

A simulation model for integrated molten carbonate fuel cell systems

Wei He

Department of Mechanical Engineering, Delft University of Technology, 2628 CD Delft (Netherlands)

Abstract

This paper investigates the static and the dynamic behaviour of integrated molten carbonate fuel cell systems operating in a load-following mode. The fundamental techniques for modelling the reformer and fuel cell are discussed. More specifically, the dominant chemical, electrochemical and physical phenomena which significantly influence the gas composition, temperature and pressure, are modelled in the reformer and fuel cell.

Introduction

An integrated fuel cell system provides a new option for the efficient, economical and environmentally acceptable production of electricity.

An integrated fuel cell system will often integrate a fuel processor, a fuel cell power generator and a conventional power generation system. This close integration of the various components in the system may cause dynamic interactions which are difficult to predict. Furthermore, evaluation of the dynamic behaviour of main components, such as the reformer and the fuel cell stack in non-conventional systems is of great interest for integrated fuel cell system demonstration projects. The results of this study are expected to be applicable to two 250 kW molten carbonate fuel cell (MCFC) system demonstration projects scheduled for operation in The Netherlands in 1995–1996.

Because of the complex chemical, electrochemical and physical phenomena in a highly integrated fuel cell system, a Ph.D. project entitled ‘Dynamic modelling and control of an integrated fuel cell system’ was initiated at the Laboratory for Thermal Power Engineering, Delft University. The first objective was to analyse the inherent process characteristics with regard to load-following control, and to identify and to investigate potential bottlenecks. The second objective was to investigate different control designs for their ability to follow load changes as rapidly and smoothly as possible. Initially, a simulation model for integrated fuel cell systems (SIFCS) was developed to obtain an improved understanding of the principal component processes in integrated fuel cell systems.

SIFCS was constructed using the recent comprehensive plant modelling code SpeedUp [1]. This code considers large-scale steady-state simulation and dynamic simulation with simultaneous solution of differential and algebraic equations. Several components in the integrated fuel cell system may be described by the available Modular Modelling System library [2] which includes the most common components in conventional power generation systems. However, the reformer and fuel cell stack models were newly developed.

Integrated fuel cell system defined by SIFCS

System description

The principle of an integrated fuel cell system was confirmed by the example shown in Fig. 1 [3]. The power output from the fuel cell is 1000 kW. The heat from the fuel cell is utilized for the production of process steam (10 bar/180 °C). The calculated gross electrical efficiency equals 50.7%. Part of the power generated in the fuel cell (7%) is used to drive pumps and blowers in the system, resulting in a net system electrical efficiency of 43.7%. The overall efficiency, i.e., heat and electricity generated, equals 70.8%.

The fuel compositions for the integrated fuel cell system correspond to natural gas or coal gas obtained by gasification.

Main components

Since an integrated fuel cell system has many alternative design parameters, it is necessary to define the main components in the SIFCS. Very flexible connections between each component can be easily executed using the SpeedUp code. The main components in the integrated fuel cell system may be identified as follows:

- (i) *Fuel processing:* external reformer or internal reformer; components used in a coal gasification system, and auxiliary combustion.
- (ii) *Thermal management:* components used in the bottoming cycle (often a conventional power generation system) or in a district heating system, and fuel or gas preheater.
- (iii) *Electricity generation:* MCFC fuel cell stack, and generator from a gas-turbine and/or steam turbine bottoming cycle with power generators.
- (iv) *Power conditioning:* d.c./a.c. inverter.
- (v) *Mass flow:* pump, blower, and compressor.

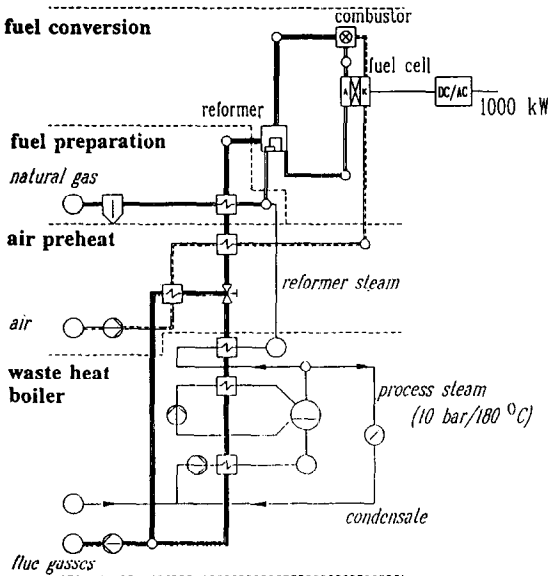


Fig. 1. Fuel cell system flow diagram.

