(m) \Rightarrow H_2O(g) + CO_2(g) + 2e^-
\]  
(3.1)

At the cathode:

\[
\frac{1}{2} O_2(g) + CO_2(g) + 2e^- \Rightarrow CO_3^{2-}(m)
\]  
(3.2)
The overall cell reaction:

$$H_2(g) + \frac{1}{2} O_2(g) + CO_{2(g)}(g) \rightarrow H_2O(g) + CO_{2(g)}(g)$$

\((\Delta H^0_{298} = -242 \text{ kJ/mol})\) (3.3)

where g and m stand for gas and molten state.

As a result of these electrochemical reactions, two mole electrons (e.g. two Faradays) are generated by consuming one mole H\(_2\) at the anode, and consuming a half mole O\(_2\) and one mole CO\(_2\) at the cathode.

The speed of the electrochemical reactions depends on the speed of transport of reactant species to the electrode surface. This transport process is estimated to be fast and to be on a time scale of 10 \(\mu\)s (Lee et al., 1996). Therefore, the process of these electrochemical reactions is modeled in steady-state.

The local generation of current by the electrochemical reactions (Eqs. 3.1 and 3.2) results from the local consumption of reactants and the liberation of products at cell unit surfaces. The consumption or liberation flow rate \(\bar{m}\) (mol/m\(^2\cdot\text{s}\)) of the gas species H\(_2\), CH\(_4\), N\(_2\), CO, CO\(_2\), O\(_2\), and H\(_2\)O is related to the local current \(i\) (A/m\(^2\)) generation:

\[
\bar{m} = \bar{n} \cdot \frac{i}{2F}
\]

where \(F\) is the Faraday constant (96,485 coulombs/mol); \(i\) is the local current density, \(\bar{n}\) stands for the stoichiometric reaction number of the gas species. For the electrochemical reaction at the anode (Eq. 3.1), \(\bar{n}\) is equal to:

\[
\bar{n}_{\text{anode}} = (-1, 0, 0, 0, 1, 0, 1)
\]

For the electrochemical reaction at the cathode (Eq. 3.2), \(\bar{n}\) is equal to:

\[
\bar{n}_{\text{cathode}} = (0, 0, 0, 0, -1, \frac{1}{2}, 1)
\]

In the fuel gas, the water-shift reaction takes place:

\[CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g)\] (3.8)

The water-shift reaction has a high reaction speed at a high operating temperature (600–700°C). The composition change due to the shift reaction \(\Delta n_{\text{shift}}\) is determined from the equilibrium constant of the reaction. The equilibrium constant \(K_{\text{shift}}\) is a function of temperature.

\[
K_{\text{shift}} = \frac{(y_{CO_2}^o + \Delta n_{\text{shift}}) \cdot (y_{H_2}^o + \Delta n_{\text{shift}})}{(y_{CO}^o - \Delta n_{\text{shift}}) \cdot (y_{H_2O}^o - \Delta n_{\text{shift}})} = e^{\frac{-\Delta G}{RT}}
\]

where superscript \(o\) denotes the gas concentration before the shift reaction, \(y\) is the molar fraction gas, \(\Delta G\) is the change in Gibbs free energy, \(R\) is the gas constant, and \(T\) is the temperature in Kelvin. \(K_{\text{shift}}\approx 2\) at 650°C (Smith and van Ness, 1987).

### 3.3.2.2 Power-generation characteristics

The cell-unit performance of the electricity generation is expressed:

\[
V = E - \Delta V_{\text{ohmic}} - \Delta V_{\text{anode}} - \Delta V_{\text{Cathode}}
\] (3.10)
where $V$ (V) is the cell working voltage, $E$ (V) is the reversible local cell potential, $\Delta V_{\text{ohmic}}$ (V) is the local voltage losses due to the internal ohmic resistance, and $\Delta V_{\text{anode}}$ (V) and $\Delta V_{\text{cathode}}$ (V) are the local voltage losses due to an overpotential at the anode and cathode respectively. $E$ is given by the Nernst potential:

$$E = E^0 + \frac{RT}{2F} \ln \frac{y_{H_2} \times y_{O_2}^{0.5} \times y_{CO_2(e)}}{y_{H_2O} \times y_{CO_2(a)}} + \frac{RT}{4F} \ln P$$

where $E^0$ (V) is the standard potential, $R$ is the gas constant (8.314 J/mol.K), $y$ (mol/mol) is the local gas concentration, $T$ (K) is the cell operating temperature, and $P$ ($10^5$ Pa) is the gas pressure.

Wilemski et al. (1985), Yuh and Selman (1991), and Watanabe et al. (1991) predicted the local dependence of the current density on the electrode structure and the local operating conditions (e.g. temperature, pressure, and gas composition). Our stack model uses the approach of Watanabe et al. (1991). This approach uses the lumped local resistance $R_{\text{local}}$ to represent the losses of the ohmic resistance and overpotentials of the anode and cathode. The Eq. 3.10 is then expressed by Eqs. 3.12 and 3.13.

$$V = E - i \times R_{\text{ohmic}} - i \times R_{\text{anode}} - i \times R_{\text{cathode}} = E - i \times R_{\text{local}}$$

$$i = \frac{E - V}{R_{\text{local}}}$$

$R_{\text{local}}$ is determined by the inherent cell characteristics and local operating conditions (e.g. the operating temperature and partial gas pressure). Appendix C.1 presents the formulation of $R_{\text{local}}$.

The potential $E$ in each cell is used in two-dimensional form. In Eq. 3.11, the gas concentrations are defined by their values at the anode and cathode surfaces, the temperature by the average value of the cell unit temperature in the stack direction, and the gas pressure by the fuel gas pressure. The pressure difference between the fuel and oxidant is a few percent of their operating pressure. Similarly, the local current density $i$ and resistance $R_{\text{local}}$ are used in two-dimensional form in each cell. However, each cell in a stack has different operating conditions. Therefore, the potential $E$, the local current density $i$, and the local resistance $R_{\text{local}}$ are different from cell to cell, and depend on the cell location in the stack.

### 3.3.2.3 Gas-transport processes

The gas-transport processes in a stack to be considered are: i) the fuel and oxidant gases flow separately through the gas manifolds in the stack direction without electrochemical reactions, ii) the fuel and oxidant gases flow along the cell channels while the reactants are consumed and products liberated at the cell unit surface, and iii) the exhaust gases from each cell are discharged through the gas output manifolds.

### 3.3.2.4 Heat generation and transfer

Analysis of the heat generation and heat transfer processes is important, because the temperature distribution is closely related to the reaction rate of the electrical and chemical reactions and to power generation characteristics. Heat is generated due to the electrochemical reaction, cell losses, and the water-shift reaction.
Heat generation due to electrochemical reaction and cell losses. The local heat generation in the cell unit arises from the electrochemical reaction and cell losses. The heat generation is assumed to be homogenous in the stack direction in the cell unit. The calculation of the volumetric heat generation sources $q_v$ (kJ/m$^3$.s) reads:

$$q_v = \frac{i \cdot (-T \Delta S + \frac{(E - V)}{2F})}{t_{cell}}$$  \hspace{1cm} (3.14)

where $\Delta S$ (kJ/(mol×K)) is the entropy change of the reaction, $\Delta H_v$ (kJ/mol) is the enthalpy change, and $t_{cell}$ (m) is the thickness of the cell unit.

When inhomogeneous heat generations in the anode, cathode and electrolyte are considered, the heat generation is defined separately for the anode, cathode, and electrolyte zones respectively.

Heat generation due to water-shift reaction. There is heat generation in the fuel gas due to the water-shift reaction. The calculation of the generated heat $q_s$ (kJ/m$^3$.s) reads:

$$q_s = \Delta H_{shift} \times \Delta n_{CO}$$  \hspace{1cm} (3.15)

where $\Delta H_{shift}$ (kJ/mol) is the enthalpy change of the shift reaction and $\Delta n_{CO}$ (mol/m$^3$.s) is the molar flow rate change in the fuel gas volume unit. The calculation of $\Delta n_{CO}$ is based on the water-shift reaction rate $\Delta n_{shift}$.

After the description of the different heat generations sources, the heat generation and heat transfer processes can be presented for the fuel gas, oxidant gas, cell unit, and separator separately.

Fuel gas. The heat generation in the fuel gas and the boundary conditions of the heat transfer are shown in Figure 3.4.

![Figure 3.4 Heat generation and heat transfer processes of fuel gas](image)

$q_s$: reaction heat of water-shift;
$Q_{SF}$: convective heat between fuel gas and cell unit;
$Q_{EF}$: convective heat between fuel gas and separator;
$Q_{MF}$: heat transfer due to mass transfer in fuel gas side.

In this section, E stands for a cell unit element, S stands for a separator element, F stands for a fuel gas element, and O stands for oxidant gas.
Oxidant gas. The heat transfer processes in a layer of oxidant gas are shown in Figure 3.5.

\[
\begin{align*}
\text{Oxidant gas} & \quad (T_O) \\
Q_{EO} & \\
Q_{SO} & \quad Q_{MO}
\end{align*}
\]

- $Q_{EO}$: convective heat between oxidant gas and cell unit;
- $Q_{SO}$: convective heat between oxidant gas and separator;
- $Q_{MO}$: heat transfer due to mass transfer in oxidant gas side.

**Figure 3.5 Heat transfer processes of oxidant gas**

The heat generation in the cell unit and the boundary conditions of the heat transfer are shown in Figure 3.6.

\[
\begin{align*}
\text{Cell unit} & \quad (T_c) \\
Q_{ES(C1)} & \quad Q_{ES(C2)} \quad Q_{ES(r1)} \quad Q_{ES(r2)} \quad Q_c \quad \text{heat generation of reaction and cell losses;} \\
Q_{EF} & \quad \text{convective heat between fuel gas and cell unit;} \\
Q_{ES(C1)} & \quad \text{conductive heat between cell unit and up-separator;} \\
Q_{ES(r1)} & \quad \text{radiative heat between cell unit and up-separator;} \\
Q_{MF} & \quad \text{heat transfer due to mass transfer in fuel gas side;} \\
Q_{MO} & \quad \text{heat transfer due to mass transfer in oxidant gas side;} \\
Q_{SO} & \quad \text{convective heat between oxidant gas and cell unit;} \\
Q_{ES(C2)} & \quad \text{conductive heat between cell unit and down-separator;} \\
Q_{ES(r2)} & \quad \text{radiative heat between cell unit and down-separator.}
\end{align*}
\]

**Figure 3.6 Heat generation and heat transfer processes of a cell unit**

Separator. The heat transfer boundary conditions of the separator are shown in Figure 3.7.

\[
\begin{align*}
\text{Up separator} & \quad (T_{S(up)}) \\
Q_{ES(C1)} & \quad Q_{SF} \quad Q_{ES(r1)} \\
Q_{ES(C2)} & \quad Q_{SO} \quad Q_{ES(r2)} \\
\text{Down separator} & \quad (T_{S(down)})
\end{align*}
\]

- $Q_{ES(C1)}$: conductive heat between cell unit and up-separator;
- $Q_{SF}$: convective heat between fuel gas and up-separator;
- $Q_{ES(r1)}$: radiative heat between cell unit and up-separator;
- $Q_{ES(C2)}$: conductive heat between cell unit and down-separator;
- $Q_{SO}$: convective heat between oxidant gas and down-separator;
- $Q_{ES(r2)}$: radiative heat between cell unit and down-separator.

**Figure 3.7 Heat transfer processes of separator**

### 3.3.3 Formulation of stack equations

This section gives the formulation of the stack equations according to the stack representation and the main processes described in Section 3.4.1 and in Section 3.4.2. The stack is divided into three computational regions: in input and output gas manifolds and in the repeated cells. The processes in the gas manifolds are relatively simple and are based on the following two considerations:

- **No reactions.** There are no electrochemical or chemical reactions in the gas manifolds. The water-shift reaction is assumed to occur and reach equilibrium instantaneously at the stack inlet. This assumption is justified because: i) the gas reaches its equilibrium rapidly at a high
temperature (around 600°C), and ii) owing to the small temperature variation in the gas manifolds the equilibrium state does not shift significantly. (The temperature variation in the gas manifold is expected to be a few percent of the temperature change along the cell direction.)

- **Laminar gas flow.** In the manifold channels, the gas flow is in laminar form. This assumption is justified because the gases flow at a low speed (usually smaller than 1 m/s) (CRIEPI, 1995) and the small cross section of the gas manifold results in a low Reynolds number.

In the repeated cells region, the cell power-generation behavior depends on the gas flow and temperature distributions. The main processes modeled are:

- Transport of fuel and oxidant gases
- Water-shift reaction in the fuel gas
- Consumption of reactants and liberation of products at the cell unit surfaces due to electrochemical reactions
- Heat generation in the cell unit due to the electrochemical reactions and cell losses
- Heat transfer between the separator, gas, and cell unit
- Heat conduction within the separator and the cell unit

The variables which essentially determine the cell power-generation behavior are the gas velocity, the gas concentration, pressure, and temperature. This section describes the stack conservation equations of gas species, energy, and momentum based on Patankar (1980).

### 3.3.3.1 Conservation of chemical species

In the presence of a velocity field \( \vec{V} \), the conservation of chemical species is expressed as

\[
\frac{\partial}{\partial t} (\rho \cdot \vec{y}) + \text{div}(\rho \vec{V} \cdot \vec{y} + \vec{J}_{\text{diffusion}}) = \vec{R}
\]  \hspace{1cm} (3.16)

Here \( \partial(\rho \vec{y})/\partial t \) denotes the mass rate change of the chemical species per unit volume. The quantity \( \rho \vec{V} \cdot \vec{y} \) is the convection flux of the species. \( \rho \) is local density (kg/m³). \( \vec{y} \) is the vector of the gas species concentration (mol/mol). \( \vec{J}_{\text{diffusion}} \) stands for the diffusion flux, which is caused by the gradients of \( \vec{y} \). The quantity \( \vec{R} \) on the right-hand side is the mass generation rate of the chemical species per unit volume (kg/s m³).

The diffusion flux \( \vec{J}_{\text{diffusion}} \) is expressed by the use of Fick's law of diffusion,

\[
\vec{J}_{\text{diffusion}} = -\Gamma \times \text{grad} \vec{y}
\]  \hspace{1cm} (3.17)

where \( \Gamma \) is the diffusion coefficient.

In the fuel gas, a local \( \vec{R} \) exists due to the water-shift reaction. The quantity of this \( \vec{R} \) is determined by the reaction rate multiplied by the stoichiometric number of the gas species. In the oxidant gas, there is no reaction. Hence, the local \( \vec{R} \) is zero.

\[
\vec{R}_{\text{fuel--gas}} = \Delta n_{\text{shift}} \cdot \vec{n}_{\text{shift}} \cdot \vec{M}_w \cdot 10^3
\]  \hspace{1cm} (3.18)

\[
\vec{R}_{\text{oxidant--gas}} = 0
\]  \hspace{1cm} (3.19)
where the $\Delta n_{\text{shift}}$ (mol/s.m$^3$) is based on Eq. 3.11. $\bar{n}_{\text{shift}}$ stands for the stoichiometric number of the reaction: $\bar{n}_{\text{shift}} = (1, 0, 0, -1, 1, 0, -1)$. $\bar{M}_w$ stands for the molecular weight (g/mol) of gas species of H$_2$, CH$_4$, N$_2$, CO, CO$_2$, O$_2$, and H$_2$O (Atkins, 1991).

For example, conservation equations for H$_2$ in fuel gas and for CO$_2$ in oxidant gas lead to:

\[
\frac{\partial}{\partial t} (\rho \cdot y_{H_2}) + \text{div}(\rho \bar{V} \cdot y_{H_2}) - \text{div}(\Gamma_{H_2} \times \text{grad} y_{H_2}) = \Delta n_{\text{shift}} \times 1 \times 2.02 \times 10^3
\]  

(3.20)

\[
\frac{\partial}{\partial t} (\rho \cdot y_{CO_2}) + \text{div}(\rho \bar{V} \cdot y_{CO_2}) - \text{div}(\Gamma_{CO_2} \times \text{grad} y_{CO_2}) = 0
\]  

(3.21)

At the boundary surfaces of the fuel and oxidant gases adjacent to cell unit, there are consumption of reactants and liberation of products due to electrochemical reactions. The gas generation is related to the local current density.

\[
\bar{R}_{\text{fuel-surface}} = \frac{i}{2F} \cdot \bar{n}_{\text{anode}} \cdot \bar{M}_w \cdot 10^3
\]  

(3.22)

\[
\bar{R}_{\text{oxidant-surface}} = \frac{i}{2F} \cdot \bar{n}_{\text{cathode}} \cdot \bar{M}_w \cdot 10^3
\]  

(3.23)

### 3.3.3.2 Conservation of energy.

The energy equation for fuel and oxidant gases can be written as

\[
\frac{\partial(h \rho)}{\partial t} + \text{div}(\rho \bar{V} h - \lambda \nabla h) = S_h
\]  

(3.24)

where $h$ (kJ/kg) is the specific enthalpy, $\lambda$ (kJ/m.K) is the thermal conductivity, $C_p$ (kJ/kg.K) is the heat capacity, and $S_h$ (kJ/s.m$^3$) is the volumetric rate of heat generation.

In the fuel gas, the heat generation $S_h$ is due to the water-shift reaction $q_\text{s}$ (Eq. 3.15). In the oxidant gas, there is no reaction heat source. Hence, $S_h$ is zero.

\[
S_h|_{\text{fuel-gas}} = q_s
\]  

(3.25)

\[
S_h|_{\text{oxidant-gas}} = 0
\]  

(3.26)

At the boundary surfaces of the fuel gas and oxidant gas adjacent to cell unit, the heat sources are:

\[
S_h|_{\text{fuel-surface(bottom)}} = Q_{EF} + Q_{MF} + Q_{ES(r1)}
\]  

(3.27)

\[
S_h|_{\text{oxidant-surface(top)}} = Q_{EO} + Q_{MO} + Q_{ES(r2)}
\]  

(3.28)

The energy equation for the separator and cell unit can be written as

\[
\rho C_p \frac{\partial T}{\partial t} - \bar{\lambda} \cdot \nabla^2 T = S_h
\]  

(3.29)

In the separator, there is no heat generation, $S_h$ is zero. In the cell unit, the heat generation $S_h$ is due to $q_e$ (Eq. 3.14).

\[
S_h|_{\text{separator}} = 0
\]  

(3.30)

\[
S_h|_{\text{cell-unit}} = q_e
\]  

(3.31)
The energy equations for separator and cell unit lead to:

\[
\rho_s C_{p(s)} \frac{\partial T_s}{\partial t} = - (\lambda_{eff, x(s)} \frac{\partial^2 T_s}{\partial x^2} + \lambda_{eff, y(s)} \frac{\partial^2 T_s}{\partial y^2} + \lambda_{eff, z(s)} \frac{\partial^2 T_s}{\partial z^2}) = 0
\]  

(3.32)

\[
\rho_e C_{p(e)} \frac{\partial T_e}{\partial t} = - (\lambda_{eff, x(e)} \frac{\partial^2 T_e}{\partial x^2} + \lambda_{eff, y(e)} \frac{\partial^2 T_e}{\partial y^2} + \lambda_{eff, z(e)} \frac{\partial^2 T_e}{\partial z^2}) = q_e
\]  

(3.33)

At the boundary surfaces of the separators to fuel and oxidant gas sides, the heat sources are:

\[
S_{h|sep} = Q_{SF} + Q_{ES(e)}
\]  

(3.34)

\[
S_{h|sep} = Q_{SO} + Q_{ES(e)}
\]  

(3.35)

### 3.3.3.3 Conservation of momentum

Since the fuel gas is a Newtonian fluid with a laminar flow pattern, the differential equation governing the momentum conservation of the fuel gas in x direction can be written as (Patankar, 1980):

\[
\frac{\partial (\rho u)}{\partial t} + \text{div}(\rho \nabla u) = \text{div}(\mu \text{grad } u) \frac{\partial p}{\partial x} + B_x + V_x
\]  

(3.36)

where \( u \) denotes the x-direction velocity, \( \mu \) is the viscosity, \( p \) is the pressure, \( B_x \) is the x-direction body force per unit volume, and \( V_x \) stands for the viscous terms that are in addition to those expressed by \( \text{div}(\mu \text{grad } u) \).

The momentum conservation of the oxidant gas in z direction can be written as:

\[
\frac{\partial (\rho w)}{\partial t} + \text{div}(\rho \nabla w) = \text{div}(\mu \text{grad } w) \frac{\partial p}{\partial z} + B_z + V_z
\]  

(3.37)

where \( w \) denotes the z-direction velocity.

### 3.3.4 Solution method of stack equations

In order to solve the stack conservation equations of gas species, energy, and momentum, this section presents the solution approach. The CFD program PHOENICS that was introduced in Section 2.8. PHOENICS provides a solver for fluid-flow, heat-transfer, chemical-reaction, and related problems ranging in complexity from one-dimensional single-phase and steady-state, to 3D multi-phase and transient. In this study, the CFD software package PHOENICS is used as a solution tool. The solution method of the 3D-stack equations is presented in Appendix C.4. It consists of: i) numerical method of PHOENICS, ii) program structure of PHOENICS, iii) implementation of 3D-stack model in PHOENICS, and iv) evaluation of the simulation results.
3.4 Performance of the Stack Model under Stationary Conditions

3.4.1 Setting-up cases

To examine the model equations dealing with the main processes at cell level under stationary conditions, three cases have been selected to show the distributions of the temperature, pressure, gas concentration, and density across cells with different flow patterns. Comparing the temperatures and pressures in cells with different flow patterns is a commonly used method to evaluate the correctness of a cell model (Watanabe, 1992 and Achenbach, 1994). Then, the stack case is set up to examine the model equations dealing with the gas flow in the manifolds, the heat transfer among cells, and the stack wall boundary conditions. Table 3.1 lists the objectives of the cases that have been set up.

<table>
<thead>
<tr>
<th>Cases</th>
<th>Illustrations</th>
<th>Objectives of demonstration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell with cross-flow</td>
<td></td>
<td>Distribution of temperature across the cell at full and partial electrical load</td>
</tr>
<tr>
<td>Cell with co-flow</td>
<td></td>
<td>Distribution of temperature, pressure, concentration, and density along the cell direction</td>
</tr>
<tr>
<td>Cell with counter-flow</td>
<td></td>
<td>Distribution of temperature and pressure along the cell direction</td>
</tr>
<tr>
<td>Stack with cross-flow</td>
<td></td>
<td>Temperature distribution across the stack and mass distribution along the stack</td>
</tr>
</tbody>
</table>
These four cases are assumed to be characterized by the following specifications:

- Each cell has an electrochemically active area of 1 m x 1 m and a thickness of 10 mm.
- The stack contains 5 cross-flow cells. The inlet and the outlet of the fuel and oxidant gases are located at the bottom of the stack. This means that the fuel or oxidant gas first goes upwards along the stack direction within the inlet manifolds, then turns along the cell flow path, and finally leaves the stack downwards via the outlet manifolds.
- The fuel and the oxidant gases are supplied by the external reformer. The inlet temperature of the fuel and oxidant gases is 600°C. The outlet gas is at atmospheric pressure. Both the fuel gas and the oxidant gas are considered as ideal (based on high temperature and a low gas pressure). The flow rates of the fuel and the oxidant gas are 0.05 mol/s and 0.8 mol/s respectively for the three cell cases. The flow rates of the fuel gas and the oxidant gas are 0.25 mol/s and 4.0 mol/s respectively for the stack case.
- The average current density is set to 1500 A/m² if without specification.

The stack operating conditions and design features (e.g. geometry and physical properties) are also described in Chapter 2 and Appendix A.6. The results of the four cases are discussed in the following sections. The height of the cell or stack in the following figures has been exaggerated by 20:1.

3.4.2 Cell with cross-flow

**Temperature distribution.** In this section the temperature distributions are examined in the fuel cell, since these effectively illustrate the basic features of the operation performance. The following three factors contribute to the temperature distribution:

- Reversible heat generated by chemical reactions
- Irreversible heat generated by electrical resistance
- Heat transfer to the surroundings

The temperature profile of the cell with cross-flow operating at an average current of 1500 A/m² and 750 A/m² is presented in Figures 3.8 and 3.9 respectively.
Figure 3.8 (a) Temperature distribution at a current density of 1500 A/m², and (b) isothermal surface of 700°C and 630°C

The main features shown in Figures 3.8 and 3.9 can be identified as follows:

- The point of maximum temperature is at 710°C and is approximately located at the outlet of oxidant gas and near the inlet of fuel gas. This may be explained qualitatively by three factors. First, the reversible heat from the chemical reactions at this location is high, since the fuel gas is relatively concentrated. The fuel gas utilization is much higher than that of the oxidant gas, which implies that the chemical reaction rate is more dependent on the fuel gas composition than that of oxidant gas. Second, the irreversible heat (i²×R_{amp}) is usually high due to a high local current density i. However, the lumped local resistance R_{local} does not have a high value at a high temperature (refer to Appendix C.1). Thirdly, the oxidant gas has been heated up as it flows through the cell channel. The temperature of the oxidant gas has more impact than that of the fuel gas, since the oxidant gas flow is much larger than the fuel gas.
As expected, the maximum temperature and the temperature gradient of a cell operating at a current density of 1500 A/m² are much higher than at 750 A/m². Hence, a greater temperature difference occurs at higher current density.

**Figure 3.9** (a) Temperature distribution at a current density 750 A/m² and (b) isothermal surface of 650°C and 610°C

### 3.4.3 Cell with co-flow

The distributions of the temperature, pressure, density, and gas compositions for a co-flow cell operating at an average current density of 1500 A/m² are discussed below. The corresponding results are shown in Figure 3.10.
The main features of Figure 3.10 can be summarized as follows:

- The temperatures of the gases and cell hardware increase in the direction of the gas flow, and the increment is largest near gas inlets. This is the result of the heat generated from the chemical reactions and from the electrical resistance. In this case, the point of maximum temperature is at 680°C, and is located around the outlet of the anode gas. However, the highest temperature gradient is near the inlet between the cathode gas and the cathode electrode.

- The pressure of the fuel and oxidant gas decreases in the direction of the gas flow as expected. The highest pressure difference is 400 Pa, which is between the inlet of the fuel and oxidant gases. It is not large because the point of maximum pressure of fuel gas corresponds to the point of maximum pressure of the oxidant.

- As expected, the H₂ concentration at the anode and CO₂ concentration at the cathode decrease in the direction of the gas flow, and the decrease is more rapid near the inlet of the gas. This implies a greater rate of the chemical reactions in the incoming gas than in the depleted gas.

- The fuel gas density significantly increases and the oxidant gas density decreases in the direction of the gas flow. In this case, the fuel gas density at the inlet is lower than 0.17
kg/m³ and is greater than 0.32 kg/m³ at the outlet, while the oxidant gas density at the inlet is greater than 0.42 kg/m³ and is lower than 0.38 kg/m³ at the outlet. The increase of the fuel gas density results from the greater percentage of heavier molecules and the greater flow rate due to the electrochemical reaction at the anode, which consumes 1 mole lighter molecules H₂, and liberates 1 mole heavier molecules H₂O and 1 mole heavier CO₂. The decrease of the oxidant gas density results from the consumption of CO₂ and O₂ due to the electrochemical reaction at the cathode. The considerable change in the fuel gas density shows that the usual assumption of constant gas density at cell or stack level is unrealistic in most models.

3.4.4 Cell with counter flow

The temperature and pressure distributions for a counter flow cell operating at an average current density of 1500 A/m² are illustrated in Figure 3.11. The main characteristics are identified as follows:

- The point of maximum cell temperature is 700°C, located near the inlet of the anode gas. The temperature gradient is more uniform than that of the co-flow cell.
- The highest pressure difference is 700 Pa, which occurs between the fuel gas outlet and the oxidant gas inlet.

![Figure 3.11 (a) Temperature of a counter-flow cell at a current density of 1500 A/m² and (b) pressure distribution (100 Pa)](image)

3.4.5 Comparison of temperature and pressure distributions in different cells

The maximum temperature and pressure difference for fuel cells with different flow patterns described in the previous sections are summarized in Table 3.2. Table 3.2 shows that the cell with cross-flow has the highest maximum temperature of 710°C and the cell with co-flow has the lowest maximum temperature of 680°C. These results are qualitatively consistent with the predicted results of Watanabe (1992). Hence, the model dealing with processes at cell level is acceptable.
Table 3.2 Maximum temperature and pressure difference in fuel cells

<table>
<thead>
<tr>
<th>Cases</th>
<th>Maximum temperature and location</th>
<th>Largest pressure difference and location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross-flow</td>
<td>710°C, at the outlet of oxidant gas and near the inlet of fuel gas</td>
<td>600 Pa, near the oxidant gas inlet and the fuel gas outlet</td>
</tr>
<tr>
<td>Co-flow</td>
<td>680°C, around the outlet of the fuel gas</td>
<td>400 Pa, between the fuel and oxidant gas inlets</td>
</tr>
<tr>
<td>Counter flow</td>
<td>700°C, near the inlet of the fuel gas</td>
<td>700 Pa, between the fuel gas outlet and oxidant gas inlet</td>
</tr>
</tbody>
</table>

The distributions of the temperature and pressure indicate the safe operating characteristics of a cell. The high local cell temperature causes electrolyte evaporation losses while the high pressure difference between the anode and cathode results in damage to the cell unit. Therefore, in stationary conditions, the two highest priority constraints of safe operating fuel cells are defined as Eq. 3.42 (the pressure constraint is given by Yochida and Inoue (1993)):

\[
\begin{align*}
T_{\text{max}} &< 750 \, ^\circ\text{C} \\
\Delta P_{\text{max}} &< 4 \, \text{kPa}
\end{align*}
\]  

(3.38)

where \(T_{\text{max}}\) is the highest cell unit temperature and \(\Delta P_{\text{max}}\) is the highest pressure difference between the anode and cathode. The maximum temperature and pressure values in Table 3.2 indicate that all cells operate within the safety constraints of Eq. 3.38.

3.4.6 Stack with cross flow

With the described model, the 3D distributions of crucial parameters across the stack can be obtained. Below, temperature profiles and mass distribution are calculated. The temperature distributions in a transverse section of the fuel gas outlet and the oxidant gas outlet are shown in Figure 3.12, at an average current density of 1500 A/m². The result indicates that the highest temperature is located at the top cell. The three temperature factors described in Section 3.6.2. indicate that the temperature differences in the stack direction depend on the mass distribution in the stack direction. A high temperature may result from a high reaction rate, which may be related to a high flow rate of fuel gas. Figure 3.13 shows that the cell with the highest temperature in Figure 3.12 is indeed related to the top cell (top cell No. 5) with the highest fuel gas flow.
Figure 3.12 Temperature across a cross-flow stack with a current density of 1500 A/m²

Mass flow along stack
(current density = 0, 750, 1500 A/M2)

Figure 3.13 Fuel gas distributions along the stack direction

Instead of assuming the gas distributions, the 3D-stack model is capable of calculating the gas distribution. Figure 3.13 shows the fuel gas distribution along the stack direction at an average current density of 0, 750 and 1500 A/m². The simulations indicate that the inhomogeneous performance among different cells is closely related to both the hydraulic resistance (relating to the stack geometry and wall roughness) and the density change of the fuel gas (relating to the electrochemical reaction).

When no current is drawn from the stack, the gas distribution can be predicted according to hydraulic resistance models (i.e. a cell located higher in the stack gets less fuel gas since it has a longer flow path). Figure 3.13 shows that the fuel gas distribution when the current density is
zero is qualitatively consistent with the prediction based on hydraulic resistance models. However, when a current is drawn from the fuel-cell stack, a cell located higher gets more fuel gas. This is assigned to the significant change in the fuel gas density (see Figure 3.10(d)). The impact of the variation in gas density on the gas distribution was indicated by Takashima (1993) and analyzed by He (1994). The gas distribution results in this case indicate that the commonly used hydraulic resistance methods, such as the model of Boersma and Machielse (1992), suit only low gas utilization conditions. However, this requires further confirmation.

Simulations for the stacks with 5, 10, and 20 cells were performed. For the stacks with 5, 10 and 20 cells, the computation times are in the time orders of hours, days, and weeks respectively on work-stations like Sun-IPX. Though the stack model is capable of calculating the gas distribution, it is not feasible to compute a 1 MW stack with several hundred cells on a normal PC. With a supercomputer, such as a CRAY, it is possible to calculate a stack with several hundred cells under steady-state conditions, but it is still too expensive to calculate such a stack under transient conditions.

The stack design usually allows gas distribution derivations of 2% for 20 cells under a no current generation situation, which is also the target for 100 cells (Hitachi, 1995). It is expected that the derivations of the gas distribution under power-generation conditions may be higher than the value under no current generation situation (refer to Figure 3.13). However, it is assumed that the derivations of the gas distribution between 100 cells under power-generation conditions are still small (in the magnitude of a few percents). In the following simulations under transient conditions, uniform gas distribution is assumed.

3.5 Performance of the Stack Model under Transient Conditions

The model equations dealing with transient conditions are illustrated in this section. The stack voltage or current output can be simultaneously manipulated to accommodate small load variations. However, when there are large variations in load, the flow-rates of fuel and oxidant gases must be changed to maintain the stack fuel and oxidant utilizations within the allowable ranges. The change of gas flow rates is slower than that of voltage or current. The stack response is illustrated for a +10% step change of the stack voltage, while the feeding gases to the stack remain the same. This case setup also represents one of the most severe operating conditions for a stack under load-up modes. This case shows the responses of the current density and temperature, because i) the response of the temperature distribution is inter-related to the response of the current, and (ii) the constraint of the temperature distribution has usually the highest operational priority. In a practical situation the current output can also be manipulated. The case in which the current is manipulated needs additional iteration between its local current and its total current output.

The time needed for the current or temperature to reach a new steady-state in such a stack is about one hour according to the experimental experience of Watanabe (1991). The simulation for the stack response is for a period of two hours. A smaller time-step is used at the beginning and is increased progressively. The simulation results are illustrated for t=40, 80, 120, 3600 and 7200 s, respectively.
Figure 3.14 Current density profile response at a transverse section (A/m²)

Figure 3.14 illustrates the current density distribution in the separator of cell unit five. Between 0 s and 80 s, the current density profile changes significantly, but not between 80 s and 120 s. The current density profile also changes significantly between 120 s and 3600 s, and also between 3600 s and 7200 s. The magnitude of the current density changes rapidly in the beginning and slowly later. For example, the maximum current density decreases by 300 A/m² (from 2500 to 2200 A/m²) between 0 s and 80 s, but decreases only by 100 A/m² (from 1800 to 1700 A/m²) between 3600 s and 7200 s. The current has an immediate response due to the variation of the voltage, and a fast response due to the gas concentration. Then the current has a slow decrease due to the slow temperature decrease. (A lower operating temperature results in a higher cell electrical losses.)
Figure 3.15 Temperature profile response at a transverse section (°C)

Figure 3.15 shows the dynamic temperature distribution in the middle layer of the separator. The temperature profile changes slowly. For example, the maximum temperature remains 670°C between 0 s and 120 s, decreases 20°C after one hour and another 10°C after another hour. The overall temperature decreases with increasing time, because the higher stack voltage provides a smaller current density corresponding to less heat generation.

A comparison of the changes of the current and temperature distributions in Figures 3.14 and 3.15 indicates the relationship between the current and temperature. Between t=80 s and 120 s, the current profile in Figure 3.14 remains almost the same, which agrees with the constant temperature profile in Figure 3.15. Due to the variation in temperature, the current density profile then changes again between 120 s and 3600 s and also between 3600 s and 7200 s.

It is also important to evaluate the safe stack operation under transient conditions. Since high local cell temperature causes electrolyte evaporation losses, and the temperature gradient causes differential expansion, maximum temperatures and gradients for safe stack operation are
imposed. However, no quantitative definitions of the temperature under transient conditions were found in the literature. Yochida and Inoue (1993) gave the pressure constraint. In this study, the three highest priority constraints for the safe operation of fuel cells are defined as Eq. 3.39 for the transient conditions:

$$
\begin{align*}
T_{\text{max}} &< 750 \, ^{\circ}\text{C} \\
\frac{T(t+60) - T(t)}{60} &< 10 \, \text{K/min} \\
\Delta P_{\text{max}} &< 8 \, \text{kPa}
\end{align*}
$$

(3.39)

The temperature distributions under transient conditions (Figure 3.15) and the gas pressure distributions (not shown here) confirm that the stack operation is within the safety constraints of Eq. 3.43.

### 3.6 Discussion of the 3D-Stack Model

Most fuel-cell studies focus on the electrochemical performance of electrodes and are conducted by chemical engineers. This study has approached fuel-cell stack from a mechanical engineering viewpoint and integrates the results of the electrochemical performance at electrode level. The results are useful for introducing fuel-cell stack into power-generation systems.

The stand-alone 3D-stack model has attained the first thesis goal (prediction of the power-generation characteristics and evaluation of whether a stack operates within the safety constraints). Though the 3D-stack model cannot be directly incorporated into the system model, it provides useful results for developing a simple stack for integration into the system model. The discussion of the 3D-stack model is focused on the following four aspects:

- Fuel-cell stack power-generation characteristics and safe operation
- Improvement and new functions
- Model reliability
- Usefulness for developing the simple stack model

#### 3.6.1 Fuel-cell stack power-generation characteristics and safe operation

**Fuel-cell stack power-generation characteristics.** The cells and the stack stationary performances with regard to power-generation are illustrated by the distributions of the temperature, pressure, gas concentration, and density at full load (current density of 1500 A/m²) or half load conditions. The prediction of the cells and the stack stationary characteristics are illustrated by the following cases:

- **Cell with cross-flow.** (i) the maximum temperature is 710 °C at a current density of 1500 A/m² and it is approximately located at the outlet of oxidant gas, near to the inlet of fuel gas, and (ii) as expected, the maximum temperature and the temperature gradient of a cell operating at a current density of 1500 A/m² is much higher than those at 750 A/m². Hence, larger temperature differences occur at higher current density.

- **Cell with co-flow.** (i) the temperatures of gases and cell hardware increase in the direction of the gas flow, and the increment is large near the gas inlets, (ii) the pressure of fuel and oxidant gas decreases in the direction of the gas flow, (iii) H₂ at the anode and CO₂ at the cathode decrease in the direction of gas flow, and the decrease is more rapid near the inlet of the gas,
and (iv) the fuel gas density significantly increases and the oxidant gas density decreases in the direction of gas flow.

- **Cell with counter-flow.** (i) the point of maximum cell temperature is located near the inlet of the anode gas. The temperature gradient is more uniform than that of the co-flow cell, and (ii) the highest pressure difference occurs between the fuel gas outlet and the oxidant gas inlet.

- **Stack with cross-flow.** (i) the calculated highest temperature is located at the top cell at a current density of 1500 A/m², and (ii) the fuel gas flow distribution along the stack direction is closely related to both hydraulic resistance and the density change of the fuel gas due to the electrochemical reaction.

The stack dynamic behavior was illustrated by the responses of the current density and temperature to a +10% step voltage change. The response of the stack output power consists of: i) an immediate response due to the electrode power-generation behavior, ii) a fast response due to the gas concentration variation (gas transport) (time order of 0.1 to 1 seconds), and iii) a slow response due to temperature variation (heat storage) (time order of 10 to 10² seconds).

**Evaluation of Fuel-cell stack safe operation.** The simulated temperature distributions show that the 1 MW stack is within the safety constraints. The maximum stack temperature and the maximum temperature gradient are lower than 750°C and 10 K/min.

### 3.6.2 Improvement and new functions

The 3D dynamic stack model computes the distributions of the crucial parameters in the stack under load-following modes. It has two advantages over most dynamic stack models in lumped form that are presented in the literature.

- **Improvement in predicting power-generation behavior.** The stack DC (direct current) power output depends on both the cell voltage and the current density distribution. The cell voltage is the same everywhere, however, the local current density has a significant difference in a reaction area of 1 m². By computing the distributions of the temperature and gas concentration, the 3D-stack model predicts the local current. Hence, the 3D-stack model gives a more accurate prediction of the stack power-generation behavior than a stack model in lumped parameter (which assumes uniform current distribution). The simulation results (Figure 3.14) show the two dimensional distributions of the current density. The variations in the current density are around 1000 A/m² in a cell reaction area of 1 m². It is difficult for a stack model in lumped or one-dimensional form to adequately represent such current output characteristics.

- **New functions of identifying safe stack operation.** The 3D-stack model has new functions that can easily determine whether operating limits are violated for a certain power generation. For example, in order to identify safe stack operation, it is necessary to know the large cell temperature gradients in stack space and in time (which give rise to differential expansion) and a high local temperature (which causes electrolyte evaporation losses). The 3D-stack model provides such temperature distributions that cannot be obtained from a stack model in lumped form.
3.6.3 Model reliability

Examining the reliability of the 3D-stack simulation tool includes three efforts: i) review and evaluation of the 3D-stack model development, ii) comparison with the available results from the literature, and iii) evaluation by colleagues.

Review and evaluation of the 3D-stack model development. The development of the 3D-stack model is reviewed and evaluated with regard to the following four aspects:

- **Stack representation.** The stack representation includes all major physical and chemical (electrochemical) processes at electrode, cell and stack levels.

- **Model equations.** The model equations are examined by three steps as follows:
  i. The model equations dealing with the main processes at cell level are examined under stationary conditions. The distributions of the temperature, pressure, gas concentration, and density across fuel cells are illustrated by different flow patterns (Figures 3.10-13). The predicted highest temperatures (Table 3.2) between cells with different flow patterns are qualitatively consistent with the predicted results of Watanabe (1992).
  
  ii. The equations at stack level (dealing with the gas flow in the manifolds, the heat transfer among cells, and the stack wall boundary conditions) are illustrated by the stack case under stationary conditions. The computed temperature distributions across the stack and the gas distributions among cells (Figures 3.12 and 3.13) show that the cell with the highest temperature is indeed related to the cell with a high fuel gas flow. Hence, the stack case indicates that the equations at stack level are acceptable.

  iii. The equations dealing with transient conditions are illustrated by computing the current and temperature distributions under a step voltage change (Figures 3.14 and 3.15). The current density profile changes rapidly at the beginning and slowly in the following stage and the temperature response is slow. A comparison of the changes in the current and temperature distributions indicates that the current change agrees with the temperature change.

- **Input parameters.** The input parameters for 3D-stack simulation consist of the stack operating conditions and design features. The input parameters with regard to the operating conditions are known. The input parameters with regard to the design features consist of i) accurate data from manufactures, ii) adopted data from general physical properties from literature, and iii) estimated gas channel geometry.

- **Solution method.** The solution of the stack equations (Section 3.3.4) and the simulation cases (Sections 3.4 and 3.5) show that PHOENICS is capable of solving the stack equations in 3D form under transient conditions. The two proposed criteria (convergence and grid-independence) are useful in initially evaluating the simulation results.

Comparison of computed results with the results from literature. Many assumptions and approximations have been made to achieve this stack model. The stack model therefore requires experimental validation. Usually, the temperatures at various locations can be measured under steady-state conditions. Measurements under transient conditions, however, are difficult (Kobayashi et al., 1989). The measurement of the current density distribution is not easy either, even under steady-state conditions, but it may be approached by using measured gas concentrations at various locations.
The model performance under steady-state conditions is evaluated by a comparison between the temperature profiles derived from simulations of the presented model and the temperature profiles derived from simulations given by Fujimura et al. (1992). Some measured temperature data are also given by Fujimura et al. (1992). A system for measuring the cell temperature distribution was described by Kobayashi et al. (1989). The 3D-stack model has been used to simulate the measured stack with cell dimensions of 0.36 m².

![Figure 3.18](image)

**Figure 3.18** Comparison of temperature distributions: (a) results from the 3D-stack model and (b) simulated profiles and measured data (°C) by Fujimura et al. (1992)

Figure 3.18a presents the computed temperature distribution in the middle layer of oxidant gas in the middle cell. Figure 3.18b gives the simulated temperature distributions (continuous lines) and measured temperatures (discrete dots) (Fujimura et al., 1992). The computed temperature profiles from the proposed stack model agree quantitatively with the simulated profiles given by Fujimura et al. (1992). Since few measured data are available, it is not feasible to draw the isothermal lines based on these data. The deviations between the isothermal lines computed with the proposed stack model and most of the measured data given by Fujimura et al. (1992) are less than 10 K (i.e. less than 2%). Nevertheless, it is recommended that validations should be made with more measured temperature data. Further validation of the stack model under transient conditions is also necessary.

With regard to the measurement of the current density distribution, Tsutsumi et al. (1992) measured the current density at four locations in a PAFC of 900 mm×900 mm under both steady-state and transient conditions. However, it is not feasible to draw current density profiles based on the data from these four locations. In order to identify the location of the highest current density under transient conditions, it is recommended that the gas concentrations should be measured at various inlets and outlets of the gas channels. The location with the highest variation in the gas concentrations indicates the location with the highest current density.

**Evaluation by colleagues.** The results of the 3D-stack model proposed above have been published in two refereed journal papers (He and Chen, 1995 and 1998). The 3D-stack model has also been presented to more than 20 leading fuel-cell groups in the USA, Canada, Japan, South Korea, Australia and in Europe (He et al., 1994, and He et al. 1996). Therefore, the 3D-stack model has been evaluated by many colleagues. The most interesting aspects are: i) the simulated distributions of crucial parameters under both stationary and transient conditions,
and ii) implementation of the 3D dynamic stack model by using a CFD program. The proposed main processes and some stack equations have been used by Ernest et al. (1996) for their design of the 2 MW MCFC demonstration projects in the USA. The stack representation and some approaches to the stack implementation in PHOENICS have been adopted by Ding et al. (1997) for their simulations to improve stack manufacturing.

3.6.4 Usefulness of developing the simple stack model

The 3D-stack model is not suitable for direct use as a component model for the system dynamic analysis (to realize the third and fourth thesis goals). The 3D dynamic simulation is extremely time consuming (e.g. days or weeks). Furthermore, the 3D-stack simulation is implemented by using the CFD program of PHOENICS, and it cannot be directly incorporated into the system model which is in the SPEEDUP program environment. A simple stack model for integration into the system dynamic model is obviously required.

The 3D-stack model provides insight for developing the simple stack model. The 3D-stack model has calculated the temperature and pressure distributions within the stack and verified that the stack operates within its safety constraints under both severe stationary and transient conditions. The simple stack model assumes that the stack operates within its safety constraints. The two requirements for developing a simple stack model are: i) accurate prediction of the stack power-generation characteristics with regard to load-following modes, and ii) suitability for integration into the system model. The simple stack emphasizes the input and output relations, not the distributions of crucial parameters in the stack.

Two main approaches to achieve the simple stack model are as follows:
- Represent the response characteristics of the 3D-stack model by using simple approximation equations
- Establish a stack model by using lumped parameters based on physical laws, and then remedy the accuracy loss by using the results from the 3D-stack model

This study explored both approaches. With regard to the first approach, Achenbach (1995) proposed a methodology to directly represent the response characteristics of the 3D SOFC stack model by using simple approximation equations. The simplified stack model uses the steady-state simulation results of the 3D-stack model as initial conditions and achieves the same response time as the 3D-stack model. The prediction of the time response is obtained by using an approximate equation (including two dimensionless governing parameters: the modified Fourier number and the source term number). The adaptation of his SOFC approach to simplify the 3D MCFC stack model is presented in Appendix C.6. This approach requires: (i) initial conditions from the 3D-stack steady-state simulations, and (ii) many 3D dynamic simulations to cover a wide range of applications for the simplified stack model.

The second approach uses a combination of modeling based on physical laws and empirical modeling techniques. It reflects the physical nature of the main processes and uses the 3D simulation results for improvement. The stack model from the second approach is integrated into the system model. Its development is given in the following section.
3.7 Development of a Simple Stack Model

The 3D-stack simulation results provide insight for developing the simple stack for integration into the system model. The development of the simple stack model consists of the following five major steps:

- Representation of simple stack
- Description of main processes
- Formulation of stack equations
- Improvement by using the 3D-stack simulation results
- Solution method for stack equations

3.7.1 Representation of simple stack

The 3D-stack simulations showed that the computation of the stack with many cells is time consuming. In order to obtain a simple stack model, the first step is to reduce the stack performance to a cell performance. Accordingly, the effects of the processes at stack level need to be neglected or to be lumped into each cell.

- **Uniform gas distributions among cells.** The 3D-stack simulations show that computing gas distributions along stack direction is time consuming (even with the simplified gas manifolds). Since there are only a small derivation (in the order of a few percents) of the gas distribution among cells (discussed in Section 3.4.6), a uniform gas distribution among the cells is assumed. The gas-transport process in the gas manifolds is neglected.

- **No heat transfer among cells.** Based on above gas distribution among cells being uniform, each cell has the same temperature and current density distribution. There is no heat transfer between cells.

- **Lumping the heat storage of the stack wall to each cell.** The 3D-stack simulation indicated that the effect of the heat storage in the stack walls is not negligible. As a simple approach, the wall weight is divided by the cell numbers and lumped to each cell.

After dealing with the process at stack level, the simple stack is represented by identical cells. The cell representation is shown in Figure 3.19. The cell consists of:

- Two end plates (each end-plate includes: a half separator and the wall weight divided by 2×cell number)
- Fuel and oxidant gas layers
- A cell unit (including anode and cathode electrodes, and electrolyte)

![Figure 3.19 Representation of a simple stack](image)
The relations between the cell and the stack (e.g. gas flow-rate, current output, and voltage) give the following equations respectively:

\[ F_{in(A)} = \frac{F_{stack-in(A)}}{N} \]  \hspace{1cm} (3.40)

\[ F_{in(C)} = \frac{F_{stack-in(C)}}{N} \]  \hspace{1cm} (3.41)

\[ I_{stack} = I_{cell}; \quad V_{stack} = V_{cell} \times N \]  \hspace{1cm} (3.42)

Where \( F_{in(A)} \) and \( F_{in(C)} \) are the fuel and oxidant gas flow-rates into the cell. \( F_{stack-in(A)} \) and \( F_{stack-in(C)} \) are the fuel and oxidant gas flow-rates into the stack. \( I_{stack} \) and \( V_{stack} \) are the voltage and current output of the stack. \( I_{cell} \) and \( V_{cell} \) are the voltage and current output of the cell. \( N \) is the number of cells in the stack.

The second simplification step is to reduce the distributed cell performance into a lumped form. This simplification is used by most simple stack models for integration into the system model (Dijkema et al., 1994, and Take, et al., 1994). The power output from a cell \( P_{cell} \) is:

\[ P_{cell} = V_{cell} \times \int_{reaction-area} i_{local} \, dx \, dz \]  \hspace{1cm} (3.43)

where \( x \) and \( z \) are the cell length and width.

The actual cell voltage \( V_{cell} \) is the same everywhere, since the separator plate is, by design, a good ohmic conductor. However, the local current density \( i_{local} \) is not the same everywhere. The 3D-stack simulations show the two dimensional current distribution and the significant variations of the current density. Therefore, the impact resulting from the simplification using uniform current density needs to be remedied by the results of the 3D simulations.

### 3.7.2 Description of main processes

Like the main processes defined for the 3D-stack model (Section 3.3.2), the four processes significant for the power-generation performance of the simple stack are: i) electrochemical and chemical reactions, ii) power-generation characteristics, iii) gas-transport, and iv) heat generation and transfer. However, these four processes are not treated locally as in the 3D-stack model. The simple stack model treats these four processes in lumped form.

The dynamic phenomena described are:

- The gas storage in fuel and oxidant gas layers
- The heat storage in the end plates and in the cell unit

### 3.7.3 Formulation of stack equations

This section gives the formulation of the stack equations according to the stack representation and the main processes described in Sections 3.7.2 and 3.7.3. The stack equations consist of ordinary differential equations of conservation (due to the lumped form) and algebraic equations to calculate the terms in the conservation equations. The algebraic equations are the same as those used in the 3D-stack equations (described in Sections 3.3.2 and 3.3.3). The stack conservation equations are given as follows.
Conservation of chemical species. The composition balance of the fuel gas results from the gas composition at the inlet and at the outlet, the rate of the water-shift reaction, and the gas transfer due to the electrochemical reaction at the anode. Accordingly, the composition balance of the fuel gas in the gas compartment is derived as:

\[ V_A \times \frac{d(\rho_A \times \tilde{y}_A)}{dt} = F_{in(A)} \times \tilde{y}_{in(A)} - F_{out(A)} \times \tilde{y}_{out(A)} + \tilde{n}_{shift} \times \text{rate}_{shift} + \tilde{n}_{anode} \times \frac{I}{2F} \]  

(3.44)

Where \( V_A \): volume (m^3) (in this case the fuel gas channel volume), \( \rho \): gas density (mol/m^3), \( \tilde{y}_{in(A)}, \tilde{y}_{out(A)}, \tilde{y}_{(A)} \): the gas concentration vectors at the gas inlet, outlet and the average value. \( F_{in}, F_{out} \): gas flow rate at the inlet and outlet (mol/s), \( \tilde{n}_{shift}, \tilde{n}_{anode} \): vectors of stoichiometric coefficients for the shift and electrochemical anode reactions, \( \text{rate}_{shift} \): shift reaction rate, and \( I \) is the total cell current generation.

The composition balance for the oxidant gas results from the gas composition at the inlet and at the outlet, as well as the gas transfer due to the electrochemical reaction at the cathode. Accordingly, the composition balance for the oxidant gas in the gas compartment is readily derived as:

\[ V_C \times \frac{d(\rho_C \times \tilde{y}_C)}{dt} = F_{in(C)} \times \tilde{y}_{in(C)} - F_{out(C)} \times \tilde{y}_{out(C)} + \tilde{n}_{cathode} \times \frac{I}{2F} \]  

(3.45)

Where \( \tilde{n}_{cathode} \) is the stoichiometric coefficient for the electrochemical cathode reaction.

Conservation of Energy. The fuel-cell power output is closely related to the temperature of the cell unit. The heat storage in the thin fuel or oxidant gas layers is much smaller than the heat storage in the cell solid part (in end plates and in the cell unit). The heat storage in the thin fuel gas or oxidant gas layers is neglected. The thin fuel or oxidant gas layers are lumped to cell unit and the gas layers are assumed to have the same temperature as the cell unit.

The energy balance of the cell unit reads (refer to Figures 3.4 to 3.6):

\[ M_p \times C_p \times \frac{dT_e}{dt} = q_s \times V_e + q_s - Q_{EC(C1)} + Q_{ES} - Q_{ES(v1)} \]

(3.46)

\[ - Q_{EC(C2)} + Q_{SO} - Q_{ES(v2)} \]

Where \( M_p \): mass of the cell unit, \( C_p \): heat capacity of the cell unit, \( T_e \): temperature of cell unit, \( q_s \): heat generated from the electrochemical reaction per volume unit, \( q_s \): heat generated from shift reaction in the fuel gas, and \( V_e \): volume of the cell unit.

The energy balances for the up and down end-plate read (refer to Figure 3.7):

\[ M_{S(up)} \times C_s \times \frac{dT_{S(up)}}{dt} = Q_{EC(C1)} - Q_{SF} + Q_{ES(v1)} \]  

(3.47)

\[ M_{S(down)} \times C_s \times \frac{dT_{S(down)}}{dt} = Q_{EC(C2)} - Q_{SO} + Q_{ES(v2)} \]  

(3.48)

Where \( M_S \): mass of the end plate (including partial wall weight), \( C_S \): heat capacity of the end plate.
3.7.4 Improvement using the 3D-stack simulation results

The simple stack model should have the same predicted power output as the 3D-stack model. The accuracy loss of the simple model due to the simplification of using uniform current density can be remedied by using the 3D results. One of the common approaches is to modify the simple stack model parameters to fit the results from the 3D-stack model. In this study, the simple stack model attempts to have the same power output as the 3D-stack model under full-load steady-state operating conditions. Since the current density is closely related to the temperature, the heat-transfer coefficient in the simple stack model is regulated. More specifically, a correction factor $K_o$ is used in computing each convective heat-transfer. For example:

$$Q_{EF} = A_{EF} \times K_{EF} \times K_o \times (T_E - T_F)$$  (3.49)

where $A_{EF}$ and $K_{EF}$ are the heat-transfer area and convective heat-transfer coefficient between the cell unit and fuel gas, $T_E$ and $T_F$ are the mean temperatures of the cell unit and fuel gas. $K_o$ is regulated to achieve the same power output as the 3D-stack model under full-load conditions.

While using a function $f(K_o)$, the simple stack model can have approximately the same power output as the 3D-stack model under a series of steady-state simulations. Further work is necessary to achieve the fitting under both a series of steady-state simulations and transient conditions.

3.7.5 Solution method of stack equations

In order to solve the described stack equations, the software package SPEEDUP (SPEEDUP, 1996) introduced in Section 2.8 is used as a solver. The implementation of the lumped stack model in SPEEDUP code is described in Appendix C.7.

3.8 Performance of the Simple Stack Model

To illustrate the performance of the simple stack model, a steady-state case and a dynamic case have been selected. The performance of a fuel cell is characterized by voltage-versus-current data for specified conditions (e.g. temperature, pressure, gas concentration and utilization of the fuel and oxidant gases). Figure 3.19 depicts the performance of the voltage-versus-current and power-versus-current of an average fuel cell. As expected, the voltage decreases significantly with increasing current density. The power density increases with increasing current density within the current density range of 500-1750 A/m². However, the power density decreases within the current density range of 1750-2000 A/m², because the effect of voltage drop is larger than that of the current increment. The simple stack model has the same power output value at full load (i.e. current density of 1500 A/m²) as the 3D-stack model, since the parameter fitting of the simple stack is based on the 3D simulation results at full load. Therefore, the performance of the simple stack model appears acceptable within its operating range.
Figure 3.19 Voltage-versus-current and power-versus-current

The simple stack model is applied to simulate the stack responses to a step change of the current density. This dynamic case gives a qualitative comparison between the dynamic performance derived from the developed simple stack model and that from the simple stack model of Achenbach (1995). The simple stack model of Achenbach is derived from his 3D-stack model (given in Section 3.6 and Appendix C.5.2).

This case uses the same current density step changes as were used by Achenbach (1995). Two current density step changes are applied: from 1000 to 1500 A/m² and from 1250 to 1500 A/m² respectively.

Figure 3.19 shows that the voltage response has an undershoot, i.e. the voltage falls beneath the new steady-state value. The amount of the voltage drop correlates with the magnitude of the current-density step. The reason for the voltage undershoot is that immediately after the current jump, the stack temperature is still low corresponding to the initial current density. Then, while the average temperature of the cell unit increases, the cell voltage also increases owing to the lower internal cell resistance at a higher temperature. Figure 3.19 shows that the average temperature of the cell unit increases due to the higher amount of waste heat produced at I=1500 A/m². Our simulated voltage and temperature response profiles are qualitatively consistent with the simulated results of Achenbach (1995).
Figure 3.19  Voltage and temperature responses to current step increase

3.9 Discussion of the Simple Stack Model

The simple stack model has been improved in comparison to the stack model, which simply multiplies the cell performance by the number of cells, as do most dynamic fuel-cell models presented in the literature. The simple stack model used the 3D-stack simulation results for making simplifications and identifying the parameters.

It is obvious that the proposed simple stack model has not fully utilized the advantages of the 3D stimulation results. The links between the simple stack and the 3D-stack models need to be further explored. Appendix C.6 gives another simple stack model by directly representing the response characteristics of the 3D-stack model using simple approximation equations. However, the physical nature of the model is difficult to evaluate. Finally, the simple stack model proposed in Section 3.7 has been selected to be integrated into the system model.

3.10 References

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4 A REFORMER MODEL

This chapter provides a reformer model to evaluate whether the reformer output gases satisfy the concentration, temperature, pressure, and flow-rate with regard to the fuel-cell stack load-following operating modes. First, a description of the reformer structure is given in Section 4.1. Secondly, a literature survey is presented to position our reformer model and to provide methodology dealing with the reforming reactions and heat-transfer processes (Section 4.2). Thirdly, the development of the reformer model is described in Section 4.3. The development of the reformer model consists of five major steps:

- Description of Main processes
- Representation of reformer
- Formulation of reformer equations in distributed form
- Formulation of reformer equations in lumped form
- Solution method of reformer equations

Fourth, the reformer is simulated under both stationary and transient conditions (Sections 4.4). Finally, the model reliability and recommendations are described in Section 4.5.

4.1 Description of the Reformer Structure

In hydrogen processing plants, a reformer operates in continuous full-load conditions. The research work is focused on optimizing reformer design to maximize the fuel conversion rate. However, the reformer operation in a fuel-cell system is essentially different from that in processing plants. The reformer in a fuel-cell system is required to operate in such a manner that the production of the gases for the fuel-cell stack always follows the changes in the power demand. It is therefore necessary to evaluate the capability of the reformer to provide gases for the fuel-cell stacks with regard to load-following operating modes.