Since the reformer and the fuel cell are new devices which are of major importance in an integrated fuel system, the first object of SIFCS was to investigate their behaviour. The modelling of these two components is described in the following sections.

Reformer modelling

Introduction

A reformer converts hydrocarbons into H_2 . This H_2 is then fed to the anode of the fuel cell as mixed fuel gas. The output gases from the fuel cell are partly recycled to the reformer or to the fuel cell, while the remaining gases are used in a bottoming cycle.

Haldor Topsoe has developed a heat-exchange reformer (HER) [4] which combines counter- and co-current flow so that the reformer temperature is controlled with low sensitivity to flue gas inlet temperature variations. This reformer design is now well proven and has been applied to fuel processing systems in MCFC and phosphoric acid fuel cell (PAFC) power plants in capacities from 100 kW to 5 MW. The IHI plate reformer [5] has a large heat-transfer area per unit volumetric capacity and good load following controllability.

Since the HER will be used in the 50 kW MCFC system in The Netherlands, it was modelled first.

Processes in the heat-exchange reformer (HER)

The HER, shown in Fig. 2, uses a patented principle with a combination of co-current and counter-current heat exchange between the process gas and the flue gas to maximize thermal efficiency and to optimize the utilization of construction materials. The hydrocarbon and steam reformer feed mixture is partly converted into CO_2 , CO

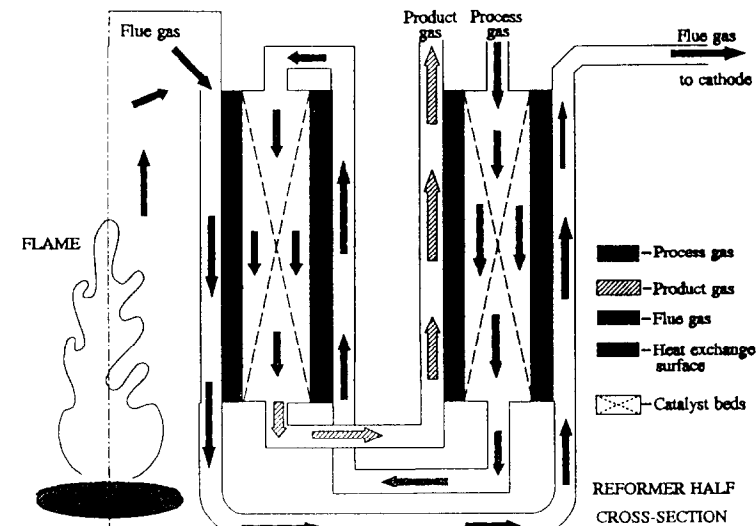
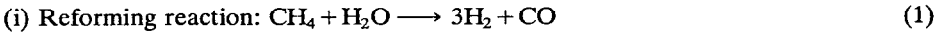


Fig. 2. Cross section of the heat-exchange reformer in a schematic representation.

and H_2 in the first catalyst bed. The heat required for the endothermic reaction and for the heating of the reaction mixture to approximately 675 °C is supplied by the partially cooled combustion gas and by the product gas leaving the second catalyst bed in counter-current flow. Nearly complete conversion of the process stream is obtained in the second catalyst bed where the process gas mixture is further heated to approximately 830 °C by heat exchange with a co-current flow of hot combustion gas.

Reactions modelled for the process gas



The above equilibrium constant for above reaction can be calculated as follows [6]:

$$-RT \ln K = \Delta G \quad (3)$$

where, R is the proportionality constant ($J \text{ mol}^{-1} \text{ K}^{-1}$), T the temperature (K), K the equilibrium constant of the CH_4 -transformation reaction (mol^{-2}), and ΔG the Gibbs energy change ($J \text{ mol}^{-1}$).