At least three types of reformers have been considered for the 1 MW MCFC system. These are: the heat exchange reformer (HER) (Christiansen and Laursen, 1991), the plate reformer (Watanabe et al., 1989), and the two-stage catalytic combustion type reformer (Uematsu et al., 1994). The HER type reformer was designed for MCFC or PAFC power plants in the range from 100 kW to 5 MW (Stahl and Laursen, 1992). HER was selected for the Dutch MCFC projects (Laag and Verbruggen, 1994). As discussed in the system design (Chapter 2), the HER was selected for the 1 MW MCFC system. Hence, the reformer model in this study uses the HER configuration for the 1 MW MCFC system. Throughout this chapter, the term 'reformer' refers to the HER.

The reformer structure is shown in Figure 4.1 (Christiansen, 1991). It consists of: (i) a pressure shell, (ii) two catalyst beds, and (iii) a combustion chamber with a burner. The two catalyst beds are connected in series and the reforming reaction takes place in these two catalyst beds. Since the
reforming reactions are strongly endothermic, a heat supply is required to maintain the operation temperature. The heat is provided by the flue-gas from the burner at the bottom of the reformer where the combustion reaction takes place.

![A heat exchange reformer](image)

**Figure 4.1 A heat exchange reformer**

It is noted that the HER operation is different from that of a conventional reformer which has one catalyst bed with an inter-connected or a separated burner. First, the process-gas conversion in the HER is carried out in two catalyst beds at two different temperatures. Secondly, the process-gas conversion is closely integrated with the heat-transfer processes. Therefore, the proposed reformer model must represent the HER operating characteristics.

### 4.2 Literature Overview

Pietrogrande and Bezzecccheri (1993) indicated that the activities for the reformer improvement can be classified into six main categories: i) metallurgy, ii) heat transfer, iii) geometry, iv) process integration, v) combustion, and vi) catalysis. This study mainly belongs to the category of the process integration, but also uses the results from the other categories. The available literature provides no HER type of reformer model for 1 MW MCFC systems with regard to load-following modes. However, the previous work is useful to position our reformer model and to provide methodology dealing with the main processes. A literature survey is given with regard to two objectives: i) decisions on the reformer approach, and ii) calculation of reaction kinetics and heat transfer.
4.2.1 Decisions on the reformer approach

**Design features of the reformer.** The reformer manufacturer (Haldor Topsoe, Inc. 1991) has provided the reformer design concept, including the reformer structure (Figure 4.1), working principle, and the designed operation conditions. The reformer design in Section 2.6.3 and Appendix A.7 gives the available design parameters from manufactures and the estimate of the gas channel geometry. The literature gives no catalyst properties or details of the reformer geometry data.

**Reformer model using CFD approach.** The 3D fuel-cell stack model indicates that the CFD approach is capable of realistically dealing with processes of fluid-flow, heat-transfer, and chemical-reactions. However, the reformer investigation using the CFD package of PHOENICS did not achieve successful results (Tilburg, 1993). The work of Tilburg (1993) indicated that: (i) the reformer model has to model processes at both macro- and micro-levels, (ii) accurate data of the catalyst properties and reformer geometry is required, and (iii) establishing a 3D reformer model is time consuming work.

**Types of the reformer investigations from literature.** Experimental investigations of the reformers are usually conducted by manufacturers to verify the design aspects. The experimental data are usually not available for the public, due to the confidential policies of the companies concerned. Nevertheless, reformer models are available from literature. These models can be classified into four types.

i. The individual reformer models developed for optimizing design (e.g. Rostrup-Nielsen et al. 1991). These models are in the distributed form and deal with stationary conditions.

ii. The individual reformer models developed for operation studies (e.g. Alatiqi and Meziou 1991). These models are in the lumped or one dimensional form and deal with transient conditions.

iii. The reformer models developed for fuel-cell system design studies are in steady-state form. These models include those of Kivisaari (1992), Laag (1993), Woudstra and Verschoor (1995).

iv. The reformer models developed for fuel-cell system operation studies deal with transient conditions (Yamaguichi et al. 1990) but these models are based on experimental data.

The above reformer model types i and iii deal with reformers only under stationary conditions, though the above reformer model type i has dealt with HER. The reformer model types ii and iv do not represent the reformer characteristics with two-stage catalyst beds and the integration of process-gas conversion and heat-transfer. Therefore, the reformer model types ii and iv do not directly apply to HER. It is necessary to establish a new reformer model which is suitable for studying the HER with regard to load-following modes.

**Proposed approach for reformer model.** First, the reformer model must represent the HER working principle. Secondly, the reformer model is focused on evaluating its capability with regard to load-following operation modes. Thirdly, based on the limited reformer design data and time, it is not feasible to present the internal behavior of the reformer. The reformer model emphasizes the input and output relation. This study develops a reformer model for direct integration into the system model, instead of first establishing a detailed dynamic reformer model.
by using CFD and then simplifying it. The proposed reformer model is focused on adapting the methodology dealing with steam-reforming reactions and heat-transfer from the literature to the HER with regard to load-following modes.

4.2.2 Calculation of reaction kinetics and heat transfer

The two essential processes determining the reformer performance are i) the kinetics of steam reforming reaction, and ii) heat transfer. The information from the literature with regard these two aspects is given as follows.

Kinetics of steam reforming reactions. The review paper of Elnashaie et al. (1988) gave a critical evaluation of the kinetic rate expressions available in the literature. The analysis indicated the limitations and contradictions in the kinetic rate expressions. More than 10 widely used kinetic rate expressions are given under the conditions (including catalyst type, particle size, and operation temperature and pressure). Three of the empirical equations developed in different decades are listed in Table 4.1.

<table>
<thead>
<tr>
<th>Table 4.1 Kinetic parameters of steam reforming of methane</th>
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<tbody>
<tr>
<td>Investigators</td>
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<tr>
<td>Bodrov (1964)</td>
</tr>
<tr>
<td>Ross &amp; Steel (1973)</td>
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<tr>
<td>Kopsel (1980)</td>
</tr>
</tbody>
</table>

Take et al. (1992) also investigated the widely used empirical kinetics equations for the steam reforming reaction on a Ni-Al\(_{2}\)O\(_{3}\) catalyst. They recommended the following empirical equation:

\[
r_{\text{CH}_4} = k_{\text{CH}_4} \times \left( P_{\text{CH}_4} - \frac{P_{\text{CO}} \times P_{\text{H}_2}^3}{P_{\text{H}_2O} \times K} \right)
\]

(4.1)

where \( r \) is the steam reforming rate. \( P \) is the partial pressure of gas participating in the steam reforming reaction. \( K \) is the equilibrium constant of the methane reforming reaction. \( k \) is the reaction rate constant.

Heat transfer. The chemical reactions are closely related to the operating temperature. The calculation of the heat-transfer processes in a reformer is crucial. The effectiveness of the heat transfer is also closely related to the gas-flow pattern. The related literature can be classified into two types.

- Gas heat transfer in pipes (without catalyst). There are well validated empirical equations to deal with the gas heat transfer in pipes, e.g. VDI (1988).
- Gas heat transfer in pipes (with catalyst). The empirical equations dealing with the heat transfer in pipes (with catalyst) depend on the catalyst properties (e.g. catalyst type and
particle size). Many research workers have attempted to improve knowledge of the mechanism of the heat transfer and to achieve accurate and general empirical equations. The empirical equation of Beek (1962) reads:

$$Nu = 2.58 \times Re_p^{1/3} \times Pr^{1/3} + 0.094 \times Re_p^{0.8} \times Pr^{0.4}; \quad \alpha = \frac{Nu \times \lambda}{D_{\text{particle}}}$$ (4.2)

where $Re_p$ is the particle Reynolds number, $Pr$ is the Prandtl number, $\alpha$ is the heat transfer coefficient, and $D$ is the equivalent diameter.

Froment and Bischoff (1979) proposed the following empirical equation:

$$Nu = 0.813 \times Re_p^{0.9} \times e^{-6 \frac{D_{\text{Particle}}}{D_{\text{tube}}}} \times \frac{Nu \times \lambda}{D_{\text{tube}}}$$ (4.3)

### 4.3 Development of a Reformer Model

#### 4.3.1 Description of main processes

The reformer output gases to the fuel-cell stacks must satisfy the temperature, pressure, concentration, and flow-rate required by the fuel-cell stack operation. The fuel-cell stack operation conditions are discussed in Section 2.3.2. The related processes are: i) the chemical reactions, and ii) heat transfer and gas flows.

#### 4.3.1.1 Chemical reactions

**Reactions in the process gas.** The major constituent of natural gas is methane. The following reactions are generally chosen to describe the steam reforming of methane (Wagner, 1992):

(i) Methane-steam reaction (also called reform reaction):

$$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow 3 \text{H}_2 + \text{CO} \quad (\Delta H_{298}^o = 206 \text{ kJ/mol})$$ (4.4)

(ii) Water-shift reaction:

$$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad (\Delta H_{298}^o = -41 \text{ kJ/mol})$$ (4.5)

(iii) Overall reaction:

$$\text{CH}_4 + 2 \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 4 \text{H}_2 \quad (\Delta H_{298}^o = +165 \text{ kJ/mol})$$ (4.6)

The overall reaction is endothermic and yields an increase in the number of moles. Hence, a higher temperature and a lower pressure favor the overall reaction. In addition, steam makes the reaction equilibrium move to the right side. Therefore, a higher steam ratio results in a higher conversion rate and output process gas with a lower methane content.

Hydrocarbons higher than CH$_4$ in the natural gas have the following reactions:

(iv) High hydrocarbon reforming:

$$C_nH_m + nH_2O \leftrightarrow (n+m/2) \text{H}_2 + n\text{CO}$$ (4.7)

(v) Hydrocracking reaction:

$$C_kH_{2k+2} + (k-1)\text{H}_2 \leftrightarrow k \text{CH}_4$$ (4.8)
Reactions in the burner. The following combustion reactions take place to provide heat for the reactions in the process gas:

\[
\begin{align*}
\text{CH}_4 + 2\text{O}_2 &\rightarrow 2\text{H}_2\text{O} + \text{CO}_2 \quad (\Delta H^\circ_{298} = -802.3 \text{ kJ/mol}) \\
\text{H}_2 + 0.5\text{O}_2 &\rightarrow \text{H}_2\text{O} \quad (\Delta H^\circ_{298} = -241.8 \text{ kJ/mol}) \\
\text{CO} + 0.5\text{O}_2 &\rightarrow \text{CO}_2 \quad (\Delta H^\circ_{298} = -283.0 \text{ kJ/mol})
\end{align*}
\]

(4.9) (4.10) (4.11)

4.3.1.2 Heat transfer and gas flows

The effectiveness of the heat transfer and the gas pressure drop are closely related to the gas flows. The gas flows in the reformer are illustrated by Figure 4.2 (derived from the reformer structure of Figure 4.1).

![Figure 4.2 Gas flows in the reformer cross section](image)

When the process gas flows through the first catalyst bed, it receives heat from both the partly cooled flue gas and the processed gas. When the process gas flows through the second catalyst bed, it receives heat from the hot flue-gas and the partly processed gas. Accordingly, the heat generation and transfer processes in the first and second beds include:

- The heat generation due to the water-shift reaction and the heat sink due to the methane-steam reaction
- The convective heat transfer between the process gas and the shell wall
- The convective heat transfer between the process gas and the catalyst particles
- The radiant heat transfer between the two shell walls
- The radiant heat transfer between the process gas and the shell walls
- The radiant heat transfer between the catalyst particles and the shell walls

The heat transfer processes in the fuel or process gas side (without catalyst bed) include:

- The convective heat transfer between the gas and the shell wall
- The radiant heat transfer between the two shell walls
- The radiant heat transfer between the gas and the shell wall
4.3.2 Representation of the reformer

In the representation of the reformer models developed for system analysis, e.g. Yamaguchi et al., (1990), Kivisaari (1992), Laag (1993), Woudstra and Verschoor (1995), a reactor with or without a burner is used. The two assumptions used in these reformer representations are not suitable for the HER reformer.

- The assumption of the gas conversion in a single catalyst bed at one temperature is not suitable. In the HER reformer, the process gas conversion is carried out in two catalyst beds at two different temperatures.
- The assumption of the output gas concentration based on the output gas temperature is not suitable for the HER reformer. The output gas concentration depends on the second catalyst bed temperature. After the second catalyst, the process gas is cooled down in pipes (without a catalyst). However, the gas concentration is assumed to remain the same.

In order to overcome the two major problems mentioned above, the proposed reformer representation includes two separate catalyst beds to deal with the chemical reactions and the inter-related heat-transfer processes.

Four simplifying assumptions are introduced to represent the reformer:
- The outside reformer wall is adiabatic.
- Since the reformer has a length of 7 m and a very thin gas channel (the ratio of length to thickness is greater than 100), the entrance and exit effects are negligible.
- The chemical reactions of the process gas only take place in two catalyst beds.
- Since the external burner is located at the bottom of the reformer, the only impact of the burner considered is the supply of high temperature flue-gas.

The reformer representation is illustrated in Figure 4.3. On the flue-gas side, the combustion process is presented by module BURNER. The heat-transfer process between the flue-gas and the catalyst bed is presented by modules BHX2 and BHX1. On the process gas side, the chemical reactions for the process gas are implemented consecutively in the first and second catalyst beds. This is presented by two modules (BED1 and BED2) which are connected in series. The heat-transfer processes between the process gas and the catalyst beds are presented by modules RHX1 and RHX2. It is also noted that two heat-transfer effects (i.e. the heat transfer between RHX1 and RHX2, and the heat transfer between the burner and BHX1) are eliminated in Figure 4.3. Based on the temperature profiles provided by the manufacture design (Stahl and Laursen, 1994), the heat transfer between RHX1 and RHX2 is expected to be small. The heat transfer between the burner and BHX1 has been lumped to the Burner module. Its impact needs to be considered.
4.3.3 Formulation of reformer equations in distributed form

4.3.3.1 Conservation of chemical species

Process gas in the catalyst bed. The gas concentration balance for the process gas (i.e. natural gas plus steam) in the first and the second catalyst bed is determined by the reaction rate of the methane-steam and water-shift. It is derived as:

\[
\frac{\varepsilon \times A}{\tilde{W}_w} \frac{\partial (\rho \times \tilde{y})}{\partial t} = \frac{\partial (F \times \tilde{y})}{\partial z} + \text{stoich}_{\text{reform}} \times \text{rate}_{\text{reform}} \times A + \text{stoich}_{\text{shift}} \times \text{rate}_{\text{shift}} \times A
\]  

(4.12)

where \(\varepsilon\) and \(A\) are the void fraction (m\(^3\)/m\(^3\)) and transverse section area (m\(^2\)) of the catalyst bed. \(\rho\) is the gas density (kg/m\(^3\)). \(F_{\text{in}}\) and \(F_{\text{out}}\) are the gas input and output flows (mol/s). \(\tilde{y}\) and \(\tilde{W}_w\) are the gas concentration (mol/mol) and molecular weight (kg/mol) for gas species of H\(_2\), CH\(_4\), N\(_2\), CO, CO\(_2\), O\(_2\) and H\(_2\)O. stoich\(_{\text{reform}}\) and stoich\(_{\text{shift}}\) are the reform and shift reaction stoichiometric numbers (stoich\(_{\text{reform}} = (3, -1, 0, 0, 1, 0, -1)\) and stoich\(_{\text{shift}} = (1, 0, 0, 0, -1, 1, -1)\)), and rate\(_{\text{reform}}\) and rate\(_{\text{shift}}\) are the conversion rate of the reform and shift reactions (mol/s.m\(^3\)).

Only the methane-steam and the water-shift reactions take place in the catalyst bed. Due to the relatively low percentage (< 3.5%) of high hydrocarbons in Dutch natural gas, and the relatively high speed of the hydrocracking reaction, it is assumed that the high hydrocarbons instantaneously hydrocrack into CH\(_4\) at the reformer inlet. The CH\(_4\) concentration at the reformer inlet is the CH\(_4\) originally in the feedstock plus the CH\(_4\) formed from the high hydrocarbons.

Process or flue gas channels without a catalyst bed. The gas concentration balance for the process and flue gas without reaction reads:

\[
\frac{A}{\tilde{W}_w} \frac{\partial (\rho \times \tilde{y})}{\partial t} = \frac{\partial (F \times \tilde{y})}{\partial z}
\]  

(4.13)
Flue-gas in burner. The composition balance for the flue gas in the burner is considered to be in lumped form and it is determined by the burning reactions of CH₄, H₂ and CO. It is readily derived as:

\[
\frac{V_{\text{burner}}}{W_w} \times \frac{d(p_{\text{out}} \times \bar{y}_{\text{out}})}{dt} = F_{\text{in}} \times \bar{y}_{\text{in}} - F_{\text{out}} \times \bar{y}_{\text{out}} + \text{stoich}_{\text{CH}_4} \times \text{rate}_{\text{CH}_4} \times V_{\text{burner}} \\
+ \text{stoich}_{\text{H}_2} \times \text{rate}_{\text{H}_2} \times V_{\text{burner}} + \text{stoich}_{\text{CO}} \times \text{rate}_{\text{CO}} \times V_{\text{burner}}
\]  

(4.14)

Where \( V_{\text{burner}} \) is the burner volume (m³), \text{stoich}_{\text{CH}_4}, \text{stoich}_{\text{H}_2} \) and \text{stoich}_{\text{CO}} \) are the stoichiometric numbers of the combustion reactions of CH₄, H₂ and CO, and \text{stoich}_{\text{CH}_4} = (0, -1, 0, -2, 0, 1, 2), \text{stoich}_{\text{H}_2} = (-1, 0, 0, -0.5, 0, 0, 1) \) and \text{stoich}_{\text{CO}} = (0, 0, 0, -0.5, -1, 1, 0).

4.3.3.2 Energy balance

Process gas in the catalyst bed. The energy storage of the process gas in the catalyst bed (BED1 and BED2) is determined by the input energy, output energy, the reaction heat, and the heat transfer to the shell wall and catalyst particles:

\[
A \times \frac{\partial (\rho \times U)}{\partial t} = W_w \times \frac{\partial (F \times h)}{\partial z} + \Delta H_{\text{reform}} \times \text{rate}_{\text{reform}} \times A + \Delta H_{\text{shift}} \times \text{rate}_{\text{shift}} \times A \\
+ \sum_{l=1,2} K_l \times \pi \times d_l \times (T_{\text{Wall}(i)} - T_{\text{gas}}) + K_c \times A_c \times \pi \times d_l \times \delta \times (T_P - T_{\text{gas}})
\]

(4.15)

where \( U \) and \( h \) are the gas internal energy (kJ/kg) and enthalpy (kJ/kg), \( W_w \) is the molecular weight of gas mixture, \( \Delta H_{\text{reform}} \) and \( \Delta H_{\text{shift}} \) are the reform and shift reaction heats (kJ/mol), \( T_{\text{Wall}} \), \( T_{\text{gas}} \) and \( T_P \) are the temperature of the shell wall, the process gas and the catalyst particles. \( d_l \) is the diameter of the shell wall and \( \delta \) is the thickness of the catalyst bed, \( K_l \) and \( K_c \) are the heat-transfer coefficients, \( A_c \) is the average external surface area of the particles per volume of catalyst bed, m²/m³.

Process or flue-gas channels without the catalyst bed. The energy storage of the process gas or the flue-gas in the gas channel without the catalyst bed is determined by the input energy, output energy, and the heat-transfer to the shell wall. The energy storage of the gas in RHX1, RHX2, BHX1, or in BHX2 has:

\[
A_l \times \frac{\partial (\rho \times U)}{\partial t} = -W_{W(l)} \times \frac{\partial (F \times h)}{\partial z} - K_l \times \pi \times d_l (T_{\text{Wall}(l)} - T_{\text{gas}})
\]

(4.16)

Shell walls. The energy storage of the shell walls is determined by the heat-transfer between the gases and the two sides of the shell wall:

\[
\rho_w \times (d_{\text{out}}^2 - d_{\text{in}}^2) \times C_{pw} \times \frac{dT_{\text{wall}}}{\partial t} = 4 \times K_{\text{out}} \times d_{\text{out}} \times (T_{\text{gas(out)}} - T_W) - 4 \times K_{\text{in}} \times d_{\text{in}} \times (T_W - T_{\text{gas(in)}})
\]

(4.17)

where \( \rho_w, C_{pw}, T_W \) are the density, heat capacity, and temperature of the shell walls, \( d_{\text{in}} \) and \( d_{\text{out}} \) are the diameters of the inside and outside shell walls, and \( K_{\text{in}} \) and \( K_{\text{out}} \) are the convective heat transfer coefficient between the gases and the inside and outside shell walls.

Catalyst. The energy balance equation for the catalyst is:

\[
C_{PC} \times \rho_{\text{catalyst}} \times \frac{dT_{\text{catalyst}}}{\partial t} = K_c \times A_c \times (T_{\text{gas}} - T_{\text{catalyst}})
\]

(4.18)
4.3.4 Formulation of reformer equations in lumped form

4.3.4.1 Two simplifications

As an initial effort, two simplifications are introduced to the reformer equations in Section 4.3.3:

- **Reduce to ordinary differential equations.** The distributed modules in Figure 4.3 are simplified to be in a lumped form. This simplification is based on the assumption that the gas-flow processes in the reformer are expected to be fast. The effect of the gas-flow processes is considered to be a pressure drop in steady-state form.

- **Process gas lumped together with catalyst bed and shell walls.** No general theoretical formula are available to calculate the heat-transfer coefficient \( K \) from the reformer shell walls to the processing gas (with catalyst bed). Frequent references (e.g. Tilbrug, 1993 and Cobben, 1994) are made according to the empirical equation of Beek (1962). The empirical equation needs the physical properties of the catalyst (e.g. the equivalent diameter of the catalyst for calculation of the particle Reynolds number). Since the catalyst properties are not available, the present approach lumps the process gas with the shell wall and catalyst bed to eliminate the uncertainty in determining the heat-transfer coefficients.

The influences of these two assumptions need to be considered. With the above two assumptions, the partial equations in Section 4.5 can be simplified as ordinary equations as follows.

4.3.4.2 Conservation of chemical species

The gas composition balance for the process gas (i.e. natural gas plus steam) in the first or the second bed (BED1 and BED2) is determined by the methane-steam and water-shift reactions. It is derived as:

\[
\varepsilon \times V \times \frac{d(\rho_{\text{out}} \times \tilde{y}_{\text{out}})}{dt} = F_{\text{in}} \times \tilde{y}_{\text{in}} - F_{\text{out}} \times \tilde{y}_{\text{out}} + \text{stoich}_{\text{reform}} \times \text{rate}_{\text{reform}} + \text{stoich}_{\text{shift}} \times \text{rate}_{\text{shift}} \quad (4.19)
\]

where \( \varepsilon \) and \( V \) are the void fraction (\( \text{m}^3/\text{m}^3 \)) and volume (\( \text{m}^3 \)), \( \rho \) is the gas density (\( \text{mol}/\text{m}^3 \)), \( F_{\text{in}} \) and \( F_{\text{out}} \) are the gas input and output flows (\( \text{mol}/\text{s} \)), \( \tilde{y} \) and \( \tilde{W}_{\text{w}} \) are the gas concentration (\( \text{mol}/\text{mol} \)) and molecular weight (\( \text{kg/mol} \)) for gas species of \( \text{H}_2, \text{CH}_4, \text{N}_2, \text{CO}, \text{CO}_2, \text{O}_2 \) and \( \text{H}_2\text{O} \), \( \text{stoich}_{\text{reform}} \) and \( \text{stoich}_{\text{shift}} \) are the reform and shift reaction stoichiometric numbers (\( \text{stoich}_{\text{reform}} = (3, -1, 0, 0, 1, 0, -1) \) and \( \text{stoich}_{\text{shift}} = (1, 0, 0, 0, -1, 1, -1) \)), and \( \text{rate}_{\text{reform}} \) and \( \text{rate}_{\text{shift}} \) are the conversion rate of the reform and shift reactions (\( \text{mol}/\text{s} \)).

The composition balance for the flue or process gases without catalyst bed is derived as:

\[
V \times \frac{d(\rho_{\text{out}} \times \tilde{y}_{\text{out}})}{dt} = F_{\text{in}} \times \tilde{y}_{\text{in}} - F_{\text{out}} \times \tilde{y}_{\text{out}} \quad (4.20)
\]

4.3.4.3 Energy balance

Within the reformer, the energy balance consists of heat sources from the reforming reactions and the heat transfers (which are presented by one counter-flow and three co-flow heat exchangers).
The process gas and the solid objects (e.g. metal wall and catalyst bed), are assumed to have the same temperature (refer to the following heat transfer section). Hence the energy balance for BED1 or BED2 sub-module can be written as:

\[
\varepsilon \times V \times \frac{d(\rho_{\text{out}}^m \times U_{\text{out}})}{dt} + \sum_{i=1,2} C_{\text{Wall}}(i) \times M_{\text{Wall}}(i) \times \frac{dT_{\text{out}}}{dt} + C_{\text{catalyst}} \times M_{\text{catalyst}} \frac{dT_{\text{out}}}{dt} = F_{\text{in}} \times h_{\text{in}} \times W_{\text{in}} - F_{\text{out}} \times h_{\text{out}} \times W_{\text{out}} + \Delta H_{\text{reform}} \times \text{rate}_{\text{reform}} + \Delta H_{\text{shift}} \times \text{rate}_{\text{shift}} + \Sigma Q
\]

(4.21)

where \( U \) (kJ/kg.K) is the internal energy of the process gas, \( \rho_{\text{out}}^m \), gas density (kg/m³), \( C_e \) (kJ/kg.K) and \( M_e \) (kg) are the heat capacity and the mass of the solid objects. \( \Delta H_{\text{reform}} \) and \( \Delta H_{\text{shift}} \) are the reform and shift reaction heats (kJ/mol). \( \Sigma Q \) (kW) of BED1 is the heat transfer from RHX1 and BHX1 to BED1. \( \Sigma Q \) of BED2 is the heat transfer from RHX2 and BHX2 to BED2.

The energy balance for the gas in the heat exchanger (RHX1, RHX2, BHX1, or BHX2) can be written as:

\[
V \times \frac{d(\rho_{\text{out}}^m \times U_{\text{out}})}{dt} = F_{\text{in}} \times h_{\text{in}} \times W_{\text{in}} - F_{\text{out}} \times h_{\text{out}} \times W_{\text{out}} - Q
\]

(4.22)

where \( Q \) (kW) is the heat transfer from RHX1, RHX2, BHX1, or BHX2 to BED1 or to BED2.

### 4.3.4.4 Principles of the algebraic equations

The algebraic equations are required to calculate the conversion rates of the chemical reactions, heat-transfer, pressure drop, and the mixture gas physical properties. The principles for the derivation of these algebraic equations are given as follows.

**Conversion rates of the chemical reactions.** To calculate the conversion rate of the reforming reaction, two common approaches are: i) to assume equilibrium conditions, or ii) to use empirical kinetic equations (Hook, 1980, Rostrup-Nielsen, 1991 and Take et al. 1992). The literature study (Section 4.3.2) indicated the limitations and contradictions of the existing empirical kinetic equations of the steam reforming reaction. Moreover, the empirical kinetic equations need the catalyst type and particle size. These data are not available in this study. Pietrogrande and Bezzeccheri (1993) mentioned that the nickel-based reforming catalyst shows a good performance. The difference between the gas composition derived from theoretical equilibrium and the actual composition is very small. The reformer also uses two long reaction beds, which maximizes the conversion rate (the rate at equilibrium conditions is the maximum). Therefore, the conversion rate calculation assumes the equilibrium state. The difference between this assumed situation and real situation is predictable (a few percents higher).

The water-shift reaction has a high reaction speed at the designed operating temperatures (around 600°C in the first catalyst bed and around 800°C in the second bed). It is also assumed to reach the equilibrium state. The calculation of the conversion rates (\( \text{rate}_{\text{reform}} \) and \( \text{rate}_{\text{shift}} \)) is given in Appendix D.1.

The reactions in the burner (\( \text{rate}_{\text{CH}4}, \text{rate}_{\text{H}2} \) and \( \text{rate}_{\text{CO}} \)) are based on the complete combustion of the methane, hydrogen, and carbon monoxide. To ensure complete combustion, an excess air ratio of 20% is used.
Heat-transfer. The Q in the equations (4.15) and (4.16) includes the heat-transfer processes among the fuel gas, processing gas, and BED1 and BED2 (including shell wall, processing gas, and catalyst bed). The heat-transfer processes between the fuel or process gas to BED1 or BED2 include the convective heat-transfer between the gas and the shell wall. The quantitative calculation is given in Appendix D.2. Heat transfer by radiation is negligible. (Appendix D.2 shows that the magnitude of the radiant heat transfer is much smaller than that of the convective heat-transfer).

Pressure drop. The calculation of the pressure drop requires either extensive computational fluid dynamics techniques or empirical equations. The present reformer model adopts the latter approach. The flue or process gas flow (without the catalyst bed) is similar to the gas flow in the heat exchanger (described in Appendix B.2), thus the gas pressure drop is related to the flow rate and the characteristics of the flow channel. The pressure drop of the process gas through the dry catalyst particles is calculated by using the Ergun equation (Ferry, 1981). The calculation of these pressure drops is described in Appendix D.3.

Physical properties of gas mixture. Ideal gas behavior is assumed for both the flue and process gas, because of the relatively high operating temperature (400 - 1400°C) and low pressure (around 300 kPa) in the reformer. When the composition of a gas mixture is known, and two gas parameters (e.g. the pressure and enthalpy), the other gas properties can be determined. The calculation of the gas properties used the built-in functions in the SPEEDUP library (SPEEDUP, 1996).

4.3.5 Solution method of reformer equations

In order to solve the reformer equations that have been described, the software package SPEEDUP (SPEEDUP, 1996) introduced in Section 2.8 is used as a solver. Setting up the reformer simulation through SPEEDUP code is fulfilled through both the user problem description and user library. The reformer problem description is composed of six input sections as follows.

- **Flowsheet.** First, the reformer problem uses seven operational units: BURNER, BHX1, BHX2, BED1, BED2, RHX1, and RHX2 based on the reformer representation shown in Figure 4.3. These seven operational units are inter-connected by the mass flow and heat flow streams as shown in Figure 4.3. Secondly, the connections between the reformer and its surroundings in the fuel-cell system are: i) on the flue-gas side, the fuel gas (anode-off gas) and air flow into the reformer burner, ii) on the process gas side, the preheated natural gas and steam flow into the reformer, iii) consequently, there are two outputs: the flue gas to fuel-cell cathode, and the processed gas to fuel-cell anode.