Kinetics for above eqn. (1) [7]:

$$r_{CH_4} = k_{CH_4} \{P_{CH_4} - [P_{CO} P_{H_2}^3 / (P_{H_2O} K)]\} \quad (4)$$

where, r is the stream reforming rate, P the partial pressure of reacting gas in the stream reforming reaction, K the equilibrium constant of the CH_4 -transformation reaction, and k the reaction rate constant.



Natural gas and refinery off-gas reformer feedstock contains hydrocarbon which are higher than CH_4 . It is assumed that the higher hydrocarbons instantaneously hydrocrack to CH_4 at the reformer inlet. This CH_4 , plus the CH_4 originally in the feedstock, is frequently termed the 'methane equivalent' of the fuel.

Reactions modelled for the flue gas



Modelling approach

Simplifying assumptions

(i) Combustion in the reformer model assumes a complete burning process with excess air.

(ii) Heat-transfer processes from flue gas to process gas are given by two standard counter-current flow heat exchangers and one co-flow heat exchanger.

(iii) The chemical reaction block is approached by a reforming reaction based on known CH_4 conversion and a water-shift reaction based on equilibrium states. The chemical reactions are carried out at a user-defined temperature and only result in gas composition changes. The reforming and shift reactions proceed simultaneously.

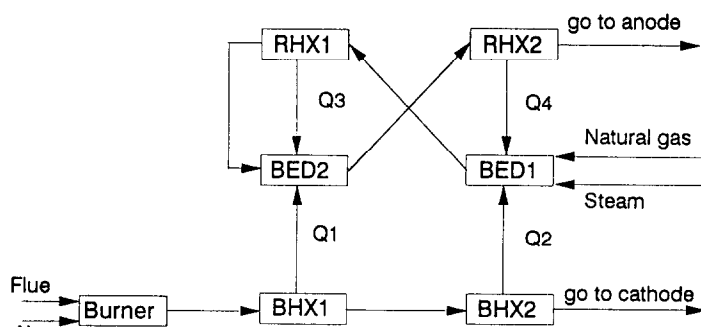


Fig. 3. Layout of the reformer modules in the SpeedUp code.

TABLE 1

Calculated hydrogen, methane composition at outlet and required heat

	600 °C	700 °C	800 °C	850 °C
product: H ₂ (mol/s, mole fraction %)	2.481 (46.4)	2.803 (50.1)	2.77 (49.3)	2.74 (48.8)
CH ₄ at outlet (mole fraction %)	2.553	0.2304	0.0184	0.00599
required heat (KJ/s)	135	167	175	177

Model structure

The structure of the reformer model is schematically depicted in Fig. 3, which has been described in the SpeedUp code.

Calculation example

Example: calculated hydrogen, methane composition at the outlet of reaction based on equilibrium.

This example was intended to investigate the behaviour of chemical reactions in the HER based on equilibrium theory. The ratio of steam to natural gas was set at 3. The composition of natural gas is 81% CH₄ and 14.5% N₂, and the flow was 1 mol/s at inlet. The results calculated at temperatures of 600, 700, 800 and 850 °C are shown in Table 1.

This example shows that more H₂ can be expected at higher temperature. The overall reaction is endothermic, and more heat is required at higher temperature. It shows that a higher steam-to-carbon ratio results in more H₂.

Fuel cell stack modelling

Introduction

A fuel cell stack is an electrochemical device which directly converts the chemical energy of reactants into low voltage d.c. electricity. A fuel cell component consists of

several parallel connected stacks. The stack usually consists of a number of series-connected individual electrical cells. The basic elements of a fuel cell consist of an electrolyte phase in contact with a porous anode and cathode on either side.

Processes in fuel cell

Simplifying assumptions

Following assumptions were introduced for fuel cell modelling:

- (i) thermally insulation on the outside;
- (ii) no vertical temperature and current distribution between cells, and
- (iii) uniform mass flow between each cell.

With above three assumptions, single cell performance and its two-dimensional distribution represent a stack performance. The reactant input mass for each cell is the input mass of the fuel cell stack divided by the number of cells.