- **Declare.** Defining the variable interconnections. The input and output variables at the reformer boundaries and between the modules are illustrated in Figure 4.4. The input variables are: the flow-rate, concentration, and enthalpy of the input streams, and the pressure of the output streams. Consequently, the output variables are the flow-rate, concentration and enthalpy of the output streams, and the pressure of the input streams.

- **Operation.** Defining the operating conditions and design data of the stack (data described in Chapter 2 and Appendix A.7).

- **Options.** Selects translation and run-time option (e.g., time steps and intervals).

- **Unit.** Seven operational units: BURNER, BHX1, BHX2, BED1, BED2, RHX1, and RHX2.
• **Models.** Three types of models have been developed. These are: the BURNER (combustion processes in the burner), BED (the processes of the process gas in the catalyst bed), and EXCH (heat-transfer).

An operational unit in SPEEDUP refers to a model which represents the physical and/or chemical processes by using mathematical equations. In order to reduce the numbers of model types, an operational unit with the same working principle often refers to a similar model type, but with different inputs for the operating and design conditions. The operational unit BURNER refers to model BURNER. The operational units RHX1 and RHX2 refer to model EXCH.

The implementation of the mathematical equations in SPEEDUP is illustrated by using model BED (assumption of module BED for operational unit of BED2). Figure 4.5 shows (i) the input variables of the flow-rate, concentration, and enthalpy of the input stream \((F_{in}, Y_{in}, H_{in})\), and the pressure of the output stream \((P_{out})\), and (ii) the output variables of the flow-rate, concentration, and enthalpy of the output stream \((F_{out}, Y_{out}, H_{out})\), and the pressure of the input streams \((P_{in})\).

The principle of the mathematical implementation of module BED is shown in Figure 4.6 (\(p\): gas density, \(T\): bed temperature, \(Q_1\) and \(Q_2\) are the heat transfer from BHX1 and RHX1 respectively). The block of the mass balance corresponds to the differential Eq. 4.19, which is the composition balance for the process gas. The block of the energy balance corresponds to the differential Eq. 4.21, which is the energy balance for the process gas at BED2. The blocks of the chemical reactions, physical properties, and pressure drop correspond to the algebraic equations used to calculate the related parameters (e.g. reaction rate and heat, and physical properties of the gas mixture) for the dynamic equations (refer to Section 4.4.4 and Appendix D). SPEEDUP simulator solved these implicit inter-connected differential and algebraic equations. The simulation of the reformer model is performed on a SUN IPX station and lead to the results presented in the following section.
4.4 Model Performance

4.4.1 Setting-up cases

To evaluate the present reformer model, one steady case and four dynamic cases have been selected as examples for demonstration. The steady-state case is used to illustrate whether the output gases from the reformer are the appropriate gases for an MCFC anode and cathode respectively. Four cases are selected to illustrate the dynamic behavior of the reformer model. The first case is related to a step change of the process gas, an event which frequently confronts a reformer. The other three cases show the dynamic reaction when step disturbances (of flue gas temperature, process gas and steam/carbon ratio) are applied to the reformer model. The operational conditions and reformer physical data refer to the system and component specifications in Appendices A, B, and D.

4.4.2 Steady-state case

The system is designed to operate at a load ranging from 30% to 100% (Ooue and Y stimulate, 1996), and the reformer should supply appropriate gases (i.e. temperature, pressure, and concentration) for the fuel-cell stacks throughout this load range. The reformer operation corresponding to the lowest system load represents one of the most severe operating conditions (the furthest from the design conditions). This case is therefore examined as follows. The crucial input data are:
Chapter 4  A Reformer Model

- On the process gas side, the process gas input is 0.62 mol/s and 450°C. The ratio of steam/natural gas is 2.5. This gives a steam input of 1.55 mol/s.
- On the flue-gas side, the natural gas flow-rate is 0.23 mol/s at 450°C (the system actually uses the anode exhaust gas, but the HER test from the literature uses mostly methane gas or natural gas). The coefficient of excess air is 1.2.

Some results from this steady-state case are depicted in Figure 4.7. On the flue-gas side, 0.23 mol/s natural gas is burned. Then the flue-gas goes through BHX1 and BHX2, while a heat of 75.7 kW and 38.3 kW are transferred to the catalyst beds BED2 and BED1 respectively. Finally, the reformer discharges 2.4 mol/s flue-gas (CO₂ concentration is 40% mol/mol). On the process gas side, 0.62 mol/s natural gas and 1.55 mol/s steam are the input streams. At the outlet of BED1, the process gas has a temperature of 561°C and a H₂ concentration of 33.4%. More conversion is carried out in BED2 at a higher outlet temperature of 834°C. Finally, the reformer delivers 3 mol/s product gas with 47% H₂ (CH₄: 1% and CO: 10%). In addition, the gas operating gas pressure is around 3 bar and the pressure drop is in the order of 0.1 bar (refer to Appendix D.3). This indicates that the output gases to the fuel-cell stack will be within the designed operating pressure range of 1 bar to 7 bar.

![Diagram of the reformer model](image)

**Figure 4.7** The reformer model performance at stationary conditions

In conclusion, the reformer supplies suitable gases for the fuel-cell stacks. The processed gas from the reformer has a temperature of 607°C, a pressure of 3.2 bar, and a concentration of H₂ of 47%. Hence, the processed gas satisfies the feeding gas requirement to the fuel-cell anode. The flue-gas from the reformer has a temperature of 633°C, a pressure of 3.3 bar, and a substantial amount of CO₂ of 40%. The flue-gas will be cooled down to about 550°C after the air heater, and it also meets the feeding gas requirement to the fuel-cell cathode.

It should be noted that the calculated CH₄ concentration (1%) of the product gas agrees with the test results (CH₄<2%) (Stahl and Laursen, 1992) and with the design requirement (CH₄<4%) (Uematsu et al., 1994). The low CH₄ concentration is a result of the assumed equilibrium conditions. Hence, the calculated low CH₄ concentration is qualitatively consistent with the fact that the conversion rate of equilibrium is higher than that for real conditions.
4.4.3 Open-loop step change cases

Four cases show the reformer responses to a frequent occurrence of reformer operating at load-following mode (step change of the process-gas flow-rate) and to three disturbances (step changes of the flue-gas temperature, the process-gas pressure, and steam/natural gas ratio) respectively.

**Step change of the process-gas flow-rate.** In order to change the flow-rate of the processed gas, the flow-rate at the process gas inlet is often manipulated. Thus, the dynamic behavior of the reformer is examined as a result of a 5% step change of the process gas flow-rate.

Figures 4.8 and 4.9 show the responses of the output process gas at different time scales. The responses of the flow-rate, temperature, and hydrogen concentration are as follows.

- The response of the output process gas flow-rate consists of a fast increase (time scale of 10 seconds) at the beginning followed by a small and slow (time scale of 1000 seconds) decrease in the following stage. The flow-rate of the output process gas increases by 0.9 mol/s (4.5%) from 20.1 to 21.0 mol/s.
- The temperature decreases 7 K from 600°C to 593°C within a time scale of $10^3$ seconds.
- The H₂ concentration decreases 0.6% from 47.0% to 46.4% within a time scale of $10^3$ seconds.

![Figure 4.8](image)

**Figure 4.8** Responses to a +5% step change of process gas flow (large time scale)
Figure 4.9  Responses to a +5% step change of process gas flow (small time scale)

Firstly, the fast increase in the output process-gas flow-rate results from the process-gas flow-rate increase at the inlet, which results in a higher rate of the reforming reaction (Eq. 4.1). The slow decrease of the flow-rate results from the lower reforming-reaction conversion-rate due to the lower temperature. Secondly, the temperature decreases due to the higher conversion rate of the reforming reaction. Thirdly, the hydrogen concentration of the process-gas decreases due to the reforming-reaction equilibrium shift corresponding to the lower operating temperature.

This case indicates that the manipulation of the flow-rate at the process gas inlet is an effective strategy for changing the output flow-rate of process gas (4.5% change in a time scale of 10 s). It should be noted that the change in the output process-gas flow-rate (4.5%) is smaller than the change at the process-gas inlet (5%), because the reforming-reaction equilibrium shifts owing to the lower temperature. In addition, there are at least two side effects: (i) the hydrogen concentration fluctuation of 0.6% and (ii) the temperature variation of 6 K at the output process gas. The process gas is fed to the fuel-cell anode. Firstly, the hydrogen concentration fluctuation of 0.6% does not have a large influence on the fuel-cell stack operation. Secondly, the operation temperature of the fuel-cell will not change by 7 K (usually less than 7 K), because there is also a large amount of cathode gas which has no such fluctuation. The fuel-cell stack is allowed to operate in a temperature range of 550°C to 750°C. Thus, the side effect of the temperature does not usually harm the fuel-cell operation. When it is necessary to reduce these side effects, the use of multiple control loops to limit the fluctuations of hydrogen concentration and temperature may be considered.

Step change of the flue-gas temperature. The temperature of the fuel gas going to the burner may fluctuate during the reformer operation (especially the fuel gas using recycled anode exhaust gas). Hence, the dynamic behavior of the reformer as a result of a +10% temperature step change of the flue-gas going to the burner is examined.
Figure 4.10 shows the responses of the temperature and hydrogen concentration of the output process gas. The responses to the +10% step change are as follows:

- The temperature of the output process gas increases only 1 K.
- The hydrogen concentration increases only 0.05%.

Figure 4.10  Responses to a +10% step change of the fuel gas temperature

The higher the temperature of the flue gas, the more heat is transferred to the process gas, which results in a higher temperature of the process gas. The higher temperature of the process gas increases the conversion rate of the reforming reaction, which absorbs more heat and results in a lower operation temperature. Consequently, the variations in the temperature and hydrogen concentration of the output process gas are small with regard to the temperature change of the flue-gas. The reformer output process gas has a low sensitivity to the temperature disturbance of the flue-gas. Usually, the reformer performance is expected to be very sensitive to the temperature change because the chemical conversion rate is an exponential function of the temperature. In this case, the higher temperature of the flue-gas results in only a 1 K increase in the output process gas temperature, thus the change in the process conversion rate is small. The heat from the flue-gas has mainly been absorbed by the high endothermic reforming reaction.

The fact that the process gas has a low sensitivity to the flue-gas temperature disturbance fits well with the reformer characteristics claimed by Stahl (1992). This characteristic has provided a good opportunity for the reformer to use the exhaust-gas from the fuel-cell power-generation subsystem. In addition, this low sensitivity behavior justifies our assumption in Section 2.6.2 that the temperature disturbance impact (temperature delay due to the water separation in the anode-recycle-gas loop) on the reformer performance should not be included in this study.

Step change of the process-gas pressure. The process pressure is an important operational parameter and the reformer usually operates around the designed optimal pressure (at 3 bar for this system). The lower gas pressure favors the reformer conversion rate. A disturbance of the process gas pressure may occur during the reformer operation. This case examines the reformer's response to a change of process gas pressure.
Figure 4.11 shows the responses to temperature and hydrogen concentration of the output process gas. The responses to the -10% step change of process gas at the reformer outlet are as follows.

- The response of the gas temperature consists of a fast decrease at the beginning and then a small fluctuation in the following slow stage. The gas temperature decreases by 2.7 K.
- The response of the H₂ concentration consists of a fast and large drop (5%) and a fast increase at the beginning, and then a small and slow decrease in the following stage. The increase of the H₂ concentration is 1.2% (from 45.2% to 46.4%).

![Graph showing temperature and concentration responses](image)

**Figure 4.11 Responses to process gas pressure -10% step change**

The lower operation pressure results in a higher reforming conversion rate. However, the higher reforming conversion rate results in a lower operation temperature. Since the influence of the lower pressure (-10%) is larger than that of the lower operation temperature (2.7 K decrease), the reformer conversion rate increases and the hydrogen concentration of the gas increases 1.2%. In addition, the change in the reforming conversion-rate due to the temperature drop is slower than the rate change due to the pressure decrease. The gas-flow change due to the pressure change is also fast. As a result, at the beginning the hydrogen concentration of the process gas has a fast drop due to the fast increase of the process-gas flow-out, and a fast increase due to the pressure decrease in the catalyst bed. In the following stage, the hydrogen concentration has a small and slow drop due to the temperature drop.

This case shows: (i) the process-gas temperature variation is 2.7 K, which will not result in a significant impact on the fuel-cell operation, but (ii) the hydrogen concentration fluctuation is 5%, which influences the fuel-cell operation. Therefore, the operational pressure of the process gas is important for the reformer performance.

**Step change of a steam/natural gas (S/N) ratio.** The S/N ratio (S/N = 1.2 steam/carbon ratio (S/C)) is an important operational parameter and the reformer usually operates around the designed optimal S/N ratio. However, the natural gas and steam are fed separately to the reformer, and the steam is generated by using the heat of the cathode exhaust gas. A disturbance
of the S/N ratio may occur during the reformer operation. This case examines the reformer response to the change of the S/N ratio.

![Graph of Change of S/N ratio](image1)

*Fig. 4.12 Responses of gas conversion to change of S/N ratio*

Figure 4.12 shows the responses of the methane concentration at the outlet of the first and the second catalyst beds as follows.

- The response of the methane concentration at the outlet of the first catalyst bed increases slowly by 1.4% (from 15.2% to 16.6%) within a time scale of $10^3$ seconds.
- The response of the methane concentration at the outlet of the second catalyst bed increases slowly by 1.1% (from 0.95% to 1.06%) within a time scale of $10^3$ seconds.

Since the lower S/N ratio reduces the reforming conversion rate as expected, the methane concentration increases both at the outlet of the first and the second catalyst beds. This case shows that the methane concentration increases only 1.1%, which is not significant. Therefore, when the S/N ratio (this case is 2.5) is higher than the required value, the reformer operation is not sensitive to S/N ratio disturbances. This reformer behavior indicating a low sensitivity to S/N disturbances justifies our modeling simplification assumption in Section 2.6.2 that the reformer operates at a fixed S/N ratio.

Operating characteristics of the reformer in the fuel-cell system are explored in more detail by the system model.
4.5 Discussion of the Reformer Model

The reformer model represents the HER working principle, which deals with the chemical reactions of the process gas at two catalyst beds under different temperatures and the interrelated heat-transfer processes. The reformer model includes the impact of the main processes which determines the output gas concentration, temperature, pressure, and flow-rate. More precisely, the reformer model calculates the steam-reforming reactions in the process gas, the combustion reactions in the reformer burner, the heat-transfer processes, and the pressure drop. However, these processes are not described in distributed form, because much of the internal design data reformer are unknown.

The present reformer attempts to have predictable performance. For example, the reaction conversion rates are calculated based on equilibrium conditions. The calculated conversion rates of the process gas are expected to be a few percentages higher than the rates under real situation. In the steady-state case, the calculated CH₄ concentration of 1% is low, which results from the high conversion rate based on equilibrium conditions. The assumption of reaction conversion rates based on equilibrium conditions suits transient conditions, since the time order of the reaction reaching equilibrium is expected to be much faster than the time order of the heat storage.

4.6 References


Laag, P. C. van der, and Verbruggen, T. W., "Conceptual designs of first-generation 250 kW MCFC demonstration plants", presented at Fuel Cell Seminar, November 28-December 1, San Diego, California, USA, 152-155


5 SYSTEM MODEL AND APPLICATIONS

This chapter provides a model of the complete MCFC system that takes into account the dynamic interactions between the reformer and fuel-cell stacks. First, the modeling simplifications at system level are reviewed. Secondly, the system model is obtained by integrating the fuel-cell stack and reformer models developed in Chapters 3 and 4, and the component models described in Appendix B. Thirdly, the system power-generation characteristics of the system are predicted. The dynamic interactions between the reformer and fuel-cell stacks are also identified during load-following modes. Finally, the effectiveness of the model is demonstrated for improving operation and design.

5.1 Introduction

The proposed system (described in Chapter 2) presents the state-of-the-art of the MCFC system development. The net electric efficiency of the system reaches 45.8% at full load. This section studies the system at partial load and under load-following conditions. The dynamic performance of the system depends not only on the stack characteristics, but also on the gases from the fuel processing sub-system and from the heat recovery sub-system. Furthermore, the anode-off gas from the fuel-cell stack is recycled to the reformer inlet. There may be dynamic interactions between the stack and reformer under load-following modes. Therefore, a system model is required to predict the power-generation characteristics of a complete MCFC system and the dynamic interactions between the reformer and fuel-cell stacks.

The previous literature study (Section 1.4.3) indicated that there is a need for a general dynamic MCFC system model with accurate component models. Chapters 3 and 4 have provided a fuel-cell stack and a reformer model. The other seven components in the system are: (1) steam generator, (2) water separator, (3) mass-transport equipment (e.g. blower, compressor, expander and pump), (4) heat exchanger, (5) DC/AC inverter, (6) splitter, and (7) mixer. The models of these components have been given in Appendix B. Therefore, the system model can be achieved by integrating all component models.

5.2 Modeling Simplifications

In order to accept the developed component models and to indicate the limitations of the system model, the modeling simplifications at system level are reviewed. The major modeling simplifications at system level described in Section 2.6 are as follows:
• The performance of the system is focused on the contributions resulting from the fuel-cell stacks and the reformer. The dynamic impacts of the steam generator and water separator are included in this study.

• The requirement of the load-following capability for a 1 MW system is estimated to be about 10%/minute (IHI, 1995). Processes with a time constant range of 10 to 10^3 seconds are influential with regard to the load-following capability of the system. Models of components which are involved in such processes must be dynamic models. Accordingly, the fuel-cell stack, reformer, and heat exchangers are modeled in dynamic form. The mass-transport equipment (e.g. blower, compressor, expander and pump), DC/AC inverter, splitter, and mixer involve fast processes and are modeled in stationary form.

_Discussions with regard to point 1_. First, the neglect of the dynamic impact of the steam generator is justified by the low sensitivity of the reformer to steam/natural gas (S/N) ratio disturbances (Section 4.5.3). However, the temperature influence due to the steam generation under transient conditions is not considered. Secondly, the neglect of the dynamic impact of the water separator is justified by the reformer having a low sensitivity to the temperature disturbances in the flue-gas going to the burner (Section 4.5.3).

_Discussions with regard to point 2_. The simulation results of the reformer show that the reformer's processed-gas flow-rate has a fast response owing to the gas transport (time order of 1 to 10 seconds), and the gas concentration has a slow response owing to the temperature change (heat storage) (time order of 10^2 to 10^3 seconds). The responses of the stack output power consist of: i) an immediate response due to the electrode power-generation behavior, ii) a fast response due to the gas concentration variation (gas transport) (time order of 0.1 to 1 second), and iii) a slow response due to temperature variation (heat storage) (time order of 10 to 10^3 seconds).

The simulated reformer and stack characteristics indicate that the system's output-power consists of a fast response (time order of 0.1 to 1 seconds) and a slow response (time order of 10 to 10^3 seconds). The system model does not include all the fast processes in dynamic form (e.g. mass-transport equipment in stationary form). Hence, the system model only applies to the prediction of the slow response, which is sufficient to evaluate the load-following capability of the system with regard to the requirement of 10%/minute (IHI, 1995).

In addition, the following simplifications and operational conditions are introduced for the simulation of the performance of the entire system.

• **Fixed ratio of steam to natural gas S/N (also steam to carbon ratio).** The transient changes in the steam generator are not considered. The steam generator provides the required steam from the reformer immediately according to S/N ratio.

• **Open-loop conditions.** Since this study emphasizes the inherent system characteristics before the control study, the system is under open-loop conditions.

### 5.3 Description of System Model

#### 5.3.1 Model structure

The system model is obtained by integrating the fuel-cell stack, reformer, and the component models described in Appendix B. Figure 5.1 gives the system's implementation in SPEEDUP
code. Q1, Q2, Q3, and Q4 are the heat transfer in the steam generator, fuel preheater, heat exchanger and air preheater respectively. The system model comprises a connected network of operational units, which emulates the flow diagram of the system. Each operational unit refers to one type of component model and is individually parameterized with design and operating data.

![System Diagram](image)

**Figure 5.1 Structure of the system diagram in SPEEDUP code**

### 5.3.2 Variables transfer between units

In the system model, the variable transfers between units must be defined. Each unit must embody mathematical consistency. The input and output variables of each unit result from both the cause-and-effect sequence of the equations in each unit and the variable transfers between units reflecting bilateral interactions (MMS, 1985). When a component model is integrated into the system, it is necessary to re-consider both its input and output variables, and its equations.

Figure 5.2 shows the variable transfers between the operational units in the fuel-cell power-generation subsystem. By manipulating the flow-rate, concentration and temperature of the processed gas or flue gas, or the required current output, the subsystem achieves various output power and results in different exhaust gases. The pressure of the exhaust gas also determines the pressure of inlet gas stream.
5.3.3 Simulation running

**Simulation under steady-state conditions.** Since the simulation results under steady-state conditions are used to initialize the dynamic simulation, the problems with regard to the steady-state simulations are firstly dealt with. When the system model runs under steady-state conditions, simulation failures often result from variables beyond the estimated limits or various divergences. Estimation of the minimum and maximum limits and default values for essential variables (i.e. temperature) effectively helps simulation convergence. In general, defining a smaller band of variable change results in an easier convergence of simulation. However, the input file for the simulation is applicable for a smaller system operation range. Multiple input files are used for simulations of the system throughout the entire operation range.

**Simulation under transient conditions.** When the system model runs under transient conditions, simulation failures often result from the two following causes:

- **Large changes in manipulated variables.** A large step change of the input variable can be approximately represented by many changes of the short time steps. For example, a 10% current step change is simulated by 100 step changes of 0.1%.

- **Long simulation time.** The selection of a time step has an important impact on both the simulation time and the accuracy. A smaller time step usually results in easier convergence in each step because smaller variations of parameters occur in each step, but results in a longer simulation time. The approach in this thesis, therefore, uses a smaller time step for the time range with fast responses and a larger time step for the time range with slow responses. To maintain simulation stability, the limit of the maximum time step should be noted (MMS, 1983).
5.4 Model Performance

5.4.1 Setting-up cases

To evaluate the model performance and to illustrate the operating characteristics of the proposed 1 MW system, nine cases listed in Table 5.1 were selected.

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<th>Objectives</th>
<th>Cases</th>
</tr>
</thead>
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<td>System efficiency throughout the load range</td>
</tr>
<tr>
<td>System load-following capability</td>
<td>Output power responses to a +5% step current change (under high fuel utilization)</td>
</tr>
<tr>
<td></td>
<td>Output power responses to a +5% step current change (under low fuel utilization)</td>
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<td></td>
<td>Output power responses to a +5% step fuel flow change</td>
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<tr>
<td>Dynamic interactions between components under load-following operation modes</td>
<td>Dynamic interactions between the fuel-cell stack and reformer under load-up operation mode</td>
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<tr>
<td>Model evaluation</td>
<td>Compare the calculated system response to the measured results from a 100 kW system</td>
</tr>
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</table>

5.4.2 System efficiencies

The illustration of the efficiency of the system through the load range is based on two reasons:
- The system's efficiency at full load can be compared with the data known from Uchijama and Segawa (1991) and the calculation by using CYCLE-TEMPO in Chapter 2.
- The system's efficiency profile throughout the load range is effective in illustrating the simulation results of the system under steady-state conditions.

The system is designed to operate in a load ranging from 30% to 100% (Ooue and Yasue 1996). It is assumed that the operational range of the system can stretch 10% beyond its maximum and minimum limits (with the same system and the component configurations). The system model was used to simulate the load level between 20% to 110% of design load.

Figure 5.3 shows the calculated overall efficiency of the system. The efficiency of the system is within the range of 40 - 50% throughout the load range. The system reaches its highest efficiency at partial load instead of at full load. This is caused by the fact that the fuel-cell stack has a higher efficiency at a lower power output (Blomen and Nugeva, 1993), but most other components in
the system still have lower efficiency at a lower power output. When the load is higher than 0.45 MW, the overall efficiency of the system decreases because the fuel-cell efficiency decrease is more significant than the efficiency increases of the other components.

![Overall system efficiency](image)

**Figure 5.3 Efficiency of System in entire load range**

The efficiency of the system at full load (1 MW) is 45.2%. This value is close to the system’s efficiency of 45% from Uchijama and Segawa (1991) and our system’s design efficiency of 45.8% calculated by using CYCLE-TEMPO in Chapter 2. In conclusion, the model performance under steady-state conditions is considered to be acceptable.

### 5.4.3 System load-following capability

As discussed in Chapter 2, the power output from the fuel-cell system refers to the output power generated by the fuel-cell stack. Manipulating fuel-cell current output or system fuel inputs can control the system power output. It is assumed that the stack operates under the fuel utilization constraints. The current output of the fuel-cell stack can be manipulated to rapidly accommodate small load variations. The DC/AC inverter achieves the current output variation. When there are large variations in load, the flow rates of fuel and air must also be changed.

This section shows: (i) the system’s responses to a step change of the required current (with fixed input gas flow), and (ii) the system’s responses to a step change of the required current and a same step change of the input fuel flow (with approximate fixed fuel utilization in the fuel-cell).

#### 5.4.3.1 Power response to current change

According to the fuel-cell characteristics discussed in Chapter 3, withdrawing a higher current output from a fuel-cell results in a higher power output within the allowable gas utilization range. However, a higher current output results in a lower reactant gas concentration, which reduces the voltage output. This voltage drop phenomena will be more significant at high gas utilization conditions. Consequently, the power output responses to current change under high and low gas utilization conditions will be illustrated. In addition, the Dutch requirement for a +5% step change power demand is that half of this must be met within 5 seconds and the remainder within 25 seconds. Therefore, our simulation shows the power response in the time range of 100 seconds.
Figures 5.4 and 5.5 illustrate the responses of the power output versus a +5% step change in current density under high and low fuel utilizations. The increase in the current results in a fast change in the gas utilization. The hydrogen utilization increases from 80% to 84% on the fuel gas side. The voltage response has a fast beginning with significant voltage drop (due to the current increase) and then a following stage of voltage recovery (due to changes in gas concentration and temperature). Based on the responses of the current and voltage, the power response consists of a fast beginning with significant power increase (due to the current change) and a following stage of power drop and slow recovery (due to the voltage change). It should be noted that the voltage drop of 23 V at high fuel utilization in Figure 5.4 is much higher than that of 14 V at low fuel utilization in Figure 5.5. Consequently, the power response under low fuel utilization is smoother than that under high fuel utilization. After the 100 seconds, the power increase is 4% under low fuel utilization, while the power increase is only 2.5% under high fuel utilization.

This case indicates that the current change can effectively manipulate the output power (with a significant change simultaneously). It should be noted that the change in the output power (4% at low fuel utilization or 2.5% at high utilization), is smaller than the change in the current (5%), because of the side effect of the voltage drop (14 V at low fuel utilization and 23 V at high utilization). The system's load-following capability under low fuel utilization is better than that at high fuel utilization.

![Figure 5.4 Power responses to a +5% step current density (high fuel utilization)](image-url)
Figure 5.5 Power responses to a +5% step current density (low fuel utilization)

5.4.3.2 System responses to fuel flow-rate change

In order to maintain the same fuel utilisations in the fuel-cell stack, the gas flow-rate should also have a change in addition to the current change in Section 5.4.3.1. This case shows the system response to a 5% step change of the required current and a 5% step change in fuel input flow. Figure 5.6 shows the system responses. At the reformer outlet, the flow rate of the process has a fast and large increase (due to step change of the fuel input) and then a decrease in the following stage (due to temperature decrease), while the hydrogen concentration has a dip (for the reformer performance refer to Chapter 4). The stack voltage has an immediate voltage drop due to the current step up, a fast change due the gas concentration in the stack, and a slow change due to the stack operating temperature variation.

The output power has a 4.2% increase with regard to 5% step changes in the current and fuel input. It should be noted that the side effect of the voltage drop (4 V) is much smaller than that from the single current manipulation in the previous case.
Figure 5.6 Power responses to a +5% step change of fuel flow (large time scale)

5.4.4 Interactions between the components

The fuel-cell system integrates the stack and the reformer. The fuel included in the anode exhaust gas is recycled to the reformer burner to provide the heat source for the reforming processes. There may be dynamic interactions between the stack and reformer. The temperature fluctuations in the reformer burner and the hydrogen used by the stack are important to the safe operation of the reformer and stack. Therefore, it is interesting to study the interactions of the reformer burner temperature and stack fuel use under load-following operations. During load-up operation, increasing both the fuel input and current output is a frequent operation. Thus, the case with a 5% step change of fuel input and a 5% step change of current output is selected.
Figure 5.7 Interactions between stack and reformer under load-up operation mode

Figure 5.7 shows that high current output in the fuel-cell stack causes high fuel utilization, which results in low hydrogen concentration at the stack outlet. The low hydrogen concentration causes the low combustion heat released and the low temperature from the flue gas, which will reduce the reforming processes and result in even higher gas utilization in the fuel-cell. In this case, the hydrogen utilization in the stack increases from around 80% to 87.5% then falls back to around 81%. The hydrogen utilization exceeds the limit of 85% (Uchijama and Segawa, 1991). This excessive hydrogen utilization results in a hydrogen concentration drop from 6.5% to 4% at the reformer burner inlet. Then the flue gas at the outlet of the burner has a temperature drop of 55 K (1228°C to 1173°C). After the lag of feeding gas transport, both the hydrogen utilization and combustion-gas temperature reach new equilibrium values. This case indicates the potential problem of excessive H₂ utilization in the stack resulting from the dynamic interaction between the fuel-cell stack and reformer during the load-up operation mode. An alternative operation to reduce the hydrogen utilization will be discussed in Section 5.5.1.

Figure 5.8 shows the dynamic interaction between the fuel-cell stack and reformer under load-down operation mode. There is a high combustion temperature in the reformer caused by the anode exhaust gas with higher H₂ concentration at lower power output.
Figure 5.8 Interactions between stack and reformer under load-down operation mode

5.4.5 Safe operation of the components

During the load-following operation modes, it is also important to know whether each component operates within its safety constraints. The highest priority safety constraint is the pressure difference in the fuel-cell (Sasaki et al., 1988), and it is evaluated.

5.4.5.1 Responses of the pressure difference in fuel-cell stack

In order to prevent damage to the cell, the constraint of the pressure difference between anode and cathode is around 4 kPa under normal operation and 8 kPa under transient conditions (Yoshida and Inoue, 1993). The responses of pressure difference between anode and cathode, pressure of anode (Pa) and cathode (Pc) are illustrated in Figures 5.7 and 5.8 under a 10% current step change.
Figure 5.9 shows the fuel-cell pressure response under a -10% current step change. The anode pressure (Pa) decreases and the cathode pressure (Pc) increases because the -10% current step change causes less electrochemical reaction, which decreases the gas phase moles at anode but increases the gas phase moles at cathode. The time constant for the pressure response is in the order of a few seconds. The response of the pressure difference has an overshoot above the new steady-state value. In this case, the overshoot of the pressure differences gives no cause for concern since it is much smaller than 8 kPa. It is important to remember that the time constant range of the process in this case is smaller than the defined time scale of the model. It is recommended that the results presented in this case are verified by the 3D-stack model.

![Figure 5.9 Pressure responses to a -10% step change of current density](image)

5.4.5.2 Response of stack temperature to gas recycling

The cathode recycling ratio regulates the stack temperature. Figure 5.10 shows the responses of the fuel-cell stack temperature and voltage when the cathode gas recycling flow rate is changed from 40% to 60%. The stack temperature is the average operational temperature of the cell solid plate.

Figure 5.10 shows that the stack temperature increases about 10 K when the cathode gas recycling ratio changes from 40% to 60%. The stack temperature response consists of a very fast beginning and a slow following stage. The rapid initial response is caused by the gas mixing process which is modeled in the steady-state form. The real situation may be slower, because of the delay in the cathode recycling gas loop. The change in the following slower stage is caused by the energy storage, which has been modeled in the dynamic state form. The voltage response consists of three stages: (i) the voltage increases resulting from the stack temperature increase at the beginning; (ii) the voltage drops resulting from the reactant concentration decrease at the cathode; (iii) the voltage increases resulting from the following stack temperature increase stage. This case indicates that the cathode gas ratio change is effective to maintain the stack operational temperature within its designed range.
Figure 5.10 Response of stack temperature to recycle-ratio change

5.4.6 Model evaluation

In principle, the proposed system dynamic model is based on fundamental physical laws and therefore should correctly predict the real behavior of the component or system. However, the outcome of this model should always be considered in a critical manner. There are at least three reasons for this:

- **Simplifications.** Each modeling step involves simplifications that are necessary for representation of each real component, the description of processes, the establishment of mathematical equations and the search of solutions. In making the models, the fundamental laws were approximated. For example, in the reformer model, the process gas in each catalyst bed was assumed to be perfectly mixed in order to derive an ordinary differential equation that is much easier to solve than a partial differential equation. Moreover, since the dynamic behavior of the auxiliary components (e.g., steam generator, water separator and transport equipment) is not included, the system model focuses on the impacts from the stack and the reformer components. The system model does not include the impacts from all the components.

- **Empirical correlation.** Although the component models are based on physical rules, a certain number of empirical or semi-empirical correlation to calculate the transfer coefficients for heat and mass are used. Such correlation is usually obtained by other investigators under their own specific experimental circumstances. Even though we have attempted to select those which have similar operating conditions to ours, deviations are almost inevitable. Moreover, the correlation themselves are not 100% accurate.

- **Input design data.** Although a system design was conducted to provide component or system design data, it could not include all engineering realization considerations. The
estimated component design data may be different from the one used in practical situations.

Validation of the results derived from our simulation tools is necessary before they can be put into use. No experimental data are available for the dynamic performance of the 1 MW system. However, a 100 kW class MCFC test plant (Yoshida and Inoue, 1993) has been set up to establish the fundamental operation techniques for the 1 MW class MCFC system. The 100 kW test system has a comparable configuration to that of the 1 MW system we studied, although it uses a dummy fuel-cell stack and different type of reformer. Therefore, the available measured data from the 100 kW MCFC system has been used to evaluate the model performance. Yoshida and Inoue (1993) described the test system and the measured responses of the stack gas utilization to a ramp change of the power from 30 kW to 100 kW. When the load demand has a ramp change, the fuel input and the current output are manipulated to have a similar ramp change to match the required power output.

Figure 5.11 (a) gives the responses of the power output and H₂ and O₂ utilization to a ramp changes of fuel input and current power derived from our simulation model. Figure 5.11 (b) gives the profile based on measured data (Yoshida and Inoue, 1993). Though power output in Figure 5.11 (a) has a small overshoot, its change matches the load demand in Figure 5.11 (b). The computed responses of H₂ and O₂ utilization qualitatively agree with the profiles of the measured results. The model validations should be continued, when the appropriate experimental data are available.

Figure 5.11 (a) Calculated responses of stack output power and gas utilizations
Figure 5.11 (b) Response of gas utilization profiles based on measured data

5.5 Model Applications

The system model is applied to improve both operation and design. The improvement in operation is carried out with regard to the reduction of the dynamic interactions between components. The effectiveness of the system model for the design of systems is demonstrated by applying it for selection of control valve location.

5.5.1 Operation improvement

As discussed in section 5.2.4, dynamic interactions exist between the fuel-cell stack and reformer during load-up operation mode. As shown in Figure 5.7, the high hydrogen utilization in the fuel-cell stack results in low operation temperature of the reformer, which reduces the reformer performance and provides the process gas with less hydrogen concentration. The process gas with less hydrogen results in higher hydrogen utilization in the fuel-cell stack. In the case shown in Figure 5.5, the hydrogen utilization exceeds its limit of 85%.
Figure 5.12 Effect of providing fuel gas to reformer combustor

In order to reduce these dynamic interactions, one approach is to decrease the dependence of the reformer burner temperature on the fuel-cell exhaust gas. We propose supplying the fuel gas directly to the combustor in the reformer. If a small amount of fuel gas (0.30 mol/s) is directly supplied to the combustor for one minute from \( t = 50 \) seconds to 110 seconds, the temperature of the flue gas (i.e., the fuel gas after combustion) at burner outlet increases in comparison with the previous temperature profile as shown in Figure 5.12. The 50 K peak temperature increase in the flue gas provides more heat for reforming reaction, which is favorable to the reforming process and reduces the excessive hydrogen use in the fuel-cell stack. Figure 5.12 also shows that the hydrogen utilization is lower than the limit of 85% under the load-up conditions. The side effect of the temperature increase of the combustor is much less than the flue gas temperature increase of 50 K, which is not very harmful in this case. This proposed operation strategy uses a small amount of fuel gas injection (around 7% of the system fuel feeding gas) for only one minute and thus the influence on the system’s efficiency is small. Therefore, this simulation model provides a valuable recommendation for system operation improvement.

This alternative operation strategy uses a small amount of fuel gas injection (around 7% of the system fuel feeding gas) for only one minute and thus the influence on the system efficiency is
small, so the proposed strategy is a valuable recommendation for the improvement of the operation of the system.

### 5.5.2 Improvement of system design

The model can also be used to select different control strategies, for example control valve location. The gas temperature at the anode inlet is around 700°C and the fuel gas at reformer inlet around 450°C (He, 1997). There are two options to control the fuel flow rate: one at the anode inlet and the other at the reformer inlet. The fuel flow rate at the reformer inlet can be controlled by a normal temperature control valve, but the gas flow at the anode inlet must be controlled by a high temperature valve. Figure 5.13 shows the possible location of these two fuel-flow control methods. In order to make the correct selection, it is important to predict the performance of the fuel-cell system by using both methods.

![Diagram](image)

**Figure 5.13 Alternative fuel-flow control with normal or high temperature valves**

Figure 5.14 illustrates the simulated power responses of a +10% step change in the fuel gas at the anode inlet or at the reformer inlet, while the current simultaneously has a +10% step change. The absolute flow rate change at the anode inlet is around 20 to 25 mol/s, which is much larger than that at the reformer inlet (around 4 to 5 mol/s). The power response to the fuel flow control at the anode inlet (high temperature control value) however, is faster and smoother. These results are expected, because the gas entering at the anode inlet immediately generates power, but the fuel gas entering at the reformer inlet has to be reformed before it enters the stack anode. It is noticed that the power response to the normal temperature control valve regulation consists of a fast power increase at the beginning, and then a dip, followed by a slow power increase to the new desired value. The fast power increase results from the simultaneous change of the current and the residual fuel gas in the stack, and the dip is caused by delay in the fuel supply from the reformer. The subsequent slower power increase is related to the slow response of the reformer. The dip is much larger under high gas utilization than that under low gas utilization.
Figure 5.14 Power responses to flow change at reformer inlet or at anode inlet

A fuel-cell system usually uses one reformer but several fuel-cell stacks (Uchijama and Segawa, 1991). The fuel-flow control at the anode inlet needs several high temperature control valves. The usual control design criteria demand the use of fewer control valves and minimum high temperature valves. Therefore, if the power response can meet the demand, it is more favorable to control the flow at the reformer inlet.
5.6 References


Uchijama, Y. and Segawa, T., 1991, "Subsequent results of a 1 MW class pilot plant development", Technology research association for molten carbonate fuel cell power generation system, Tokyo, Japan.

Yoshida, T. and Inoue, T, 1993, "Test results of 100 kW class MCFC system and control test plant, Ishikawajima-Harima Heavy Industries Co., Ltd., note, pp. 5
6 CONCLUSIONS AND RECOMMENDATIONS

This thesis describes the development of a 3D fuel-cell stack model, a reformer model, and a fuel-cell system model. The four main questions proposed with regard to the operating characteristics of the fuel-cell stack, reformer, and the 1 MW fuel-cell power-generation system have been answered.

6.1 3D Fuel-cell Stack Model

The 3D-stack model presents the internal behavior of the stack. It includes all the processes that contribute to the stack power-generation behavior with regard to load-following modes. More precisely, it describes: i) the gas transport, chemical reactions, and heat transfer at cell level, ii) the heat and gas transport at stack level, and iii) the current and heat generations due to the electrochemical reactions at the electrodes. The 3D-stack model has been implemented by using a computational-fluid-dynamics (CFD) program PHOENICS. The 3D-stack model has two advantages over most of the dynamic stack models in lumped form presented in the literature.

- **Improvement in predicting power-generation behavior.** The 3D-stack model predicts the current density distribution from the temperature and gas concentration distributions. The 3D-stack simulation results show the two dimensional distributions of the current density in each cell (cross-flow). A calculated case shows that the variations in the current density reach around 1000 A/m² in a cell reaction area of 1 m². It is difficult for a stack model in lumped or one-dimensional form to adequately represent such current output characteristics, which are crucial for an accurate power-output prediction.

- **New functions identifying stack safety operation.** The 3D-stack model has new functions indicating whether operating limits are violated for a certain power generation. For example, in order to identify safe stack operation, the 3D-stack model provides the temperature distributions that cannot be obtained from a stack model in lumped form.

The performance of the 3D-stack model under steady-state conditions is evaluated by a comparison between the temperature profiles derived from simulations of the model that is presented and the temperature profiles derived from simulations given in the literature. The predicted temperature profiles from the model presented agree qualitatively with the simulated profiles given in the literature. Furthermore, the variations between the isothermal lines computed with the proposed model and most of the measured data given in the literature are less than 10 K (i.e. less than 2%).

With regard to the first main question, the fuel-cell stack power-generation characteristics and the safe stack operation are demonstrated as follows:

- The dynamic behavior of the stack was illustrated by the simulated responses of the current density and temperature to a +10% voltage-change step. The response of the stack output
power consists of: i) an immediate response due to the electrode power-generation behavior, ii) a fast response (time order of 0.1 to 1 second) due to the gas concentration variation (gas transport), and iii) a slow response (time order of 10 to 10² seconds) due to temperature variation (heat storage).

- The simulation results of the 1 MW stack have shown that the temperature distribution under transient conditions is within the safety constraints (i.e. a maximum temperature lower than 750°C and a maximum temperature gradient smaller than 10 K/min).

In addition, the 3D-stack simulation results are used in developing a simple stack model for integration into the system model. For example, the 3D results are used for making simplifications and identifying the model parameters to reach the same power output value as the 3D-stack model at full load.

6.2 Reformer Model

The development of the reformer model has focused on two aspects: i) the representation of the HER working principle, and ii) the HER capability with regard to load-following operation modes.

With regard to the second main question, the reformer operating characteristics are demonstrated by the following cases:

- In the stationary case, the processed gas from the reformer has a temperature of 607°C, a pressure of 3.2 bar, and a concentration of H₂ of 47%. Hence, the processed gas suits the feeding gas requirements of the fuel-cell anode. The flue-gas from the reformer has a temperature of 633°C, a pressure of 3.3 bar, and a substantial amount of CO₂ of 40%. The flue-gas will be cooled down to about 550°C after the air heater, and it also suits the feeding gas requirements of the fuel-cell cathode.

- Four cases show the reformer responses to a frequently occurring load-following mode and three disturbances (variations of flue-gas temperature, process gas pressure, and steamcarbon ratio respectively). Manipulation of the input process gas is effective in controlling the feeding gas to the fuel-cell anode, though it leads to two side effects: fluctuations of the hydrogen concentration and temperature. The reformer shows a low sensitivity to disturbances of the input-gas temperature to the burner and the ratio of steam/natural gas, but a high sensitivity to the process operating pressure. Four cases are as follows:
  i. Manipulating the input process gas is effective in controlling the supply of the feeding gas to the fuel-cell anode. However, there are at least two side effects: (i) a hydrogen concentration fluctuation, and (ii) a temperature fluctuation. When the flow-rate of the process inlet gas has a +5% step change, the feeding gas to the fuel-cell anode has an increase of 4.5%, which is in a time scale of 10 s. The two side effects are the hydrogen concentration fluctuation of 0.6% and the temperature increase of 7 K. These two side effects are not harmful to the fuel-cell operation. The simulation results of the reformer show that the reformer processed-gas flow-rate has a fast response due to the gas transport (time order of 1 to 10 seconds), and the gas concentration has a slow response due to the temperature change (heat storage, time order of 10² to 10³ seconds).
  ii. The reformer has a low sensitivity to the temperature disturbance of the flue-gas going to the burner. The temperature of the output process gas increases only 1K and the hydrogen concentration increases only 0.05% to a +10% step change of the flue-gas
temperature. This indicates that there is a good opportunity for the reformer to use the exhaust-gas from the fuel-cell power-generation subsystem.

iii. The reformer operation is very sensitive to the operating pressure. The hydrogen concentration of the output process gas has a fluctuation of 5% to a 10% step change of the process gas pressure.

iv. The reformer operation is not very sensitive to steam/natural gas (S/N) ratio disturbances. When the S/N ratio drops from 3 to 2.5, the methane concentration of the output process gas increases by only 1.1%.

6.3 Fuel-cell System Model

The system model is obtained by integrating the fuel-cell stack model, reformer model, and the other component models that constitute parts of the system. The system model has been implemented in a recent dynamic simulation program SPEEDUP. The system model comprises a connected network of operational units, which emulates the system flow diagram. Each operational unit refers to one type of component model and is individually parameterized with design and operating data. The system model is evaluated by one comparison. The simulated utilization of H₂ at the fuel-cell anode and CO₂ at the cathode under load-ramp change is qualitatively consistent with the H₂ and CO₂ profiles derived from the 100 kW test data given in the literature.

With regard to the third main question, the system power-generation characteristics are simulated. The results are:

- **System efficiency.** The system electric efficiency of the system is in a range of 40 - 50% throughout the load range. The system reaches its highest efficiency at partial load instead of at full load. This is caused by the fact that the fuel-cell stack has a higher efficiency at a lower power output, but most other components in the system still have lower efficiency at a lower power output.

- **System load-following capability with regard to current change.** The manipulation of the current results in a fast change in the power output, but a large voltage drop. For a +5% step current change, the power output increases 2.5% within a time order of 10 seconds, but the voltage drops 23 V (3.3%) at high fuel utilization (80%). The manipulation of the current is more effective at low gas utilization. For the same +5% step current change, the power output increases 4% within a time order of 10 seconds with a voltage drop of 14 V (1.8%) at low fuel utilization (40%).

- **System load-following capability with regard to both current and fuel changes.** With both +5% step current and fuel changes, the output power increases 4.2%. The side effect of the voltage drop (4 V) is much smaller than the 23 V or 14 V that occurred in the above cases with the single current manipulation.

With regard to the fourth main question, the interactions between the fuel-cell stacks and reformer are predicted. The results are:

- **Excessive hydrogen utilization in the stack under load-up mode.** High current output in the fuel-cell stack causes high fuel utilization, which results in low hydrogen concentration at the stack outlet. The lower hydrogen concentration causes less combustion heat to be released in the reformer. This reduces the effectiveness of the reforming processes and results in even higher gas utilization in the fuel-cell stack. During a load-up operation (e.g. +5% step change
in both fuel input and current output), the \( H_2 \) utilization in the stack increases from about 80\% to 87.5\%, and then falls back to 80\% in a time order of 100 seconds. The \( H_2 \) utilization exceeds the limit of 85\% during the first hundred seconds of operation.

- **High reformer-combustor temperature under load-down mode.** During a load-down operation, the fuel utilization in the stack decreases and the anode exhaust gas has higher \( H_2 \) concentration. This higher \( H_2 \) concentration results in a higher combustion temperature in the reformer burner, which increases the effectiveness of the reforming processes and results in even lower fuel utilization in the fuel-cell stack.

It has also been demonstrated that the proposed system model is useful for improving system operation and design. More specifically, the system model can be effectively used to access an alternative operation strategy to reduce the dynamic interactions, and to select a suitable location for a control valve. Two applications are as follows.

- **System Operation.** Reducing the dynamic interactions by supplying a small amount of fuel gas directly into the reformer combustor for a short period provides an effective way to solve the problem of excessive hydrogen use during load-up operation. With a fuel injection of 7\% of the system fuel feeding directly to the reformer combustor for one minute, the high \( H_2 \) utilization can be kept within the limit of 85\%.

- **System design.** The fuel-flow control at the anode inlet is more effective than that at the reformer inlet with regard to the rapid, smooth load-following capability. However, the fuel-flow control at the anode inlet needs more higher temperature control valves. If the power response can meet the demand, it is more favorable to control the flow at the reformer inlet.

In conclusion, this thesis has answered the proposed four main questions. Hence, it provides the insight required both introduction of the fuel-cell stack and reformer into power-generation systems. The results of this study are interesting to a designer or an operator engaged in optimizing the design and operation of fuel-cell stacks and systems.

### 6.4 Recommendations

The recommended improvement work and extension of the applications are as follows:

- **Simplification of the 3D-stack model.** The proposed 3D dynamic stack model has made progress towards accurately predicting the power-generation performance of an individual stack. However, the 3D-stack model must be simplified prior to incorporation into the whole system model. The two simplifying approaches which we have tried have major disadvantages. The first approach attempts to represent the response characteristics of the 3D-stack directly. However, the physical nature of this approach is difficult to evaluate. The second approach uses a combination of modeling based on physical laws and empirical modeling techniques. (The second approach has been integrated into the system model). The performance of the simple model under stationary conditions has been improved by the 3D simulation results. It is obvious that the proposed simple stack model has not fully utilized the advantages of the 3D simulation results. The links between the simple stack and the 3D-stack models need to be further explored.

- **Inclusion of the dynamic impacts.** As mentioned in the modeling simplifications at system level, the current system model is focused on the contributions resulting from the fuel-cell stack and reformer. Further work to include the dynamic impacts of the steam generator and water separator is necessary.
• Application to control study. The results of this study do not directly apply to designing control systems. To design a control system, mathematical models of the fuel-cell stack, reformer and system in the form of either transfer function or state space are required. Such mathematical models can be derived from the models developed in this study.

• Adaptation to a fuel-cell system with internal reforming. A fuel-cell system with internal reforming has a more complicated fuel-cell stack model, but simpler system integration. By adding the reforming reaction, the proposed 3D-stack model can be adapted to produce fuel-cell stack with internal reforming. The proposed system model can then be extended to systems with internal reforming.
Appendix A System Design

This section complements the system design described in Chapter 2.

A.1 View of a 1 MW MCFC Plant

Figure A.1 gives a perspective view of the 1 MW MCFC Japanese pilot plant (MCFC, 1995), which indicates the plant layout and the dimensions of our system. The dimensions of the plant are about 10 m x 10 m x 10 m. The general factors considered for the location of the components are: (i) convenience for the operation and maintenance of components, (ii) piping systems, (iii) convenience for the delivery, (iv) the weight and the geometry of the component, and (v) the classification of the area because of the presence of the hydrogen in the anode exhaust.

Figure A.1 Perspective view of the 1 MW MCFC Japanese pilot plant
A.2 Specification of the System Feed Streams

The feed streams for the system are: natural gas, air, and water. The specifications are listed in Table A.1 (Nederlandse Gasunie, 1989).

Table A.1 Specification of the feed streams

<table>
<thead>
<tr>
<th>Feed stream</th>
<th>Value</th>
<th>Unit</th>
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<td>Natural gas:</td>
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<td></td>
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<tr>
<td>Pressure</td>
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<td>bar</td>
</tr>
<tr>
<td>Temperature</td>
<td>15</td>
<td>°C</td>
</tr>
<tr>
<td>Composition: CH₄</td>
<td>81.29</td>
<td>% (mol/mol)</td>
</tr>
<tr>
<td>C₂H₆, C₃H₈, C₄H₁₀, C₅H₁₂, C₆H₁₄</td>
<td>2.87, 0.28, 0.15, 0.04, 0.05</td>
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</tr>
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<td>N₂</td>
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<td>% (mol/mol)</td>
</tr>
<tr>
<td>O₂</td>
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<td>% (mol/mol)</td>
</tr>
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<td>CO₂</td>
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<td>% (mol/mol)</td>
</tr>
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<td>Air:</td>
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<td>bar</td>
</tr>
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<td>°C</td>
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<td>% (mol/mol)</td>
</tr>
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</tr>
<tr>
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<td>bar</td>
</tr>
<tr>
<td>Temperature</td>
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<td>°C</td>
</tr>
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</table>

A.3 Minimum Steam-to-carbon Ratio

This section computes the minimum steam-to-carbon ratio (Alkasab and Lu, 1985), which gives a back-up evaluation on the selected steam-to-carbon ratio in Section 2.3.2 in Chapter 2.

The following reactions are generally chosen to describe the steam reforming of methane (Wagner, 1992).
(i) Methane-steam reaction (also called reform reaction):

\[ \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow 3 \text{H}_2 + \text{CO} \]  \hspace{1cm} (A.1)

(ii) Water-shift reaction:

\[ \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \]  \hspace{1cm} (A.2)

(iii) Carbon deposit reactions:

\[ \text{CH}_4 \leftrightarrow \text{C} + 2\text{H}_2 \]  \hspace{1cm} (A.3)

\[ \text{CO} + \text{H}_2 \leftrightarrow \text{C} + \text{H}_2\text{O} \]  \hspace{1cm} (A.4)

\[ 2\text{CO} \leftrightarrow \text{C} + \text{CO}_2 \]  \hspace{1cm} (A.5)
The carbon deposit reactions (A.3-5) should be avoided. When the ratio of steam to methane in the feed is sufficiently high, carbon cannot be present at equilibrium. In order to determine the minimum steam ratio required to prevent carbon deposit, a constrained minimization problem is set up as follows:

Objective function: Minimum (ratio)  \hspace{1cm} (A.6)

Constraints:

\[
\begin{align*}
(K_{\text{reform}}) & = \frac{(rate_{\text{reform}} - rate_{\text{shift}}) \times (3 \times rate_{\text{reform}} + rate_{\text{shift}}) \times P^2}{(1 - rate_{\text{reform}}) \times (ratio - rate_{\text{reform}} - rate_{\text{shift}}) \times (1 + ratio + 2 \times rate_{\text{reform}})} \\
(K_{\text{shift}}) & = \frac{rate_{\text{shift}} \times (3 \times rate_{\text{reform}} + rate_{\text{shift}})}{(rate_{\text{reform}} - rate_{\text{shift}}) \times (ratio - rate_{\text{reform}} - rate_{\text{shift}})} \\
(K_{1,\text{carbon}}) & > \frac{rate_{\text{shift}} \times (1 + ratio + 2 \times rate_{\text{reform}})}{(3 \times rate_{\text{reform}} + rate_{\text{shift}}) \times (rate_{\text{reform}} - rate_{\text{shift}}) \times P} \\
(K_{2,\text{carbon}}) & > \frac{rate_{\text{shift}} \times (1 + ratio + 2 \times rate_{\text{reform}})}{(3 \times rate_{\text{reform}} + rate_{\text{shift}}) \times P} \\
(K_{3,\text{carbon}}) & > \frac{rate_{\text{shift}} \times (1 + ratio + 2 \times rate_{\text{reform}})}{(rate_{\text{reform}} - rate_{\text{shift}}) \times P} \\
rate_{\text{reform}} - rate_{\text{shift}} & > 0
\end{align*}
\]

where ratio is the steam-to-carbon ratio, rate$_{\text{reform}}$ and rate$_{\text{shift}}$ are moles of CH$_4$ and CO converted by reform and shift reaction respectively, $K_{\text{reform}}$ and $K_{\text{shift}}$ are the equilibrium constants of the reform and shift reactions, $K_{1,\text{carbon}}$, $K_{2,\text{carbon}}$, and $K_{3,\text{carbon}}$ are the equilibrium constants of the carbon deposit reactions, and $P$ is the operation pressure (bar). When the initial CH$_4$ is 1 mole, the equilibrium moles are:

- CH$_4$: 1-rate$_{\text{reform}}$
- H$_2$O: ratio-rate$_{\text{shift}}$-rate$_{\text{reform}}$
- CO: rate$_{\text{reform}}$-rate$_{\text{shift}}$
- CO$_2$: rate$_{\text{shift}}$
- H$_2$: 3-rate$_{\text{reform}}$+rate$_{\text{shift}}$
- Total moles: ratio+1+2-rate$_{\text{reform}}$

The above minimization problem is a typical optimization problem and can be solved by the available software. The solutions found by using program (Kirschsten, 1997) are listed in Table A.2.
### Table A.2 Calculated minimum steam-to-carbon ratio

<table>
<thead>
<tr>
<th>$P$ (bar)</th>
<th>$T$ (°C)</th>
<th>450</th>
<th>500</th>
<th>550</th>
<th>600</th>
<th>650</th>
<th>700</th>
<th>750</th>
<th>800</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>0.94</td>
<td>1.18</td>
<td>1.35</td>
<td>1.38</td>
<td>1.28</td>
<td>1.15</td>
<td>1.05</td>
<td>1.01</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.75</td>
<td>0.97</td>
<td>1.15</td>
<td>1.26</td>
<td>1.25</td>
<td>1.16</td>
<td>1.07</td>
<td>1.01</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.66</td>
<td>0.85</td>
<td>1.03</td>
<td>1.16</td>
<td>1.19</td>
<td>1.15</td>
<td>1.07</td>
<td>1.01</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.60</td>
<td>0.78</td>
<td>0.96</td>
<td>1.09</td>
<td>1.14</td>
<td>1.12</td>
<td>1.06</td>
<td>1.00</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>0.56</td>
<td>0.73</td>
<td>0.90</td>
<td>1.03</td>
<td>1.10</td>
<td>1.10</td>
<td>1.05</td>
<td>0.99</td>
</tr>
</tbody>
</table>

### A.4 Temperatures in Heat Recovery Subsystem

The determination of the temperatures in the heat recovery subsystem is based on the known values from the 1 MW Japanese system (Uchijama and Segawa, 1991) and the criteria of the conventional power-generation (Haywood, 1991). These temperature values used in the heat-recovery subsystem are as follows.

- The natural gas is preheated to 450°C by the fuel preheater.
- The super-heated steam from the steam generator has a temperature of 450°C.
- The anode-off gas is cooled down to 600°C by the fuel preheater and further cooled down to 400°C by the heat exchanger.
- The working temperature of the water separator is at 85°C.

### A.5 Representation of the Main Components in CYCLE-TEMPO

To compute the system shown in Figure 2.1, the representation of the main components in CYCLE-TEMPO is listed in Table A.3.
### Table A.3 Representation of the main components in CYCLE-TEMPO

<table>
<thead>
<tr>
<th>Component name</th>
<th>Model representation</th>
<th>Main assumptions</th>
<th>Processes modeled</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel-cell stack</td>
<td>Fuel-cell</td>
<td>• Shift reaction taking place before entering active anode area.</td>
<td>• Three mass balances: i) anode gas in and out, ii) cathode gas in and out, and iii) gas transfer between anode and cathode due to electrochemical reaction</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Heat exchange between the anode and cathode gases is not considered.</td>
<td>• Total energy balance</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Same temperature of outlet gases</td>
<td>• Conversion rates of the shift and electrochemical reactions based on equilibrium and the required current output</td>
</tr>
<tr>
<td>Reformer</td>
<td>Reformer and combustor</td>
<td>Reformer:</td>
<td>Reformer model:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Conversion rate of the steam reforming is based on equilibrium</td>
<td>• Steam reforming of natural gas</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Combustor:</td>
<td>• Heat transfer from flue-gas to process gas</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Combustion of anode exhaust gas with air</td>
<td>Combustor model:</td>
</tr>
<tr>
<td></td>
<td>General surface heat exchanger</td>
<td></td>
<td>• Mass balance related to complete reactions with an excess of air</td>
</tr>
<tr>
<td></td>
<td>Water separator</td>
<td></td>
<td>• Energy balance related to reaction heat</td>
</tr>
<tr>
<td>Fuel preheater, air heater and heat exchanger</td>
<td>General surface heat exchanger</td>
<td>• Heat transfer between the hot and cold gases</td>
<td></td>
</tr>
<tr>
<td>Water separator</td>
<td>Water separator</td>
<td></td>
<td>• Mol-fraction of the water in outlet gas is based on the saturated partial pressure</td>
</tr>
<tr>
<td>Steam generator</td>
<td>Steam generator</td>
<td>Represented by a preheater, an evaporator (with a drum and pump), and a superheater models</td>
<td>• Heat transfer from the cathode exhaust gas to water (reaches its saturation temperature) in preheater</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Heat transfer from the cathode exhaust gas to evaporate water in evaporator</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Heat transfer from the cathode exhaust gas to heat the steam further in superheater</td>
</tr>
<tr>
<td>Mass-transport equipment</td>
<td>Pump, compressor, and turbine</td>
<td></td>
<td>• Determine specific enthalpy at the inlet or at the outlet according to the isentropic efficiency.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Isentropic efficiency depends on equipment.</td>
</tr>
<tr>
<td>DC/AC inverter</td>
<td>Lumped to fuel-cell model</td>
<td></td>
<td>• A fixed power conversion efficiency from DC to AC</td>
</tr>
<tr>
<td>Mixer</td>
<td>Junction</td>
<td>Mixing several streams adiabatically to give one outlet stream</td>
<td>• The pursuer of the output stream is the minimum pressure of the input stream</td>
</tr>
<tr>
<td>Splitter</td>
<td>Splitter</td>
<td>Dividing one input stream into several similar output streams</td>
<td>• Enthalpy of the output stream is based on energy balance</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• The pressure and temperature of the output streams are the same as that of the input stream.</td>
</tr>
</tbody>
</table>
A.6 Component Operating Conditions and Design Data

To compute the system performance at full load, the input file to compute the system performance by using CYCLE-TEMPO consists of:

- System diagram
- Specifications of the system feed streams
- Component operating conditions and design data at full load

The system diagram and the feed streams have been given by Figure 2.1 in Chapter 2 and Table A.1 in this appendix respectively. With regard to the above component data, Table 2.2 in Chapter 2 lists the input data for the fuel-cell stack and reformer. Table A.4 gives the input data for the other components in the system.
## Table A.4 Input data of components

<table>
<thead>
<tr>
<th>Component models</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water separator</td>
<td>Operating conditions:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Gas outlet temperature (°C)</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>Design features:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Water separator efficiency (%)</td>
<td>95%</td>
</tr>
<tr>
<td>Steam generation</td>
<td>Operating conditions:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Pressure of drum (bar)</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>• Temperature of output steam (°C)</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td>Design features:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Pressure drop in preheater, heater or superheater (bar)</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>• Isentropic efficiency of pump (%)</td>
<td>75</td>
</tr>
<tr>
<td>Fuel preheater</td>
<td>Operating conditions:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Outlet temperature of fuel gas (°C)</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td>Design features:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Pressure drop in both gas sides (bar)</td>
<td>0.1</td>
</tr>
<tr>
<td>Heat exchanger</td>
<td>Operating conditions:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Temperature of gas to reformer (°C)</td>
<td>510</td>
</tr>
<tr>
<td></td>
<td>Design features:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Pressure drop in both gas sides (bar)</td>
<td>0.1</td>
</tr>
<tr>
<td>Air preheater</td>
<td>Operating conditions:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Temperature of the air to reformer (°C)</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>Design features:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Pressure drop in both gas sides (bar)</td>
<td>0.1</td>
</tr>
<tr>
<td>Anode gas blower</td>
<td>Operating conditions:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Pressure difference (bar)</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>Design features:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Isentropic efficiency (%)</td>
<td>75%</td>
</tr>
<tr>
<td>Recycling blower</td>
<td>Operating conditions:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Pressure difference (bar)</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>Design features:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Isentropic efficiency (%)</td>
<td>75</td>
</tr>
<tr>
<td>Air compressor</td>
<td>Operating conditions:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Pressure difference (bar)</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>Design features:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Isentropic efficiency (%)</td>
<td>75</td>
</tr>
<tr>
<td>Expander</td>
<td>Operating conditions:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Pressure difference (bar)</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Design features:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Isentropic efficiency (%)</td>
<td>75</td>
</tr>
<tr>
<td>Pump</td>
<td>Operating conditions:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Pressure difference (bar)</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Design features:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Isentropic efficiency (%)</td>
<td>75</td>
</tr>
</tbody>
</table>
A.7 Energy Output or Heat Exchange within the Component

Table A.5 lists the energy output and heat exchange within the components. These data are used for the system efficiency analysis and determination of the components.