Mass-flow processes

The fuel and air flow configurations considered in the cells were cross flow, count flow and co-flow. The fuel and air pass over the anode and cathode, respectively. On the anode side, a certain percentage of H_2 continuously reacts with the electrolyte, and the H_2O and CO_2 products are released on the anode side. On cathode side, a certain percentage of CO_2 and O_2 is continuously absorbed into the electrolyte and then is released on the anode side after reacting with H_2 .

Chemical processes

(i) At anode side:

- the electrochemical reactions:

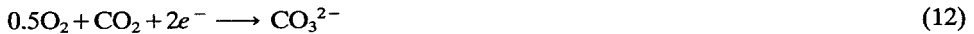


- the shift reaction:



(ii) At cathode side:

- the electrochemical reaction:



Heat-transfer processes

For the study of heat transfer, a fuel cell is divided into small elements. Each element is further divided into a fuel element, an air element, an electrode and electrolyte element and a separator element. Heat conduction, convection, radiation and mass transfer occur between the fuel element, air element, electrode and electrolyte element and the separator element. The details of the heat-transfer calculation are given in ref. 8.

Electrical characteristics

The maximum electrical work obtainable (W_{el}) in a fuel cell operating at constant temperature and pressure is given by the change in Gibbs free energy (ΔG) of the electrochemical reaction:

$$W_{el} = \Delta G = -nFE \quad (13)$$

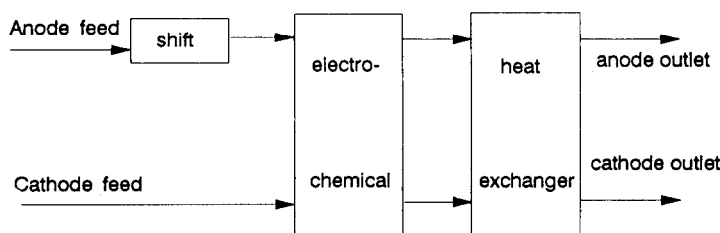


Fig. 4. Layout of the fuel cell modules in the SpeedUp code.

Several sources contribute to irreversible losses in a practical fuel cell. The losses primarily from three sources: (i) ohmic polarization; (ii) concentration polarization, and (iii) activation polarization. These losses result in a cell voltage for a fuel cell which is less than its reversible potential.

The voltage-current characteristic is:

$$V = E - IR_p \quad (14)$$

where, E is the open-circuit voltage (V), R_p the local resistance (Ω), and I the current density (A).

Modelling approach

Model integration

The integration of the reformer model is schematically depicted in Fig. 4, which was implemented in the SpeedUp code.

Conclusions

The development of SIFCS is continuing. As an initial effort, the basis of the model for the main components in an integrated fuel cell system is presented in this paper. The modelling approach to the reformer and fuel cell includes dominant chemical, electrochemical and physical phenomena, which has provided valuable insight into their operating characteristics in integrated fuel cell system.

Acknowledgements

This research was conducted at the Laboratory for Thermal Power Engineering of the Delft University under the guidance of Professors R.W.J. Kouffeld and O.H. Bosgra.

References

- 1 *User Manual, SpeedUp Release, 5.4.*, Aspen Technology, Inc., Cambridge, MA, USA, 1993.
- 2 *Modular Modelling System, Program Manual*, Babcock and Wilcox Company, Lynchburg, VA, USA, 1987.
- 3 A. de Groot, Exergy analysis of a fuel cell system, *Forschung in der Kraftwerkstechnik, Feb., 24-25, 1993*, EA, VGB-TB 231, Assen, Germany.

- 4 Endurance testing of a high-efficiency steam reformer for fuel cell power plants, Haldor Topsoe Inc., *EPRJ AP-6071, Project 2192-1, Final Rep.*, Oct. 1988.
- 5 IHI, Development of Reformer for Fuel Cell System, 10-kW Class Test, *IHI Eng. Rev. (Jpn.)* 26 (No. 1) 1991.
- 6 M. Smith and H.C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*, McGraw-Hill Chemical Eng. Ser., Singapore, 4th edn., 1987.
- 7 T. Take, *Fuel Cell Seminar, Tucson, AZ, USA, Nov. 29-Dec. 2, 1992*, pp. 477-480.
- 8 T. Watanabe, *Development of Molten Carbonate Fuel Cell Stack Performance Analysis Model*, Part 1, W90028, CRIEPI, Japan, 1991 (in Japanese).