<table>
<thead>
<tr>
<th>Components</th>
<th>Energy output (kW)</th>
<th>Heat exchange within component (kJ/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel-cell stacks</td>
<td>979 (AC)</td>
<td>-</td>
</tr>
<tr>
<td>Reformer</td>
<td>0</td>
<td>566</td>
</tr>
<tr>
<td>Turbo-compressor</td>
<td>50 (expander: 235; compressor: 185)</td>
<td>-</td>
</tr>
<tr>
<td>Water separator</td>
<td>-</td>
<td>580</td>
</tr>
<tr>
<td>Fuel preheater</td>
<td>-</td>
<td>328</td>
</tr>
<tr>
<td>Heat exchanger</td>
<td>-</td>
<td>234</td>
</tr>
<tr>
<td>Air heater</td>
<td>-</td>
<td>102</td>
</tr>
<tr>
<td>Compressors and pumps</td>
<td>-91</td>
<td>-</td>
</tr>
</tbody>
</table>

A.8 Design of Fuel-cell Stack for Dynamic Modeling

A.8.1 Selection of a stack on 1 MW scale

In practice, a fuel cell system often uses multiple components with smaller capacity instead of one component with large capacity. For example, the 1 MW Japanese system uses four parallel connected fuel cell components of 250 kW. The alternatives for the fuel-cell component selection are: (i) one 1 MW, (ii) two 500 kW, or (iii) four 250 kW. In our modeling approach, one fuel cell component of 1 MW has been used. A stack with smaller capacity usually has a faster response than the one with larger capacity, therefore this approach will not neglect the problems related to the system's load-following speed.

A.8.2 Available design parameters from manufactures

The comparison between the designed and the required performances (at full load) is listed in Table A.6. The design data are derived from references (Abe et al., 1996 and MCFC, 1995). The required performance is derived from the determined operating conditions (Section 2.3.2) and the calculated system performance at full load by CYCLE-TEMPO (Section 2.5). Table A.6 indicates that the selected fuel-cell stack satisfies the required performance at full load.
Table A.6 Comparison between the designed and required performances

<table>
<thead>
<tr>
<th>Fuel-cell performance criteria</th>
<th>Manufacturer specifications</th>
<th>Required performance at full load</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC Power generation capacity (kW)</td>
<td>1000</td>
<td>1019 (979 AC)</td>
</tr>
<tr>
<td>Fuel utilization (%)</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Maximum fuel or oxidant gas utilization limit (%)</td>
<td>85</td>
<td>within the constraints</td>
</tr>
<tr>
<td>Limit of pressure difference between electrodes (kPa)</td>
<td>4 (normal operation); 8(transient conditions)</td>
<td>*within the constraints</td>
</tr>
<tr>
<td>Stack operation temperature (°C)</td>
<td>around 650</td>
<td>around 650</td>
</tr>
<tr>
<td>Max. temp. increase between cell inlet and outlet (°C)</td>
<td>150</td>
<td>&lt;150</td>
</tr>
<tr>
<td>Stack operation pressure range (bar)</td>
<td>3 - 7</td>
<td>around 3</td>
</tr>
<tr>
<td>Gas pressure drop (bar)</td>
<td>&lt;0.50</td>
<td>0.2</td>
</tr>
</tbody>
</table>

*The calculation in Chapter 3 will confirm that the pressure difference between electrodes is within the design range.

The stack specifications are listed in Table A.7. These data are derived from references (Kahara et al., 1996, Abe et al., 1996, Masuda at al., 1996, and MCFC, 1995).

Table A.7 Stack geometry and physical properties

<table>
<thead>
<tr>
<th>Stack design items</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell number</td>
<td>900</td>
</tr>
<tr>
<td>Gas manifold</td>
<td>Internal type</td>
</tr>
<tr>
<td>Gas flow</td>
<td>cross type with rectangular gas channels</td>
</tr>
<tr>
<td>Cell active area (m²)</td>
<td>1</td>
</tr>
<tr>
<td>Density of cell separator (kg/m³)</td>
<td>8027</td>
</tr>
<tr>
<td>Heat capacity of cell unit (kJ/kg. K)</td>
<td>1.0467</td>
</tr>
<tr>
<td>Heat capacity of cell separator (kJ/kg, K)</td>
<td>0.5024</td>
</tr>
<tr>
<td>Density of cell unit (electrolyte matrix with electrodes) (kg/m³)</td>
<td>2611</td>
</tr>
<tr>
<td>Thermal conductivity of cell unit in cell direction (W/m K)</td>
<td>50</td>
</tr>
<tr>
<td>Thermal conductivity of cell unit in stack direction (W/m K)</td>
<td>5.0</td>
</tr>
</tbody>
</table>

A.8.3 Evaluation and estimation of the stack design

The stack structure is illustrated in Figure 3.1 in Chapter 3. To provide adequate voltage, a fuel-cell stack successively piles up single cells connected in series. Each cell contains a cell unit (including electrolyte, anode and cathode), two half-separators, a layer of fuel gas and a layer of oxidant gas as shown in Figure A.2.
Figure A.2 Representation of a fuel cell

The stack design relevant to power-generation, and mass and heat storage under transient conditions is crucial for determining a stack dynamic performance. This section first evaluates the stack power-generation characteristics, then estimates the gas channel geometry and determines the gas flow pattern.

Stack power-generation characteristics. The designed performance of electrodes is not known. The simple approach is to use a lumped resistance to represent the cell voltage and current relation. For the full-load calculation by CYCLE-TEMPO, the lumped electric resistance of 1.45 $\Omega \text{cm}^2$ is used.

With the stack operating temperature of 650°C, the results from Eqs. 2.10 and 2.11 lead to cell voltage and stack output power as follows:

$$ V = E - i \times A_{\text{reaction}} \times R_{\text{resistance}} = 0.95 - 1.5 \times 900 \times 1.45 \times 10^{-4} = 0.75 \ (V) $$

$$ P_{\text{fuelcell(DC)}} = i \times A_{\text{reaction}} \times V \times n_{\text{cell-number}} = 1.500 \times 1 \times 0.75 \times 900 = 1013 \ (kW) $$

The stack power-generation characteristics at full load are close to (<2%) the stack designed power output (1000 kW) or required power output (1019 kW). The parameter values of the cell reaction area $A_{\text{reaction}}$, cell number $n_{\text{cell-number}}$, and the electrode performance appear acceptable at this stage.

Estimation of gas channel and flow. The gas channel geometry is estimated according to the gas flow rate at full load and the assumed gas average velocity. Then the Reynolds number is calculated and the gas flow pattern is determined.
### Table A.8 Estimation of fuel-cell geometry and flow pattern

<table>
<thead>
<tr>
<th>Estimation</th>
<th>Input data and assumptions</th>
<th>Calculation</th>
</tr>
</thead>
</table>
| Geometry of anode-gas channel   | \( F_{in(A)} = 0.328 \text{ (m}^3/\text{s}) \), \( F_{out(A)} = 0.587 \text{ (m}^3/\text{s}) \) | \( A_{total-cross(A)} = \frac{F_{average}}{u_{average}} \) \[
\begin{align*}
A_{total-cross(A)} &= \frac{F_{average}}{u_{average}} \\
&= \frac{(F_{in(A)} + F_{out(A)})/2}{0.5} \\
&= \frac{(0.328 + 0.587)/2}{0.5} = 0.915 \text{ (m}^2) \\
A_{cell-cross(A)} &= \frac{A_{total-cross}}{n_{cell}} = \frac{0.915}{900} = 0.001 \text{ (m}^2) \\
h_{gas(A)} &= \frac{A_{total-cross}}{1 \times 0.5} = 0.002 \text{ (m)} \\
V_{gas(A)} &= 0.002 \times 1 \times 1 \times 0.5 = 0.001 \text{ (m}^3) 
\end{align*}
\] |
| Geometry of cathode-gas channel | \( F_{in(A)} = 2.91 \text{ (m}^3/\text{s}) \), \( F_{out(A)} = 3.24 \text{ (m}^3/\text{s}) \), \( u_{average} = 3.4 \text{ (m/s)} \) | \( A_{total-cross(C)} = 0.915 \text{ (m}^2) \) \[
\begin{align*}
A_{cell-cross(C)} &= 0.001 \text{ (m}^2) \\
h_{gas(C)} &= \frac{A_{total-cross}}{1 \times 0.5} = 0.002 \text{ (m)} \\
V_{gas(C)} &= 0.002 \times 1 \times 1 \times 0.5 = 0.001 \text{ (m}^3) 
\end{align*}
\] |
| Flow pattern of anode gas       | \( \rho_{in(A)} = 0.54 \text{ (kg/m}^3) \), \( \rho_{out(A)} = 1.05 \text{ (kg/m}^3) \), \( u_{average} = 0.5 \text{ (m/s)} \), \( \mu = 2 \times 10^{-5} \text{ Pa.s} \) | \( Re_{(A)} = \frac{\rho \times u \times d}{\mu} = \frac{(0.54 + 1.05)/2 \times 0.5 \times 0.005}{0.2 \times 10^{-4}} = 99 < 2000 \text{ Laminar flow} \) |
| Flow pattern of cathode gas     | \( \rho_{in(C)} = 1.3 \text{ (kg/m}^3) \), \( \rho_{out(C)} = 1.04 \text{ (kg/m}^3) \), \( u_{average} = 3.4 \text{ (m/s)} \), \( \mu = 2 \times 10^{-5} \text{ Pa.s} \) | \( Re = 995 < 2000 \text{ Laminar flow} \) |

According to the above fuel-cell geometry, the cell weight \( W_{cell} \) leads to:

\[
W_{cell} = 2 \times W_{separators} + W_{cell-unit} = 2 \times 0.002 \times 1 \times 1 \times 0.5 \times 8027 + 0.002 \times 1 \times 1 \times 2611 = 21.28 \text{ (kg)}
\]

The cell weight of 21.28 kg is around the cell design weight of 20 kg according to MCFC (1995).
A.9 Design of Reformer for Dynamic Modeling

A.9.1 Available design parameters from manufacturers

The comparison between the designed and the required performances (at full load) is listed in Table A.9. The designed data are derived from references (Stahl and Laurse, 1992, MCFC, 1995, Uematsu et al., 1994 and Abe et al., 1996). The required performance is derived from the determined operating conditions (Section 2.3.2) and the system performance at full load calculated by CYCLE-TEMPO (Section 2.5). Table A.9 indicates that the selected reformer satisfies the required performance at full load.

<table>
<thead>
<tr>
<th>Reformer operation criteria</th>
<th>Manufacturer specifications</th>
<th>Required performance at full load</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed gas</td>
<td>natural gas</td>
<td>natural gas</td>
</tr>
<tr>
<td>Natural gas flow range (kg/h)</td>
<td>50 - 500</td>
<td>140</td>
</tr>
<tr>
<td>Steam/carbon ratio in volume (%)</td>
<td>&gt;=3.0</td>
<td>3</td>
</tr>
<tr>
<td>Outlet methane content in volume (%)</td>
<td>&lt;=4</td>
<td>2</td>
</tr>
<tr>
<td>Operation temperature of first catalyst bed (°C)</td>
<td>around 600</td>
<td>*</td>
</tr>
<tr>
<td>Operation temperature of second catalyst bed (°C)</td>
<td>around 800</td>
<td>800</td>
</tr>
</tbody>
</table>

*The reformer model in CYCLE-TEMPO only calculates the temperature of the second catalyst bed*

The reformer structure is illustrated in Figure 4.1 in Chapter 4. The specifications of the geometry and physical properties of the reformer are listed in Table A.10. The data are derived from literature (Okano et al., 1996, Christiansen and Laursen, 1991 and MCFC, 1995).

Table A.10 Reformer geometry and physical properties

<table>
<thead>
<tr>
<th>Specification</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Height of reformer (m)</td>
<td>7</td>
</tr>
<tr>
<td>Diameter (m)</td>
<td>1</td>
</tr>
<tr>
<td>Density of catalyst beds (kg/m³)</td>
<td>1281.48</td>
</tr>
<tr>
<td>Heat capacity of catalyst beds (kJ/kg. K)</td>
<td>1.026</td>
</tr>
<tr>
<td>Density of shell walls (kg/m³)</td>
<td>8027.17</td>
</tr>
<tr>
<td>Thickness of shell walls (m)</td>
<td>0.020</td>
</tr>
<tr>
<td>Heat capacity of walls (kJ/kg. K)</td>
<td>0.6113</td>
</tr>
</tbody>
</table>
A.9.2 Estimation of the reformer design

Estimation of gas channel and flow. The gas channel geometry is estimated according to the gas flow rate at full load and the assumed gas average velocity. Then the Reynolds number is calculated and the gas flow pattern is determined.

Table A.11 Estimation of reformer geometry and flow pattern

<table>
<thead>
<tr>
<th>Estimation</th>
<th>Input data and assumptions</th>
<th>Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometry of flue gas channel</td>
<td>$F_{in(F)}=0.80$ (m$^3$/s), $F_{out(F)}=0.49$ (m$^3$/s)</td>
<td>$A_{cross(F)} = \frac{F_{average}}{u_{average}} = \frac{(F_{in(F)} + F_{out(F)})}{2}$</td>
</tr>
<tr>
<td></td>
<td>Gas average velocity $u_{average}=5$</td>
<td>$u_{average} = \frac{(0.80 + 0.49)}{2} = 0.629$ (m$^3$/s)</td>
</tr>
<tr>
<td></td>
<td>Gas channel is a thin circular cylinder with diameter 1 m</td>
<td>$\delta(F) = \frac{A_{cross(F)}}{\pi \times d} = \frac{0.129}{\pi \times 1} = 0.041$ (m)</td>
</tr>
<tr>
<td>Geometry of process gas</td>
<td>$F_{out(F)}=0.32$ (m$^3$/s)</td>
<td>$A_{cross(F)} = 0.664$ (m$^2$)</td>
</tr>
<tr>
<td></td>
<td>Gas average velocity $u_{average}=5$</td>
<td>$\delta(F) = \frac{A_{cross(F)}}{\pi \times d \times ratio} = \frac{0.664}{\pi \times 1 \times 0.5} = 0.020$ (m)</td>
</tr>
<tr>
<td></td>
<td>Ratio of gas area=0.5,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gas channel is a thin circular cylinder with diameter 1 m</td>
<td></td>
</tr>
<tr>
<td>Flow pattern of flue gas</td>
<td>$\rho_{in(F)}=0.97$ (kg/m$^3$), $\rho_{out(F)}=1.60$ (kg/m$^3$)</td>
<td>$*Re_{(F)} = \frac{\rho \times u \times d \times (1-k)}{\mu} = \frac{(0.97 + 1.60)}{2 \times 5 \times 1 \times \frac{0.041}{0.5}} = 2 \times 10^{-5} = 26343 &gt; 2000$ (Turbulent flow)</td>
</tr>
</tbody>
</table>

*for flow through an annulus, $k=1-\delta$/$R_c$ (Bird et al., 1960)

Estimation of pressure drops. When the process gas flow through dry catalyst particles, the pressure drop is calculated by using the Ergun equation (Perry, 1981):

$$\frac{dP}{dL} = -10^{-5} \times \left( \frac{150 \times (1 - \varepsilon_v)}{Re_p} + 1.75 \right) \times \frac{F^2}{\rho \times D_p} \times \frac{1}{\varepsilon_v^3}$$ (A.7)

where $\varepsilon_v$ is the fraction of the empty space in the catalyst bed. When $Re_p=5 \times 10^5$ (diameter of catalyst of 1 mm) and $\varepsilon_v=0.5$, $\frac{150 \times (1 - \varepsilon_v)}{Re_p} = 0.015 << 1.75$

Therefore, the pressure drop of the process gas can be simplified as:

$$\Delta P = 1.75 \times 10^{-5} \frac{F^2}{\rho \times D_p} \times \frac{1}{\varepsilon_v^3} \times L$$ (A.8)

With Eq. A.16, the pressure drop of the process gas going through one catalyst bed with length of 7 m is $\Delta P \approx 0.2$ bar. Since the reformer has two-catalyst beds and gas-flow channel, the estimated total pressure is 0.5 bar at full load.
### A.10 Design of Heat Exchangers for Dynamic Modeling

#### Table A.12 Estimation of air preheater

<table>
<thead>
<tr>
<th>Estimation</th>
<th>Input data and assumptions</th>
<th>Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of tubes</td>
<td>$F_{\text{in(C)}}=0.10$ (m$^3$/s), $F_{\text{out(C)}}=0.18$ (m$^3$/s)</td>
<td>$A_{\text{tube(in)}} = \frac{F_{\text{average}}}{u_{\text{average}}} = \frac{(0.10 + 0.18)/2}{5} = 0.028$ (m$^2$)</td>
</tr>
<tr>
<td></td>
<td>Gas average velocity $u_{\text{average}}=5$ m/s</td>
<td>$n_{\text{min}} = \frac{A_{\text{tube(in)}}}{\pi \times d^2/4} = \frac{0.028}{\pi \times 0.030^2} = 39.6$</td>
</tr>
<tr>
<td></td>
<td>Diameter of tube $D_{\text{tube(in)}}=30$ mm</td>
<td>$n = 40$</td>
</tr>
<tr>
<td>Flow pattern of cold gas</td>
<td>$\rho_{\text{air(C)}}=2.83$ (kg/m$^3$)</td>
<td>$Re_{(F)} = \frac{\rho \times U \times d}{\mu} = \frac{(2.83 + 1.61)/2 \times 10 \times 0.025}{27.8 \times 10^{-5}} = 19864 &gt; 2000$</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{air(out)}}=1.61$ (kg/m$^3$)</td>
<td>Turbulent flow</td>
</tr>
<tr>
<td></td>
<td>Gas average velocity $u_{\text{average}}=5$ m/s</td>
<td>$A_{\text{tube(in)}} = \frac{F_{\text{average}}}{u_{\text{average}}} = \frac{(0.49 + 0.43)/2}{5} = 0.092$ (m$^2$)</td>
</tr>
<tr>
<td></td>
<td>Diameter of tube $D_{\text{tube(out)}}=44$ mm</td>
<td>$A_{\text{tube(in)}} = \frac{\pi \times (D_{\text{shell(in)}}^2 - D_{\text{tube(out)}}^2)}{4}$</td>
</tr>
<tr>
<td></td>
<td>$\Rightarrow D_{\text{shell(in)}} = 0.065$ (m)</td>
<td></td>
</tr>
<tr>
<td>Inside diameter of shell</td>
<td>$F_{\text{in(H)}}=0.49$ (m$^3$/s), $F_{\text{out(H)}}=0.43$ (m$^3$/s)</td>
<td>$Re_{(H)} = 13861 &gt; 2000$</td>
</tr>
<tr>
<td></td>
<td>Gas average velocity $u_{\text{average}}=5$ m/s</td>
<td>Turbulent flow</td>
</tr>
<tr>
<td></td>
<td>Dynamic viscosity: $\mu=2.78 \times 10^{-5}$ Pa.s</td>
<td></td>
</tr>
<tr>
<td>Flow pattern of hot gas</td>
<td>$\rho_{\text{air(H)}}=1.60$ (kg/m$^3$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{air(out)}}=1.79$ (kg/m$^3$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gas average velocity $u_{\text{average}}=5$ m/s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dynamic viscosity: $\mu=2.25 \times 10^{-5}$ Pa.s</td>
<td></td>
</tr>
<tr>
<td>Heat transfer coefficients</td>
<td>Heat conductivity: $\lambda=0.05$ W/m.K</td>
<td>$Nu = 0.23 \times Re^{0.8} \times Pr^{0.33}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\Rightarrow \alpha_{\text{tube(in)}} = 50(W/m^2K)$, $\alpha_{\text{tube(out)}} = 150(W/m^2K)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_{\text{total}} = \frac{1}{\frac{1}{\alpha_{\text{tube(in)}}} + \frac{1}{\lambda} + \frac{1}{\alpha_{\text{shell(in)}}}}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$= \frac{1}{\frac{1}{50} + \frac{0.002}{\lambda} + \frac{1}{150}} = 15(W/m^2K)$</td>
</tr>
<tr>
<td>Length of tubes</td>
<td>$A_{\text{area}}$ plus 20%</td>
<td>$Q = k_{\text{total}} \times A_{\text{min}} \times \Delta T$  $\Rightarrow A_{\text{min}} = 1.54$ (m$^2$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\frac{A}{n} = \pi \times D_{\text{tube(in)}} \times L$  $\Rightarrow L = 0.4$ (m)</td>
</tr>
</tbody>
</table>
This section provides a simple estimate of the heat exchanger parameters (e.g. gas storage volumes and metal mass) with regard to its dynamic modeling. The type of heat exchanger is assumed to be of the double-pipe counter mode (comparison to a realistic heat exchanger is given). The design only considers the required gas flow and the heat transfer at full load. The required flow rate at full load is used to calculate the flow area and to estimate the number of pipes. Then the required heat-transfer quantity is used to calculate the heat-transfer area and to determine the length of the pipes. The estimation approach to the air preheater is listed in Table A.12.

The engineering design of a heat exchanger (GPSA, 1998) considers more technical factors than those in Table A.12, e.g. the availability of the standard heat exchanger and cost. The outcome of the selection is usually not exactly the same as the estimated data. This assumes that the selected heat exchanger has the same data as the theoretical estimation data. The input data for dynamic modeling air preheater is listed in Table A.13.

<table>
<thead>
<tr>
<th>Table A.13 Input data for air preheater geometry and properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of tubes</td>
</tr>
<tr>
<td>Internal diameter of tube (mm)</td>
</tr>
<tr>
<td>Thickness of tube wall (mm)</td>
</tr>
<tr>
<td>Internal diameter of shell (mm)</td>
</tr>
<tr>
<td>Thickness of shell wall (mm)</td>
</tr>
<tr>
<td>Length of tubes (m)</td>
</tr>
<tr>
<td>Density of shell or tube (kg/m$^3$)</td>
</tr>
<tr>
<td>Thermal conductivity of tube or shell (kJ/kg.K)</td>
</tr>
<tr>
<td>Heat capacity of tube or shell (kJ/kg. K)</td>
</tr>
</tbody>
</table>

The above heat exchanger only includes the double pipes not the supporting material and gas in and out manifolds. Since a heat exchanger with 50 double pipes is not economic, a practical option is to use 50 single pipes and a larger shell wall. The above simplified heat exchanger also approximately represents the practical option with a larger shell wall based on the conditions as follows:

- The surface area of the shell wall can be reduced to 1/4 (however the wall thickness may increase 2 times).
- A practical heat exchanger has to include the supporting material and gas manifolds (the same mass as the shell wall).
- The heat-transfer coefficient in the shell wall is assumed to be similar to that in the double pipes based on the same average gas speed.

With the same approach as the air preheater, the input data for fuel preheater and another heat exchanger are listed in Tables A.14 and A.15.
### Table A.14 Input data for fuel preheater geometry and properties

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of tubes</td>
<td>25</td>
</tr>
<tr>
<td>Internal diameter of tube (mm)</td>
<td>20</td>
</tr>
<tr>
<td>Thickness of tube wall (mm)</td>
<td>2</td>
</tr>
<tr>
<td>Internal diameter of shell (mm)</td>
<td>55</td>
</tr>
<tr>
<td>Thickness of shell wall (mm)</td>
<td>3</td>
</tr>
<tr>
<td>Length of tubes (m)</td>
<td>0.5</td>
</tr>
<tr>
<td>Density of shell or tube (kg/m³)</td>
<td>8027.17</td>
</tr>
<tr>
<td>Thermal conductivity of tube or shell (kJ/kg.K)</td>
<td>0.050</td>
</tr>
<tr>
<td>Heat capacity of tube or shell (kJ/kg.K)</td>
<td>0.60</td>
</tr>
</tbody>
</table>

### Table A.15 Input data for heat exchanger geometry and properties

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of tubes</td>
<td>50</td>
</tr>
<tr>
<td>Internal diameter of tube (mm)</td>
<td>30</td>
</tr>
<tr>
<td>Thickness of tube wall (mm)</td>
<td>2</td>
</tr>
<tr>
<td>Internal diameter of shell (mm)</td>
<td>70</td>
</tr>
<tr>
<td>Thickness of shell wall (mm)</td>
<td>3</td>
</tr>
<tr>
<td>Length of tubes (m)</td>
<td>0.7</td>
</tr>
<tr>
<td>Density of shell or tube (kg/m³)</td>
<td>8027.17</td>
</tr>
<tr>
<td>Thermal conductivity of tube or shell (kJ/kg.K)</td>
<td>0.050</td>
</tr>
<tr>
<td>Heat capacity of tube or shell (kJ/kg.K)</td>
<td>0.60</td>
</tr>
</tbody>
</table>
Appendix B Component Models

B.1 Modeling Approach

In order to achieve the system model, all component models must be set up. As defined in Chapter 2, all components in the system are represented by nine types of component models: (1) fuel-cell stack, (2) reformer, (3) heat exchanger, (4) water separator, (5) steam generator, (6) mass-transport equipment (e.g. blower, compressor, expander and pump), (7) DC/AC inverter, (8) mixer, and (9) splitter. Among these nine types of component models, only the fuel-cell stack, reformer, and heat exchanger models are in dynamic form. Chapters 3 and 4 described the development of the fuel-cell stack and reformer models. This appendix presents the other seven types of component models.

The modeling approaches to these seven types of component model are general available from the commercial libraries, e.g., the MMS (1983), the library of SPEEDUP (1996), and CYCLE-TEMPO (Woudstra and Verschoor, 1995). Accordingly, the modeling approach emphasizes adapting the available component models to the 1 MW system operating conditions.

B.2 Heat Exchanger Model

There are three gas/gas heat exchangers (fuel preheater, air preheater and anode heat exchanger) in the system. The fuel preheater uses the anode-off gas (approximated at 700 °C) to heat the system input natural gas from 15 °C to about 400 °C for the processing gas of the reformer. The air preheater uses the exhaust flue gas (approximated 700 °C) from the reformer to heat the air from 180 °C to about 500 °C. The anode heat exchanger further utilizes the anode-off gas after the fuel preheater to heat the recycled anode gas from 120 °C to about 500 °C. The working principles for these three gas heat exchangers are similar, however, these three gas heat exchangers do not have the same the gas flow-rate, temperature or the required heat transfer flux. Accordingly, these three gas/gas heat exchangers are modeled as the same type but with different inputs for geometry and physical properties. The modeling procedure for gas/gas heat exchanger is illustrated by the development of the fuel preheater.

In order to reduce the computational time, the heat exchanger models in MMS (1983) lump the tube metal energy together with the fluid, which is a good approximation when the tube metal energy storage is less than 20% of the total. However, in a gas/gas heat exchanger, the energy stored in the tube metal may be not small compared to the energy stored in the gases. Therefore, the energy storage in the tube metal is calculated separately.
The structure of the fuel preheater has a simple type of counter-current, double-pipe heat exchanger. The hot anode exhaust gas flows inside the tube while the cold natural gas flows outside the tube. The gas flow is assumed to be fully developed turbulent flow. The convection and radiation heat transfer can be characterized by a logarithmic mean temperature difference.

The dynamic processes modeled are:
- Gas storage
- Energy storage of the gas
- Energy storage of the heat exchanger tube metal

The mass storage in the anode-off gas (A) and in the natural gas (N) is modeled separately.

\[ \frac{d(\rho_A V_A)}{dt} = F_{A\text{in}} - F_{A\text{out}} \]  \hspace{1cm} (B.1)

\[ \frac{d(\rho_N V_N)}{dt} = F_{N\text{in}} - F_{N\text{out}} \]  \hspace{1cm} (B.2)

where \( \rho \) is the gas density, and \( F \) is the gas flow rate.

The energy storage in the anode-off gas, tube metal (M), and natural gas are considered separately. The energy balance yields:

\[ C_p \rho_m \frac{dT}{dt} = Q_1 - Q_2 \]  \hspace{1cm} (B.3)

\[ \frac{d(V_A \times \rho_A \times U_A)}{dt} = F_{A\text{in}} \times h_{A\text{in}} - F_{A\text{out}} \times h_{A\text{out}} - Q_1 \]  \hspace{1cm} (B.4)

\[ \frac{d(V_N \times \rho_N \times U_N)}{dt} = F_{N\text{in}} \times h_{N\text{in}} - F_{N\text{out}} \times h_{N\text{out}} + Q_2 \]  \hspace{1cm} (B.5)

where \( U_A \) and \( U_N \) are the internal energy of the anode-off gas and natural gas.

In the above energy equations the heat transfer \( Q \) reads:

\[ Q_1 = A_{AM} \times K_{AM} \times \Delta T_{LM(AM)} \]  \hspace{1cm} (B.6)

\[ Q_2 = A_{MN} \times K_{MN} \times \Delta T_{LM(MN)} \]  \hspace{1cm} (B.7)

where, \( A_{AM} \) and \( A_{MN} \) stand for the heat transfer surface areas between the anode exhaust gas and the tube metal, and between the tube metal and the natural gas respectively. \( K_{AM} \) and \( K_{MN} \) stand for the overall heat transfer coefficients between the anode exhaust gas and the tube metal, and between the tube metal and the natural gas respectively. \( \Delta T_{LM(AM)} \) and \( \Delta T_{LM(MN)} \) stand for the logarithmic mean temperature differences between the anode exhaust gas and the tube metal, and between the tube metal and the natural gas respectively.

To calculate the \( Q \), the heat-transfer coefficients refer to MMS (1993) and read:

\[ U = 0.023(\frac{\lambda}{D}) \times Re^{0.8} \times Pr^{0.4} \]  \hspace{1cm} (B.8)

where, \( \lambda \): thermal conductivity of fluid; \( D \): characteristic dimension; \( Re \): Reynold's number and \( Pr \): Prandil number.

For the dynamic simulation, the following simplified formulations are used:

\[ U_{AM} = K_{AM} \times F_A^{0.8} \]  \hspace{1cm} (B.9)
\[ U_{MN} = K_{MN} \times F_{N}^{0.8} \]  \hspace{1cm} (B.10)

where, \( K_{AM} \) and \( K_{MN} \) are multiple factors that are determined by the design aspects.

The above Equations B.9 and B.10 usually have sufficient accuracy for a dynamic model. A dynamic model predicts the changes from the design conditions instead of the initial design conditions. In the present heat exchange model, the Equations B.9 and B.10 are used to calculate the heat-transfer coefficients, while \( K_{AM} \) and \( K_{MN} \) are determined by the results from Equation B.8.

### B.3 Water Separator

The water separator is used to separate the water from the cooled anode-off gas. The three principles used to achieve physical separation of gas and liquids are momentum, gravity settling, and coalescing. The basic equipment for separating liquid from vapor uses both gravitational and centrifugal force. The gravitational force is utilized by reducing velocity so the liquid can settle out in the space provided. Centrifugal force is utilized by changing the direction of flow. The typical liquid retention time is the order of 1 to 10 minutes (Campell, 1998). Since the capacity of the water separator is small, the water retention time is expected to be short, i.e. around 1 minute.

The water drop greater than 10 µm may be separated by properly designed equipment. The calculation of the particle size is provided by (Campell, 1998, and GPSA, 1998). In this study, ideal water separation is assumed. The minimum mol-fraction of the water in outlet gas can be determined by the partial pressure with regard to the operating temperature. The extra water is condensed. The heat of condensation is then removed via the cooling water. It is assumed that the cooling water is a large quantity and the heat of condensation can be sufficiently released. When the working temperature of the separator remains around 85°C, its water saturated partial pressure is around 0.578 bar. The mass and energy balances are modeled.

The mass balance is as follows:

\[ F_{\text{in}} \times \bar{y}_{\text{in}} = F_{\text{water(out)}} \times \bar{y}_{\text{water(out)}} + F_{\text{vapor(out)}} \times \bar{y}_{\text{vapor(out)}} \]  \hspace{1cm} (B.11)

where \( F_{\text{in}} \), \( F_{\text{water(out)}} \), and \( F_{\text{vapor(out)}} \) are the flow rate at the input stream, output water and vapor streams. \( \bar{y}_{\text{in}} \), \( \bar{y}_{\text{water(out)}} \), and \( \bar{y}_{\text{vapor(out)}} \) are the concentrations at the input stream, output water and vapor streams.

The mol-fraction of the water at the outlet gas stream is equal to its partial pressure. The energy conservation balance is as follows:

\[ F_{\text{in}} \times h_{\text{in}} = F_{\text{water(out)}} \times h_{\text{water(out)}} + F_{\text{vapor(out)}} \times h_{\text{vapor(out)}} + Q_{\text{cooling}} \]  \hspace{1cm} (B.12)

\[ Q_{\text{cooling}} = K \times A \times \Delta T_{LM} \]  \hspace{1cm} (B.13)

where \( h \) is the enthalpy, \( Q_{\text{cooling}} \) is the heat for gas condensation. \( K \) is the heat-transfer coefficient. \( A \) is the heat-transfer area. \( \Delta T_{LM} \) is the logarithmic mean temperature.
B.4 Steam Generator

The steam generator uses the heat of the cathode exhaust gas to generate the super-heated steam for the reformer. The steam generator is comprised of a preheater, an evaporator (a heater with a drum and a pump), and a superheater. The water is first heated to saturation, then evaporated, and further heated in the superheater, while the cathode-off gas is cooled down. The principle of the steam generator model can refer to the heat exchanger model. The steam generator provides the required steam to the reformer according to the fixed steam-to-carbon ratio.

B.5 Mass Transport Equipment

The mass transport equipment includes the blower, compressor, pump and expander in the fuel cell system. These four components are approximately modeled as the same type but with different inputs of characteristic functions. There are both dynamic and steady-state models available for rotation equipment in the SpeedUp library (1996). The model in dynamic form includes the energy storage for the rotating wheel. In this study, the transport equipment uses the model in steady-state form in the SpeedUp library.

B.6 DC/AC Invertor

The DC/AC invertor in the fuel cell power-generation system includes power conditioning, current control, DC to AC inversion (unless the application is DC), and stepping the voltage up through a transformer. The conversion efficiency of electric power is in terms of power, frequency, phase number, voltage and current. The response of the DC/AC invertor is estimated to be much faster than the time constants of the system dynamics, accordingly, no dynamic aspects are simulated. The present DC/AC invertor model is modeled in a steady-state form and is represented by fixed power conversion efficiency.

B.7 Mixer and Splitter

The mixer and splitter models are from the SpeedUp library (1996). The models are in steady-state form. The MIXER model from the SpeedUp library mixes streams of any phase adiabatically to give one outlet stream. The SPLITTER model in the SpeedUp library divides one input stream into several similar output streams, each identical in composition, temperature, pressure and specific enthalpy. The mass and energy balances over the unit are preserved.
Appendix C Implementation of Fuel-cell Stack Models

This appendix complements the fuel-cell stack models described in Chapter 3.

C.1 Calculation of Fuel-cell Electric Resistance

The lumped local resistance $R_{\text{local}}$ in Eq. 3.13 in Chapter 3 is calculated by using the empirical equation proposed by Watanabe et al. (1991). The lumped local resistance $R_{\text{local}}$ is comprised of ohmic, anode, and cathode resistances:

$$R_{\text{local}} = A_R \exp\left(-\frac{\Delta H_R}{RT}\right) + \exp\left(-\frac{\Delta H_A}{RT}\right) \ln\left(R_{\text{an}} \cdot P_{H_2A} \cdot P_{\text{CO}_2A} \cdot P_{\text{H}_2\text{O}_4} \right)$$

$$+ \exp\left(-\frac{\Delta H_C}{R}\right) \ln\left(R_{\text{oc}} \cdot P_{\text{O}_2C} \cdot P_{\text{CO}_2C} \right) \tag{C.1}$$

where $A_R$ is the frequent factor of the resistance; $\Delta H_R$, $\Delta H_A$ and $\Delta H_C$ are the activation energy of internal resistance (J/mol.K), anode reaction and cathode reaction respectively; $R_{\text{an}}$ and $R_{\text{oc}}$ are anode and cathode resistance which is independent of the gas pressure; $P_i$ is partial gas pressure of a species $i$. Superscripts from a to e are coefficients which are related to the cell inherent performance. These coefficients are identified from the experimental data. Therefore, the lumped resistance $R_{\text{local}}$ depends on the electrode inherent characteristics and operational conditions (e.g., the temperature and the gas partial pressures).

Watanabe et al. (1991) identified the parameters in the Equation C.11 based on their experimental results of small size test cells under various test conditions. This study has used their empirical equation in the following form:

$$R_{\text{local}} = 2.71 \cdot 10^{-3} \exp\left(\frac{409 \cdot 10^3}{RT}\right) + \exp\left(-\frac{19 \cdot 10^3}{RT}\right) \ln\left(1.24 \cdot P_{H_2A}^{-2.82} \cdot P_{\text{CO}_2A}^{-2.12} \cdot P_{H_2\text{O}_4}^{-3.55} \right)$$

$$+ \exp\left(\frac{102 \cdot 10^3}{R}\right) \cdot 10^{-7} \ln\left(365 \cdot P_{\text{O}_2C}^{-3.85} \cdot P_{\text{CO}_2C}^{-2.78}\right) \tag{C.2}$$

The following Tables C.1 and C.2 indicate the magnitude of the $R_{\text{local}}$ value. The fuel utilization is 75% and more detailed conditions refer to Watanabe at al. (1991). Table C.1 gives the range of the $R_{\text{local}}$ value (from the inlet to the outlet of co-flow cell) under different cell operating temperature (with assumption of isothermal cell). Table C.2 shows the average $R_{\text{local}}$ value under different operating pressure.

Table C.1 Range of $R_{\text{local}}$ ($\Omega \text{ cm}^2$) value at 1 bar

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>600</th>
<th>650</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range of $R_{\text{local}}$ from inlet to outlet</td>
<td>2.70 - 3.07</td>
<td>1.62 - 2.04</td>
<td>1.14 - 1.56</td>
</tr>
</tbody>
</table>
Table C.2 Average value of $R_{\text{local}}$ ($\text{\Omega cm}^2$) at 650°C under different pressure

<table>
<thead>
<tr>
<th>Pressure (1bar)</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{\text{local}}$</td>
<td>1.75</td>
<td>1.45</td>
<td>1.31</td>
<td>1.22</td>
</tr>
</tbody>
</table>

The comparison of the Equation C.2 with the other empirical approaches from the literature (Selman, 1988 and PSI, 1985) according to Dekker (1992) indicated that the performance of the Equation C.2 appears acceptable.

C.2 Estimation of the Time Scale of the Main Processes

As described in Chapter 3, the main processes modeled in a fuel-cell stack are: gas transport, chemical and electrochemical reactions, electrical power-generation, and heat generation and heat transfer. These processes have different time scales, which is important for modeling assumptions and evaluation of simulation results. Estimates of such time scales can be obtained from the literature, experimental investigation, analytical and simulation results, and expert prediction. The estimates usually depend on various design and operation conditions, and it is difficult to make a general conclusion. Some simple estimates and information are provided as follows.

**Processes at micro-level.** The impacts of the processes within the electrodes and electrolyte (at micro-level) are represented by: (i) the instantaneous consumption of reactants and the liberation of products at the electrode surface, (ii) heat generations within the electrodes and electrolyte, and (iii) power-generation characteristic. These processes at micro-level are estimated on a time scale of 10 μs (Lee at al., 1996). These processes are fast, their dynamics are often neglected on a large time scale.

**Gas transport processes.** The fuel and oxidant gases are fed into the stack separately via the anode and cathode input gas manifolds and then they are distributed to each cell, where electrochemical reactions take place. The gas-transport in each cell involves the diffusion of the reactant and product gases to their electrode surfaces and their flow along cell channels. Finally, the exhaust gases from each cell are discharged through the gas output manifolds. Since the gas manifolds have a short flow path and large cross-section in comparison with the cell gas channel, the gas transport by the manifold is often negligible. The time scale of the gas flow along cell channels reads: $t = L$ (length of cell channel)/ $u$ (gas flow velocity). When the cell channel is around 1 m and the gas velocity is around 0.1 m/s ~ 1 m/s, the time scale of the gas flow along cell channels will be around 1 s to 10 s. This process, therefore, should be considered in the dynamic processes. This process is dealt with in dynamic form by the 3D-stack model, however, it is not dealt with in dynamic form by the simple stack model.

There is no simple calculation available for the time scale of the diffusion process of the reactant and product gases to their electrode surfaces. However, since the small gas channel geometry (width or depth in mm) and the gas velocity of 0.1 m/s ~ 1 m/s, this diffusion process is considered to be very fast. The 3D stack included this dynamic process, however, the simple stack model neglected the dynamic of this process.
The above gas transport processes determine the change in the local gas concentration at electrode electrochemical reaction region, which decides the power-generation characteristics.

**Chemical and electrochemical reactions.** The water-shift reaction in the fuel gas is considered. When the fuel gas is at a temperature of 600°C to 700°C, the water-shift reaction is considered to be fast (Smith and Ness, 1987). The water-shift reaction is therefore assumed to reach reaction equilibrium instantaneously. The electrochemical reactions are considered to be very fast, and modeled in steady-state form.

**Electrical power-generation characteristics.** The cell power-generation performance is assumed to result instantaneously from the imposed current output (or voltage), the cell’s inherent characteristics, local temperature, and the gas partial pressure.

**Heat generation and heat transfer.** The heat generations result from the chemical and electrochemical reactions, as well as electric losses, thus they are assumed to be fast and modeled in steady-state form.

The heat storage in the gases, in the cell unit, and in the separator (or end plate) is important to cell response. Both the 3D and the simple stack models included these processes. The time scale of the heat storage in the cell unit computed by our 3D and the direct simple stack model is about 100 s ~ 1000 s. The expert prediction of the time scale for the temperature response of our stack will be around several 1000 s (Watanabe, 1996).

### C.3 Gas Flow Conditions

The PHOENICS input file includes the gas flow conditions. The gas flow conditions can be either laminar or turbulent. The flow condition is determined from the Reynolds number \( \text{Re} \). The Reynolds number is defined as:

\[
\text{Re} = \frac{\rho \times u \times d_n}{\mu}
\]

(C.3)

where \( \rho \): gas density, \( u \): fluid average velocity, \( d_n \): hydraulic diameter, \( \mu \): dynamic viscosity of the gas.

The hydraulic diameter \( d_n \) for a rectangular section reads:

\[
d_n = \frac{2 \times a \times b}{(a + b)}
\]

(C.4)

where, \( a \) and \( b \) are the width and length of the gas flow section.

Once the Reynolds number has been determined for a particular flow field, the flow condition is found by comparing it with the critical Reynolds number \( \text{Re}_{\text{critical}} \). Values are determined experimentally. The \( \text{Re}_{\text{critical}} \) values for the rectangular cross section with a smooth entrance are usually in the range of 4300 to 7000 (Bossel and Ferguson, 1989). In this case, the Reynolds number of the gas is much smaller than the \( \text{Re}_{\text{critical}} \). The gas flow condition is therefore defined as laminar flow.
C.4 Solution Method of 3D-Stack Equations by Using CFD program

In order to solve the stack conservation equations of gas species, energy, and momentum, this section presents the solution approach. The CFD program PHOENICS has been introduced in Section 2.8. PHOENICS provides a solver for fluid-flow, heat-transfer, chemical-reaction, and related problems ranging in complexity from one-dimensional single-phase and steady-state, to 3D multi-phase and transient. In this study, the CFD software package PHOENICS is used as a solution tool. The implementation of the 3D-stack model in PHOENICS consists of: i) numerical method of PHOENICS, ii) program structure of PHOENICS, iii) implementation of 3D-stack model in PHOENICS, and iv) evaluation of the simulation results.

C.4.1 Numerical method of PHOENICS

Due to the similarity in form of the above conservation equations, the Eqs. 3.16, 3.24 and 3.37 in Chapter 3 can be written as a general equation (Patankar, 1980):

$$\frac{\partial}{\partial t}(\rho \phi) + \text{div}(\rho V \phi - \Gamma_\phi \text{grad} \phi) = S_\phi$$  \hspace{1cm} (C.5)

$\phi$ stands for any one of the dependent quantities: gas species (y), energy (h), momentum (u) and continuity (1), and $S_\phi$ is the source or sink term.

Since there is no exact mathematical solution for the general conservation Eq. C.5, numerical methods have to be introduced to provide the discrete solution. The numerical method employed by PHOENICS is the finite control volume method. The numerical methods consist of two major procedures: i) integrating the partial differential equations over the finite control volume of a computational cell and over a finite time (for transient change); and ii) solving a set of non-linear algebraic equations resulting from the first procedure.

Following the numerical schemes of Patankar (1980), a general form of the algebraic equations was derived from the partial differential equations by integrating Eq. C.5:

$$\phi_p = \frac{a_E \phi_E + a_W \phi_W + a_N \phi_N + a_S \phi_S + a_L \phi_L + a_H \phi_H + a_T \phi_T - S_o}{a_E + a_W + a_N + a_S + a_L + a_H - S_p}$$  \hspace{1cm} (C.6)

where $a_E, a_W, a_N, a_S, a_L, a_H, a_T$ are the coefficients of the finite-domain equation for main cell variable $\phi$ (Patankar, 1980), $\phi_p$ is the value at one time step forward, $P$, $E$, $W$, $N$, $S$, $L$, and $H$ denote the locations at which this variable is computed in accordance with the east-west-north-south-low-high convention. So and $Sp$ are the coefficients of the linearized source term $S_\phi$.

In the source term, $\phi$ is presumed uniform through-out the control cell, thus:

$$\iint_{V} S_\phi dV = V_p \times S_\phi$$  \hspace{1cm} (C.7)

where $V_p \times S_\phi$ is expressed in the linearized form

$$V_p \times S_\phi = S_o + S_p \times \phi_p$$  \hspace{1cm} (C.8)
C.4.2 Program structure of PHOENICS

PHOENICS consists of two essential computer codes and two auxiliary ones (CHAM, 1995). The essential ones are a pre-processor called SATELLITE and a processor called EARTH. The auxiliary ones are a pro-processor called PHOTON and separate self-instruction program called GUIDE. The relationships between them are illustrated in Figure C.1.

![Diagram of PHOENICS structure](image)

**Figure C.1 Structure of PHOENICS**

SATELLITE is an interpreter that turns instructions provided by a user into a data file containing the instructions that EARTH can understand and obey. The normal way for a user to give SATELLITE instructions is to establish a Q1 file, which is written in the PHOENICS Input Language (PIL). For example, in our case, the problem is a 3D, dynamic gas flow problem.

Earth contains the main flow-simulation software. It reads the data file provided by SATELLITE and executes the corresponding commutations and then produces output files that can be read by the user and also by PHOTON, or by EARTH itself for further computations. In addition, EARTH possesses FORTRAN subroutines that are accessible to the user. These subroutines are sorted in GROUND standing for “ground station”. The main function of GROUND is to supply the necessary boundary conditions, source, fluid properties, and output control features that are not contained within EARTH. If the user’s needs are not satisfied by what the standard GROUND subroutines already contain, she may attach the Fortune subroutines and insert programs of her own, thereafter re-compiling and re-linking before execution.

PHOTON code is an interactive program which picks up the output file written by EARTH and represents the computed grid and flow pattern graphically on a computer screen or a printer.

GUIDE is the computer code that provides a source of helpful information about PHOENICS and its usage.
C.4.3 Implementation of the 3D-stack model

Setting up a fuel-cell stack simulation through PHOENICS is fulfilled through setting up fuel-cell stack simulations in the Q1 and in the GROUND files.

Setting up fuel-cell stack simulations in Q1 file. Data settings in Q1 are arranged into 24 groups (CHAM, 1995). Q1 consists of three key aspects as follows:

- Specifications of the stack geometry and physical properties (data are described in Appendix A.8).
- Definitions of the boundary conditions, and mass and heat sources: (i) input gas velocity, concentration, temperature and pressure of output gas, (ii) the heat transfer between the stack walls and surroundings (e.g. fixed-flux), (iii) the required output voltage (or the required current), (iv) the gas sources in the fuel gas due to the shift reaction and the gas consumption and liberation due to the current generation on the surfaces of the fuel and oxidant gases adjacent to the cell unit, and (v) the heat generation sources in the fuel gas due to the water-shift reaction and in the cell unit due to the electrochemical reaction.
- The variables to be solved in the conservation equations are the gas velocity in the x, y, and z directions, the gas composition and pressure, and also the temperature in the repeated cells (including gas, separator and cell unit), in the stack walls, and in the gas manifolds. Since it is required to calculate the temperature distribution in fuel gas, oxidant gas and immersed solids simultaneously, the heat transfer is defined as being conjugate.

To specify the stack geometry and physical properties in PHOENICS, the computational grid for a stack must be defined. The computational grid for a stack consists of the grid for walls, gas manifolds, and for a series of repeated cells. Each cell contains a cell unit (including electrolyte, anode, and cathode), two half-separators, a layer of fuel gas, and a layer of oxidant gas. The selection of the computational grids for a cell unit has an important impact on both the simulation time and the accuracy and it is crucial to a successful simulation. A denser grid in x, y, or z direction usually results in greater accuracy and a denser time grid results in easier convergence in each step. However, a denser grid requires a longer simulation time.

Figure C.2 illustrates the grid definition for an analysis unit of 20 mm × 20 mm. A cell unit with dimensions of 1m × 1m will consist of 50 × 50 basic units. The x, y, and z-axes represent the fuel gas channel direction, the stack direction, and oxidant gas direction, respectively. The cell height (in the y direction) is scaled up for the illustration and it has five zones: two for half-separators and three for fuel gas, cell unit, and oxidant gas. The grid definition is based on the requirement of the minimum grids. The minimum grids in y direction are one for each of the two half-separators, three for the cell unit (two electrodes and electrolyte), five for fuel gas and five for oxidant gas (parabolic gas velocity). The minimum grids in x- and z-directions are not straightforward. The grid in the x direction is denser than that in the z direction because the variation in the fuel gas composition is more significant than that of oxidant gas (the designed fuel gas utilization is higher than that of oxidant gas). The grids eight and ten have been used for x- and z-directions, and appear feasible.
As the simulation is conducted under transient conditions, fine time steps are needed for a step or ramp change. For example, a +10% step change in voltage is simulated by a 100 step changes of +0.1% voltage within 0.1 second.

**Setting up fuel-cell stack simulation in GROUND file.** The stack simulation has to incorporate the micro-process in the cell unit (i.e. electrodes and electrolyte) and to deal with the gas property variations due to the local chemical reaction and the current generation. Subroutines in the GROUND file have been developed to represent the micro-process by using i) local power and heat generation, and ii) gas sources. The subroutines are also developed to calculate the local gas properties.

The subroutines developed for local power and heat generation are as follows:

- Average cell unit temperature in the stack direction  \( T = \left( \frac{\int_{y_0}^{y_0 + \Delta y} T_{dy}}{\Delta y} \right) / \Delta y = (T_1 + T_2 + T_3) / 3 \)
- Local cell reversible potential  \( E \) (Eq. 3.11)
- Cell voltage  Eq. 3.12
- Local current  \( i \) (Eq. 3.13)
- Heat generation due to electrochemical reaction and cell losses in the cell unit (Eq. 3.14)
- Heat generation due to shift reaction in the fuel gas (Eq. 3.15).

The subroutines developed for the gas sources are as follows:

- Consumption of reactants and liberation of products due to a local current generation at the boundary surface of the fuel gas adjacent to cell unit (Eq. 3.22)
- Consumption of reactants and liberation of products due to a local current generation at the boundary surface of the oxidant gas adjacent to cell unit (Eq. 3.23)
- Change in the fuel gas composition due to the water-shift reaction (Eq. 3.18)
The subroutines for gas properties are also developed to calculate the properties of the gas mixtures, e.g. the density, enthalpy, molecular weight, and the viscosity. The equations for the thesis calculations are described in Appendix C.5.

C.4.4 Convergence and grid-independence

Accomplishing a fuel-cell stack simulation is a process of trial-and-error. There are no universal rules for successful solutions. This study evaluates the simulation results by two criteria: convergence and grid-independence. One should patiently check the intermediate solutions with respect to different iteration sweeps and different grids, to find out whether or not the iteration process and grid-fineness are satisfactory.

Convergence. Since a stack simulation by using the PHOENICS approach involves many iteration processes, determination of the convergence is crucial. In fact, to check the convergence is one of the most difficult problems met by users. In transient conditions, the simulation results at one time step serve as the initial conditions for the next time step. Consequently, the convergence of calculations at each step is necessary.

We use the procedure of first conducting an additional steady-state simulation under the final state of the transient condition, and then comparing the results of the transient simulation over a long time with those of the steady-state simulation. The agreement between the transient simulation results over a long time and those for the steady-state simulation is the necessary condition for acceptance of the transient results. Our simulation tests have found that some transient simulation results over a long time are not consistent with the corresponding steady-state simulation results, though the convergence criteria have been reached at each time step.

Grid independence. The grid independence of a PHOENICS solution is another critical factor. To be sure that the solutions are independent of the grid fineness, the simulation test computations under different grid definitions are required. Before accepting the results from a simulation, an additional simulation with double dense grids of x, y, z, and time step is conducted.

C.5 Properties of the Gas Mixture

The fuel and oxidant gases are assumed to be an ideal mixture of ideal gas species of H₂, CH₄, N₂, CO, CO₂, O₂ and H₂O. This assumption is based on the stack operation range (high temperature 600–700°C and relative low pressure around 0.3 MPa). Thus, all the thermodynamic equations applicable to the ideal gas can be used. The main parameters for the gas mixture are given as follows.

The density ρ_mix, enthalpy h_mix and molecular weight m_mix of the gas mixture read:

$$\rho_{\text{mix}} = \frac{P}{RT} \frac{1}{\sum_{i=1}^{k} \frac{y_i}{m_i}}$$  \hspace{1cm} (C.9)
Appendix C  Implementation of Fuel-cell Stack Models

\[ h_{\text{mix}} = \sum_{i=1}^{N} x_i \cdot h_i \]  
(C.10)

\[ m_{\text{mix}} = \sum_{i=1}^{N} x_i \cdot m_i \]  
(C.11)

The viscosity \( \mu \) of the gas mixture refers to Wilke formula (CRIPI, 1995) and reads:

\[ \mu_{\text{mix}} = \sum_{i=1}^{N} \frac{\mu_i}{1 + \frac{1}{\sum_{i=1}^{N} x_i \cdot \phi_{ij} \left( i \neq j \right)}} \]  
(C.12)

\[ \phi_{ij} = \frac{1}{\sqrt{2}} \left[ \frac{m_i}{m_j} \right]^{1/2} \]  
(C.13)

where \( y_i \) and \( x_i \) are the gas molar fraction and the weight fraction, \( m_i \) is the gas molecular weight (g/mol), \( P \) is the gas pressure, \( T \) and \( h \) are the temperature and enthalpy, \( R \) is the gas constant and \( i \) and \( j \) are the gas species, and \( N \) is the total number of gas species.

C.6 Simplification of 3D-Stack Model

As discussed in Chapter 3, one approach to simplifying the 3D-stack model is to directly represent the response characteristics of the 3D-stack model by using simple approximation equations. Achenbach (1995) has proposed an approach to represent the response performance of his 3D-SOFC stack. The stack response time depends on the design parameters and the operating conditions, and is approached by using a simple approximation equation including two dimensionless governing parameters. His approach is based on the assumption of the stack response being strongly related to the transient temperature distribution of the solid stack structure. This section adapts his SOFC approach to our 3D-MCFC stack.

C.6.1 Stack representation

The simplified stack attempts to have the same impact as that of our 3D-stack model to the overall system. More specifically, the simplified stack model aims at the same performance as the 3D-stack model under steady-state conditions, and also the same response time as the 3D-stack model. The simplified stack model uses the 3D-stack simulation results under steady-state conditions as direct input, and represents the stack response time by a simple algorithm.

When a stack consists of many cells, the 3D-stack model simulation under steady-state conditions still takes a long time (e.g., a few hours on a PC-Pentium or workstations like Sun-Sparc-IPX). The two assumptions described in Section 3.9.2 are added to simplify the fuel-cell stack. Then the stack performance can be simply represented by cell performance. The simplified stack model usually takes several minutes to run a steady-state case.
C.6.2 Simplification of dynamic equations in the 3D-stack model

In order to determine the stack response time by a simple algorithm. The governing parameters related to the stack response time must be identified. Since compared with the dissipation of heat in the stack, the processes of chemical reactions, mass-transfer, and electrical power and heat generation are fast. Appendix C.2 indicates the magnitude of the response time for each process. The dynamic term only considers the energy balance of the solid structure (including separator and cell unit). This means that a quasi steady-state solution of the problem is achieved at each time step except for the temperature of the separator and cell unit. The energy balance for the separator and cell unit reads:

\[
(\rho C_p)_{s} \frac{\partial T_s}{\partial t} + \left( \lambda_{eff x} \frac{\partial^2 T_s}{\partial x^2} + \lambda_{eff y} \frac{\partial^2 T_s}{\partial y^2} + \lambda_{eff z} \frac{\partial^2 T_s}{\partial z^2} \right) = S_h
\]

where \( T_s \) is the local solid temperature. The thermal conductivity, \( \lambda_{eff} \), of the quasi homogeneous stack structure is an effective quantity which must be separately determined for each of the spatial co-ordinates according to Achenbach (1995). The source term \( S_h \) is the heat produced or consumed in the chemical and electrochemical processes and the heat transferred from the fuel and the oxidant gases to the separator or cell unit.

Eq. C.10 can be written in a dimensionless form by introducing the following quantities:

\[
\theta = \frac{T - T_E}{T_o - T_E}; \quad \tau = \frac{t}{\Delta t} \quad (C.15)
\]

\[
\xi = \frac{x}{h_{eff}}; \quad \eta = \frac{y}{h_{eff}}; \quad \zeta = \frac{z}{h_{eff}} \quad (C.16)
\]

\( \Delta T = T_o - T_E \) is the difference between the outlet and entrance temperatures of the oxidant gas. The quantity \( \Delta t \) means a characteristic time interval, which is defined as the period necessary to reach 90% of the new steady-state value. \( h_{eff} \) is a characteristic length defined by Achenbach (1995).

The total heat, \( P_w \), to be removed from the cell is related to the electric output \( P_e \) of the cell and the efficiency \( \eta_e \):

\[
P_w = \frac{P_e (1 - \eta_e)}{\eta_e} = \frac{V \cdot i \cdot (1 - \eta_e)}{\eta_e} \quad (C.17)
\]

With Eqs. (C.11-C.13), Eq. C.10 yields the dimensionless form of the energy balance of the solid:

\[
\frac{\partial \theta}{\partial \tau} = \frac{\lambda_s \Delta T}{(\rho C_p)_{s} h_{eff}^2} \left( \frac{\lambda_{eff x} \frac{\partial^2 \theta}{\partial x^2} + \lambda_{eff y} \frac{\partial^2 \theta}{\partial y^2} + \lambda_{eff z} \frac{\partial^2 \theta}{\partial z^2} + (1 - \eta_e) \frac{V \cdot i}{\eta_e \lambda_s \Delta T / h_{eff}} \right) \quad (C.18)
\]

The solution of Eq. C.14 depends on two dimensionless groups. The first is the Fourier number \( F_o \), and reads:

\[
F_o = \frac{\lambda_s \Delta T}{(\rho C_p)_{s} h_{eff}^2} \quad (C.19)
\]

The second group derives from the source term \( S_o \) and leads to:

\[
S_o = \frac{(1 - \eta_e) \frac{V \cdot i}{\eta_e \lambda_s \Delta T / h_{eff}}} \quad (C.20)
\]
The term $S_o$ gives the ratio between two heat fluxes, i.e., the waste heat flux compared with a heat flux resulting from heat conduction through a plate when $h_{eff}$ is its thickness, $\lambda_s$ its thermal conductivity and $\Delta T$ the temperature difference.

The 3D-stack model simulation under transient conditions can reveal the co-relation between $F_o$ and $S_o$. Since the $S_o$ number only contains known design data, the $F_o$ number can be determined from the co-relation and hence the temperature response time will be known. That is, the stack temperature response can be predicted.

Figure C.3 shows the values of $F_o$ and $S_o$ from the 3D-stack model simulation under transient conditions. A simple proposed relation between $F_o$ and $S_o$ proposed reads:

$$F_o = \alpha S_o^\beta$$  \hspace{1cm} (C.21)

![Graph showing $F_o$ vs $S_o$]

**Figure C.3** An approximate equation for stack temperature response.

The values of $\alpha$ and $\beta$ are estimated based on the values of $F_o$ and $S_o$ from the 3D-stack model. In this case, $\alpha=0.27$ and $\beta=-1.1$. Therefore, an approximate equation for the stack temperature response prediction has been derived. In Figure C.3, the points with $\times$ are the simulation results of the 3D-stack model and the point with $\bullet$ is the dynamic case in Section 3.7 in Chapter 3.

This simplification approach has several deficiencies. First, it is still necessary to run the 3D stack model to provide the initial conditions for its dynamic simulation. Secondly, a general approximate equation C.17 strongly depends on the quality and quantity of the 3D-stack model simulation results. The relevant parameters (e.g., $V$, $i$, $\eta_e$ and $\Delta T$) should vary to cover a wide range of applications.

### C.7 Solution Method of the Lumped Stack in SPEEDUP Code

In order to solve the stack equations that have been described, the software package SPEEDUP (SPEEDUP, 1996) introduced in Section 2.8 is used. The structure of a SPEEDUP software package is shown in Figure C.4. It consists of: (i) SPEEDUP Executive Translator (which turns a user problem description file into a data file which SPEEDUP solver can understand and obey), (ii) SPEEDUP Solver (which compiles and links the user library, mathematical solution library and physical property library), and (iii) Output. SPEEDUP which can simultaneously solve implicit differential conservation equations (e.g., mass and energy balances) and algebraic equations (e.g. chemical reactions), initialize model variables, and has access to the
physical property library. In addition, the simple stack model can be integrated later into the system model that is in SPEEDUP code.

![Figure C.4 Structure of SPEEDUP software package](image)

Setting up the simple stack simulation through SPEEDUP code is fulfilled by using both the user problem description and user library. The stack problem description is composed of six input sections as follows:

- **Flowsheet.** The connections of the stack are: i) the fuel and oxidant gas input to the stack anode and cathode respectively, ii) two exhaust gases, and iii) power output.

- **Declare.** Defining the variable interconnections. The stack input variables are: i) the flow-rate, concentration, and temperature of the input gas stream, ii) pressure of the output gas streams, and iii) the required current output. The stack output variables are: i) the flow-rate, concentration, and temperature of the output gas streams, ii) pressure of the input gas streams, and iii) the power output.

- **Operation.** Defining the operating and design conditions of the stack (data described in Chapter 2 and Appendix A.6).

- **Options.** Selects translation and run-time option (e.g., time steps and intervals).

- **Unit.** An operational unit refers to the simple stack.

- **Model.** Implementation of the stack by using ordinary differential and algebraic equations.
Appendix D Algebraic Equations for Reformer Model

This section provides the algebraic equations for the calculation of the chemical conversion rates, heat transfer and pressure drop used in the reformer model in Chapter 4.

D.1 Conversion Rates of the Process Gas

The methane-steam and the water-shift reactions of the process gas in the two catalyst beds are assumed to reach equilibrium state. The equilibrium constants $K_{\text{reform}}$ and $K_{\text{shift}}$ are a function of temperature only (Smith and Ness, 1987) and these constants are:

$$K_{\text{reform}} = e^{-\frac{\Delta G_{\text{reform}}}{RT}}$$  \hspace{1cm} (D.1)

$$K_{\text{shift}} = e^{-\frac{\Delta G_{\text{shift}}}{RT}}$$  \hspace{1cm} (D.2)

The relation between the equilibrium constant and ideal-gas composition is (Smith and Ness, 1987):

$$P^{-n} \times K = \Pi(y_i)^{n_i}$$  \hspace{1cm} (D.3)

where $n_i$ is the reaction stoichiometric number and $n = \Sigma n_i$. For reforming and shift reactions, $n$ is 2 and 0 respectively. $P$ is the gas pressure in bars. Furthermore, $y_i$ is the mole fraction. When two or more independent reactions proceed simultaneously, the mole fraction $y_i$ reads:

$$y_i = \frac{F_{\text{in}(i)} + \sum_j (n_{i,j} \times \text{rate}_i)}{F_{\text{in}} + \sum_j (n_j \times \text{rate}_j)} = \frac{F_{\text{in}(i)} + n_{i,\text{reform}} \times \text{rate}_{\text{reform}} + n_{i,\text{shift}} \times \text{rate}_{\text{shift}}}{F_{\text{in}} + 2 \times \text{rate}_{\text{reform}}}$$  \hspace{1cm} (D.4)

where $F$ is the flow rate in mol/s, rate (mol/s) is the conversion rate of the reaction taking place.

Application of Eq. D.3 to reforming and shift reactions gives:

$$P^{-2} \times K_{\text{reform}} = \frac{y_{\text{CO}} \times y_{\text{H}_2}}{y_{\text{CH}_4} \times y_{\text{H}_2O}}$$  \hspace{1cm} (D.5)

$$K_{\text{shift}} = \frac{(F_{\text{in}} \times y_{\text{in}(CO)} - \text{rate}_{\text{shift}} + \text{rate}_{\text{reform}}) \times (F_{\text{in}} \times y_{\text{in}(H_2)} + \text{rate}_{\text{shift}} + 3 \times \text{rate}_{\text{reform}})^3}{(F_{\text{in}} \times y_{\text{in}(CO)} - \text{rate}_{\text{reform}}) \times (F_{\text{in}} \times y_{\text{in}(H_2O)} - \text{rate}_{\text{shift}} - \text{rate}_{\text{reform}}) \times (F_{\text{in}} + 2 \times \text{rate}_{\text{reform}})^2}$$  \hspace{1cm} (D.6)

The conversion rates of reforming and shift reactions rate_{reform} and rate_{shift} therefore can be obtained by solving Eqs. D.5 and D.6.

According to Eqs. D.1 and D.2, some values of the equilibrium constants at different temperatures are listed in Table D.1.
Table D.1 shows that the equilibrium constant of the reform reaction is highly dependent on the operation temperature. The temperature is the major factor determining the gas (i.e. CH₄) conversion rate and the higher operation temperature favors the CH₄ conversion rate. The shift reaction depends on the temperature as well.

D.2 Heat-transfer without Catalyst Bed

D.2.1 Estimation of the heat transfer magnitudes

The heat transfer processes between the fuel or process gas to BED1 or BED2 include: (i) the convective heat transfer between the gas and the shell wall, (ii) the radiant heat transfer between the two shell walls, and (iii) the radiant heat transfer between the gas and the shell wall. This section estimates the magnitude of these heat transfers (in units of kJ/s·m²) and provides a basis for our approach in the following section. The quantitative calculations of these heat transfer processes are given as follows (heat transfer in kJ/s·m²):

**Convective heat transfer.** The general equation to describe the convective heat transfer between the gas and the shell wall is:

\[
q_{\text{convection}} = \alpha \times \Delta T_{\text{mean}} \tag{D.5}
\]

where, \( \alpha \) is the convective heat transfer coefficient and \( \Delta T_{\text{mean}} \) is the mean temperate difference. Usually, \( \alpha \) and \( \Delta T_{\text{mean}} \) are inter-connected. In order to calculate \( q_{\text{convection}} \), the convective heat transfer coefficient \( \alpha \) needs to be determined.

With regard to the gas flow pattern in the reformer (e.g. turbulent), the simplified form of Nusselt number calculation is (Cobben, 1994):

\[\text{Nu} = 0.0214 \times (\text{Re}^{0.8} - 100) \times \text{Pr}^{0.4} \times (1 + (D_c/L)^{2/3})\]  \tag{D.6}

and the Nusselt number reads:

\[\text{Nu} = \frac{\alpha \times (D_a - D_l)}{\lambda}\]

Furthermore, since \( \text{Re}^{0.8} \gg 100 \) and the other parameters being almost constant, the Eq. D.6 leads to the following relations:

\[\text{Nu} \sim \text{Re}^{0.8}; \quad \alpha \sim u^{0.8}; \quad \alpha \sim F^{0.8}\]

Where \( u \) is the gas velocity. The convective heat transfer coefficient \( \alpha \) is given by the following approximation:

\[\frac{\alpha}{\alpha_0} = \frac{F^{0.8}}{F_0^{0.8}}\] \tag{D.7}
Appendix D  Algebraic Equations for Reformer Model

Where \( \alpha_0 \) and \( F_0 \) are the convective heat transfer coefficient and flow rate under the designed full load conditions. The convective heat transfer coefficient \( \alpha_0 \) is calculated from Eq. D.6 under the designed full load conditions. The convective heat transfer coefficient \( \alpha_0 \) is in the order of 1 \( \text{kJ/s.m}^2.\text{K} \) and the convective heat \( q_{\text{convection}} \) is in the order of 100 \( \text{kJ/s.m}^2 \).

**Radiant heat transfer between two walls.** The radiant heat transfer between two cylinder walls is:

\[
q_{1 \rightarrow 2} = \frac{\varepsilon_{w1} \times \varepsilon_{w2}}{\varepsilon_{w1} + \varepsilon_{w2} \times (1 - \varepsilon_{w1}) \times \frac{D_2}{D_1}} \times \sigma \times (T_{w1}^4 - T_{w2}^4)
\]  
(D.8)

where \( \sigma \) is the Stefan Boltzmann constant \( 5.67 \times 10^{-11} \text{kJ/s.m}^2.\text{K}^4 \), the \( \varepsilon_{w1} \) and \( \varepsilon_{w2} \) are the wall emission coefficients and use 0.8 according to the oxidized steel property, \( T_{w1} \) and \( T_{w2} \) are the wall temperatures, \( D_1 \) and \( D_2 \) are the diameters of the two walls. When \( T_{w1} = 1300 \text{ K} \) and \( T_{w2} = 1100 \text{ K} \), \( q_{1 \rightarrow 2} \) is in the order of 10 \( \text{kJ/s.m}^2 \).

**Radiant heat transfer between gas and wall.** The gas components of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) have the radiant heat transfer to wall. The radiant heat transfer between the gas and wall per square meters reads:

\[
q_{g \rightarrow w} = \frac{\varepsilon_g}{1 - (1 - \varepsilon_g) \times (1 - A_v)} \times \sigma \times (\varepsilon_g T_g^4 - A_v T_w^4)
\]  
(D.9)

where the \( \varepsilon_g \) and \( \varepsilon_g \) are the wall and gas emission coefficients, \( A_v \) is the gas absorption coefficient, \( T_g \) and \( T_w \) are the gas and wall temperatures.

The gas radiant heat transfer consists of the gas components of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) to the wall, and \( \varepsilon_g \) and \( A_v \) have:

\[
\varepsilon_g = \varepsilon_{\text{H}_2\text{O}} + \varepsilon_{\text{CO}_2} - (\Delta \varepsilon)_g
\]  
(D.10)

\[
A_v = A_v_{\text{H}_2\text{O}} + A_v_{\text{CO}_2} - (\Delta A)_v
\]  
(D.11)

\[
A_v_{\text{H}_2\text{O}} = \varepsilon_{\text{H}_2\text{O}} T_g \times \left( \frac{T_g}{T_w} \right)^{0.45}
\]  
(D.12)

\[
A_v_{\text{CO}_2} = \varepsilon_{\text{CO}_2} T_g \times \left( \frac{T_g}{T_w} \right)^{0.65}
\]  
(D.13)

where the gas emission coefficients refer to VDI (1998). When \( T_g = 1500 \text{ K} \) and \( T_w = 1200 \text{ K} \), \( q_{g \rightarrow w} \) is in the order of 10\(^9\) \( \text{kJ/s.m}^2 \).

**D.2.2 Calculation of the heat transfer processes**

According to the estimate of the heat transfer magnitude, the heat transfer processes includes only the convective heat transfer. The total heat transfer \( q_{\text{total}} \) is:

\[
q_{\text{total}} = \alpha_0 \times \frac{F^{0.8}}{F_0^{0.8}} \times \Delta T_{\text{mean}}
\]  
(D.14)

Eq. D.14 shows that the heat transfer depends on the temperature difference \( \Delta T_{\text{mean}} \) and the gas flow-rate.
The Eq. D.14 is used. The convective heat-transfer coefficient $\alpha_0$ is calculated from Eq. D.6 under the designed full load conditions. When there are uncertainties about the parameters in Eq. D.6 and there are design data available (e.g. temperature and flow rate), the $\alpha_0$ can also be estimated according to the design requirements.

### D.3 Heat-transfer with Catalyst Bed

With regard to the heat transfer from the reformer inner wall to the processing gas (with catalyst bed), general theoretical formula is available. The literature survey provided by Cobben (1994) indicated the uncertainty of the empirical equations from the literature. The frequent references are made to the Beek equation (1962) for the overall heat-transfer coefficient, which needs catalyst properties. The estimates of the overall heat-transfer coefficient are in the order of $10^3$ J/s.m$^2$.K by using the Beek equation (Tilburg, 1993 and Cobben 1994), which indicates the fast heat transfer from the process gas to the reformer inner wall.

Since the catalyst properties are not available, to eliminate the difficulty in determining the heat-transfer coefficient, the present approach lumps the shell wall, processing gas and catalyst bed together. This approximation is also justified, based on the fast heat transfer between the process gas and the reformer inner wall.

### D.4 Pressure Drop

The calculation of the pressure drop requires either extensive computational fluid dynamics techniques or empirical equations. The present reformer model adopts the latter approach.

**Gas pressure drop without catalyst bed.** The pressure drop of the flue or process gas is (VDI, 1988):

$$\Delta P = 10^{-5} \times \xi \times \frac{L}{D} \times \frac{F^2}{2 \times \rho} \quad (D.15)$$

where $\xi$ is the resistance factor. $\xi$ tends to be constant when Re has high value (VDI, 1988). When $\xi$ is almost constant, the pressure drop depends only on the gas flow rate and density and it has:

$$\Delta P \sim \frac{F^2}{\rho}$$

The pressure drop can be simplified as:

$$\frac{\Delta P}{\Delta P_o} = \frac{\rho_o}{\rho} \times \frac{F^2}{F_o^2} \quad (D.16)$$

Our reformer model uses the Eq. D.16. In principal, the pressure drop $P_o$ is calculated from Eq. D.15 under the designed full load conditions. When there are uncertainties about the parameters in Eq. D.15 and there are design conditions available (e.g., pressure drop and flow rate), the $P_o$ can be identified from the design conditions and it is in the order of 0.1 bar.
Gas pressure drop with catalyst bed. The process gas flow through dry catalyst particles and the pressure drop in the process gas used the Ergun equation (Perry, 1981) as:

$$\frac{dP}{dL} = -10^{-5} \times \left( \frac{150 \times (1 - \varepsilon_v)}{\text{Re}_p} + 1.75 \right) \times \frac{F^2}{\rho} \times \frac{1}{D_p} \times \frac{1}{\varepsilon_v^3}$$  \hspace{1cm} (D.17)

where $\varepsilon_v$ is the fraction of the empty space in the catalyst bed. When $\text{Re}_p = 5 \times 10^3$ and $\varepsilon_v = 0.6$, 

$$\frac{150 \times (1 - \varepsilon_v)}{\text{Re}_p} = 0.012 << 1.75$$

Therefore, the pressure drop of the process gas can be simplified as:

$$\Delta P = 1.75 \times 10^{-5} \frac{F^2}{\rho} \times \frac{1}{D_p} \times \frac{1}{\varepsilon_v^3} \times L$$  \hspace{1cm} (D.18)

Therefore, the pressure drop depends on the square of the gas flow rate and the gas density as:

$$\Delta P \sim \frac{F^2}{\rho}$$

and the pressure drop can be simplified as:

$$\frac{\Delta P}{\Delta P_0} = \frac{\rho_0}{\rho} \times \frac{F^2}{F_0^2}$$  \hspace{1cm} (D.19)

Our reformer model uses the Eq. D.19. In principal, the pressure drop $P_0$ is calculated from Eq. D.18 under the designed full load conditions. When there are uncertainties about the parameters in Eq. D.18 and there are design conditions available (e.g., pressure drop and flow rate), the $P_0$ can be identified from the design conditions and it is in the order of 0.1 bar.
Appendix E Appendices References


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Samenvatting

Een gesmolten-carbonaat brandstofcel (MCFC) is een nieuwe en veelbelovende optie voor een efficiënte omzetting van fossiele brandstoffen in elektriciteit. De twee cruciale componenten in een MCFC-systeem, de brandstofcel-stack en de reformer, zijn nieuwe apparaten voor elektriciteitsopwekkingssystemen. Om een hoog systeemrendement te behalen, zijn deze apparaten door middel van kringlopen met elkaar geïntegreerd. Hierbij kunnen dynamische interacties tussen genoemde apparaten optreden.

Om de brandstofcel-stack en de reformer in een elektriciteitsopwekkingssysteem te kunnen opnemen, moeten eerst hun werkingseigenschappen geïdentificeerd worden bij een bedrijfsvoering waarbij de elektriciteitsproductie de vraag volgt (load-following mode). Vervolgens kan het complete systeem worden onderzocht.

De belangrijkste obstakels bij de bedrijfsvoering van een MCFC-systeem kunnen worden geformuleerd aan de hand van vier hoofdvragen. Dit proefschrift legt de nadruk op de beantwoording van deze vier vragen, die een rode draad vormen door het proefschrift:

i. Wat zijn de karakteristieken van de elektriciteitsopwekking van een brandstofcel-stack en opereert een brandstofcel-stack binnen de veiligheids marges?
ii. Kan de reformer de gassen leveren met condities die voldoen aan de eisen van de brandstofcel-stack (volumestroom, samenstelling, temperatuur en druk)?
iii. Wat zijn de karakteristieken van de elektriciteitsopwekking van een compleet MCFC-systeem?
iv. Wat zijn de dynamische interacties tussen de reformer en brandstofcel-stacks?

Om deze vragen te beantwoorden worden in dit proefschrift vier hoofdzaken onderzocht:

- Systeemontwerp
- Modellen voor de brandstofcel-stack
- Reformermode
- Systeemmodel

Systeemontwerp
Het systeemontwerp bepaalt het raamwerk waarin de vier hoofdvragen zullen worden beantwoord. De belangrijkste resultaten van het systeemontwerp zijn:

- Een state-of-the-art 1 MW MCFC-systeem is geselecteerd en aangepast aan de Nederlandse situatie (onder andere verschil in aardgas-samenstelling en apparaat-type).
- De kwalitatieve analyse laat zien dat het systeem geschikt is voor praktische toepassing en voldoet aan de eisen voor een veilige en efficiënte bedrijfsvoering.
- De kwantitatieve analyse van het systeem is uitgevoerd met het programma CYCLE-TEMPO, dat is ontwikkeld door de vakgroep energievoorziening van de Technische Universiteit Delft. Het systeem heeft een netto elektrisch rendement van 45.8% bij ontwerpmogelijkheden.
- De geometrie en fysische eigenschappen van de brandstofcel-stack, reformer en warmtewisselaars zijn berekend ter bepaling van de dynamische modellen.
Modellen voor de brandstofcel-stack
Er zijn twee typen modellen ontwikkeld voor de brandstofcel-stack. Een driedimensionaal (3D) dynamisch stack-model poogt een antwoord te geven op de eerste hoofdvraag. Een vereenvoudigd dynamisch stack-model is ontwikkeld voor gebruik in het systeemmodel. Dit model is niet plaatsafhankelijk maar alleen tijdsafhankelijk (zg. "lumped").

- Nieuwe functies om een veilige werking van de stack te kunnen identificeren. Het 3D-model heeft nieuwe functies om te kunnen detecteren of de veiligheidsmarges niet worden overschreden. Het model levert bijvoorbeeld temperatuurgradiënten (in plaats en tijd) in de stack, wat niet mogelijk is met een lumped model.

De prestaties van het 3D-model bij stationaire condities zijn geëvalueerd door temperatuurprofielen berekend met het model te vergelijken met temperatuurprofielen van simulaties uit de literatuur. Deze zijn kwalitatief in overeenstemming. De isothermen berekend met het 3D-model wijken minder dan 10 K (minder dan 2%) af van de meetdata uit de literatuur.

Ter beantwoording van de eerste hoofdvraag, worden de karakteristieken voor de elektriciteitsopwekking van de brandstofcel-stack en een veilige werking van de stack gedemonstreerd door de volgende twee simulaties:

- Het dynamisch gedrag van de stack wordt geïllustreerd door de gesimuleerde respons van de stroomdichtheid en de temperatuur op een +10% stapverandering van de spanning. De respons van het uitgaande vermogen van de stack bestaat uit: i) een onmiddellijke respons veroorzaakt door het elektriciteitsopwekkingsgedrag van de elektrode, ii) een snelle respons (in de orde van 0.1 tot 1 seconde) veroorzaakt door variatie in de gasconcentratie (gastransport), en iii) een langzame respons (in de orde van 10 tot 10² seconde) veroorzaakt door temperatuurvariabelen (warmteopslag).
- De simulatieresultaten van de 1 MW stack laten zien dat de temperatuurverdeling en gradiënt binnen de veiligheidsmarges blijven (een temperatuur lager dan 750°C en een temperatuurgradiënt kleiner dan 10 K/min).

De resultaten van de simulaties met het 3D-model zijn ook gebruikt voor de ontwikkeling van een lumped stack-model dat geschikt is voor integratie in het systeemmodel. Hierbij is uitgegaan van twee verschillende benaderingen:

- Geef de respons van het 3D-model weer door het gebruik van eenvoudige vergelijkingen met geschatte parameters.
Maak een stack-model met globale parameters gebaseerd op fysische wetten en gebruik de resultaten van het 3D-model om de nauwkeurigheid te verhogen. Bij de eerste aanpak is een methodologie uit de literatuur, waarin een 3D SOFC-stack-model werd vereenvoudigd, aangepast om het 3D MCFC-stack-model te vereenvoudigen. De tweede aanpak gebruikt een combinatie van modelleertechieken gebaseerd op fysische wetten en empirische relaties. Het beschouwt de fysische natuur van de processen en gebruikt de resultaten van de 3D-simulaties ter verbetering van het model. Met deze tweede aanpak is een stack-model gemaakt dat geïntegreerd is in het systeemmodel.

Reformermodel
De reformer in een brandstofcel systeem is afgeleid van reformers uit de procesindustrie. Een belangrijk verschil is dat een reformer in de procesindustrie voornamelijk stationair wordt bedreven. Bij een brandstofcel systeem moet de reformer de gasproductie aanpassen aan de vermogensvraag. Er is gekozen voor het gebruik van een Heat Exchange Reformer (HER) van Haldor Topsoe. In de HER vindt de conversiereactie plaats in twee katalysatorbedden die werken op twee verschillende temperatuurniveaus. Bij de ontwikkeling van het reformermodel is veel aandacht besteed aan twee aspecten: Het werkingsprincipe van de HER en het kunnen volgen van de vermogensvraag.
Om de tweede hoofdvraag te beantwoorden worden de werkingsgeigenschappen van de reformer gemonstreerd aan de hand van de volgende simulaties:
- Stationaire simulatie: Het uitgaande procesgas van de reformer heeft een temperatuur van 607°C, een druk van 3.2 bar en een waterstofconcentratie van 47%. Hiermee voldoet het gas aan de eisen gesteld door de brandstofcelenode. Het rookgas van de reformer heeft een temperatuur van 633°C, een druk van 3.3 bar en een kooldioxideconcentratie van 40%. Het rookgas wordt tot 550°C afgekoeld en is dan geschikt voor de brandstofcelkathode.
- Vier simulaties waarbij de respons van de reformer op vermogensvariaties en de respons op drie verstoringen wordt bekeken. Manipulatie van de procesgas-toevoer naar de reformer is effectief voor de controle van de anodegas-toevoer. Er zijn echter twee neveneffecten, namelijk fluctuaties van de waterstofconcentratie en van de temperatuur. De reformer heeft een lage gevoeligheid voor veranderingen in de temperatuur van het stookgas naar de brander en voor de stoom/gas-ratio. De gevoeligheid voor de druk is echter groot.

Systeemmodel
Het systeemmodel is geïmplementeerd in het dynamisch simulatieprogramma SPEEDUP en bestaat uit een koppeling van de modellen voor de brandstofcel-stack, reformer en overige componenten. Voor elke component worden de parameters vastgesteld met ontwerp- en werkgegevens.
Simulaties uitgevoerd met het systeemmodel zijn vergeleken met meetgegevens van een 100 kW systeem uit de literatuur. De gesimuleerde benutting van waterstof aan de anode en kooldioxide aan de kathode bij een stijgend vermogen zijn kwalitatief consistent met de meetgegevens.
Om de derde hoofdvraag te beantwoorden is het gedrag van de elektriciteitsopwekking gesimuleerd:
- Systeemrendement. Het elektrisch rendement van het systeem ligt tussen de 40 en 50% over het hele vermogensbereik. Het systeem behaalt het hoogste rendement bij een laag vermogen.
• **Vermogensverandering door het veranderen van de stroom.** Het aanpassen van de stroom resulteert in een snelle verandering van het vermogen maar ook in een grote spanningsval. Bij een 5% toename van de stroom stijgt het vermogen met 2.5% binnen een tijdsomspanne van 10 seconden. De spanning daalt dan met 23 V (3.3%) bij een hoge waterstofbenutting (80%). De manipulatie van de stroom is effectiever bij een lage waterstofbenutting. Bij dezelfde 5% toename van de stroom stijgt het vermogen met 4% binnen een tijdsomspanne van 10 seconden met een spanningsval van 14 V (1.8%) bij een waterstofbenutting van 40%.

• **Vermogensverandering door een verandering van stroom en brandstof.** Bij een 5% toename van tegelijkertijd de stroom en de brandstof stijgt het uitgaande vermogen met 4.2%. De spanningsval (4 V) is hier veel kleiner dan de 23 V en 14 V bij enkel een stroomtoename.

Om de vierde hoofdvraag te beantwoorden zijn de dynamische interacties tussen de brandstofcel-stack en de reformer geïdentificeerd. De resultaten zijn:

• **Excessieve waterstofbenutting in de stack bij stijgend vermogen.** Een hoge stroomopbrengst in de brandstofcel-stack veroorzaakt een hoge brandstofbenutting wat resulteert in een lage waterstofconcentratie aan de stack-uitgang. Dit resulteert in een lagere verbrandingstemperatuur in de brander van de reformer. Hierdoor wordt de effectiviteit van het reformproces gereduceerd, wat resulteert in een nog hogere gasbenutting in de brandstofcel-stack. Bij stijgend vermogen (5% staptoename van brandstofvoevoer en stroom) stijgt de waterstofbenutting in de stack van 80% naar 87.5% en valt daarna terug naar 80% in een tijdsomspanne van 100 seconden. De waterstofbenutting overstijgt dan de limiet van 85%.

• **Hoge verbrandingstemperatuur in de reformer bij dalend vermogen.** Bij een dalend vermogen neemt de brandstofbenutting in de stack af, waardoor het uitgaande anodegas een hogere waterstofconcentratie behoudt. Dit resulteert in een hogere verbrandingstemperatuur in de brander van de reformer. Hierdoor neemt de effectiviteit van de reformreactie toe wat resulteert in een nog lagere brandstofbenutting in de brandstofcel-stack.

Het voorgestelde systeemmodel is bruikbaar voor verbetering van het systeemontwerp en de werking. Het systeemmodel is bruikbaar om een alternatieve bedrijfsstrategie te bepalen ter vermindering van dynamische interacties en om de locatie van een regelklep te optimaliseren.

Dit proefschrift heeft de vier hoofdvragen beantwoord en geeft inzicht bij de introductie van een brandstofcellsysteem en reformer in een systeem voor electriciteitsopwekking. De resultaten van deze studie zijn interessant voor een ontwerper die betrokken is bij de optimalisatie van het ontwerp en de bedrijfsvoering van brandstofcel-stacks en systemen.
ABOUT THE AUTHOR

The Author, Wei He was born in Shanghai, China. She obtained her MSc. in Mechanical Engineering from Southeast University, China and her MBA from the European University, the Hague, the Netherlands. She was employed as a mechanical design engineer for nuclear, coal, and gas power-generation plants in China, followed by one year designing wind energy systems at the Riso National Laboratory, Denmark. She broadened her industrial working experience at N.V. KEMA, the Netherlands, where she developed optimization tools for planning the Dutch electric power distribution network. She then worked on the fuel-cell project at Laboratory of Thermal Power Engineering, Faculty of Mechanical Engineering, Delft University of Technology, the Netherlands. This thesis includes her research results achieved in the field of fuel-cell systems. She is currently working as a senior process engineer in the field of oil and energy at Norsk Hydro, Oslo, Norway.

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