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STEADY-STATE AND TRANSIENT ANALYSIS OF A STEAM REFORMER BASED SOLID OXIDE FUEL CELL SYSTEM

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Sridharan Narayanan

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STEADY-STATE AND TRANSIENT ANALYSIS OF A STEAM REFORMER BASED SOLID OXIDE FUEL CELL SYSTEM

By

Sridharan Narayanan

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Mechanical Engineering

2008

ABSTRACT

STEADY-STATE AND TRANSIENT ANALYSIS OF A STEAM REFORMER BASED SOLID OXIDE FUEL CELL SYSTEM

By

Sridharan Narayanan

In this thesis we perform a model-based analysis of a Solid Oxide Fuel Cell (SOFC) system with an integrated steam reformer and with methane as fuel. The objective of this study is to analyze the steady-state and transient characteristics of this system for varying current demand. For the analysis, we develop a control-oriented model of the system that captures the heat and mass transfer, chemical kinetics and electrochemical phenomena. We express the dynamics of the reformer and the fuel cell in state-space form. By applying coordinate transformations to the state-space model, we derive analytical expressions of steady-state conditions and transient behaviors of two critical performance variables, namely utilization and steam-to-carbon balance. Using these results, we solve a constrained fuel optimization problem in steady-state using linear programming. Our analysis is supported by simulations. The results presented in this thesis can be applied in predicting transient response and will be useful in control development for SOFC systems. To my parents

ACKNOWLEDGMENTS

I would like to thank everyone who contributed towards the completion of my thesis.

I sincerely thank my advisor Dr.Mukherjee for his direction, advice and support. I cannot thank my co-advisor Dr.Tuhin Das enough for his time, guidance, patience, insight and attention he gave me all through the process and I hereby express my sincere gratitude for him. I really appreciate the members of my MS committee: Dr.Ranjan Mukherjee, Dr.Tuhin Das, Dr.Andre Benard and Dr.Fang Zheng Peng for the flexibility extended to me and for all their valuable suggestions.

I am extremely grateful to my parents whose love, blessings and encouragement have always been a constant source of strength for me.

I would also like to thank all my fellow graduate students in the Dynamics and Controls Laboratory for their companionship and for making the whole experience so wonderful.

Also, my special thanks to the entire Mechanical Engineering department and staff for making this voyage unique and memorable.

Sridharan Narayanan

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CHAPTER 1

NOMENCLATURE

A	Cross sectional area for heat transfer (m^2)
Ā	Cross sectional area for heat transfer in discretized model (m^2)
C	Specific heat(J/kg/K)
C_p	Specific heat at constant pressure $(J/kg/K)$
C_v	Specific heat at constant volume (J/kg/K)
D_H	Hydraulic diameter (m)
d_p	Catalyst ring equivalent spherical diameter (m)
E	Reformer bed emmisivity
E_I, E_{II}, E_{III}	Activation energy of reactions (I), (II), (III)
	in Eqs. (3.17) and (3.38) (J/mol)
F	Faraday's constant (= 96485.34 Coulomb/mol)
${\cal H}$	
	Convective heat transfer coefficient $(W/m^2/K)$
h	Convective heat transfer coefficient(W/m ² /K) Molar enthalpy (J/mole)
h h _{rate}	Convective heat transfer coefficient(W/m ² /K) Molar enthalpy (J/mole) Molar enthalpy change (J/mole)
h h _{rate} i	Convective heat transfer coefficient(W/m ² /K) Molar enthalpy (J/mole) Molar enthalpy change (J/mole) Current draw (A)
h h _{rate} i K _{cv}	Convective heat transfer coefficient(W/m ² /K) Molar enthalpy (J/mole) Molar enthalpy change (J/mole) Current draw (A) Convective contribution to the heat transfer coefficient
h h _{rate} i K _{cv}	Convective heat transfer coefficient(W/m ² /K) Molar enthalpy (J/mole) Molar enthalpy change (J/mole) Current draw (A) Convective contribution to the heat transfer coefficient in reformer(W/m ² /K)

K_r	Convective contribution to the heat transfer coeficient
	in reformer($W/m^2/K$)
$\mathcal{K}_{I},\mathcal{K}_{III}$	Equilibrium constant of reactions (I) and (III)
	in Eqs. (3.17) and (3.38) (Pa ²)
\mathcal{K}_{II}	Equilibrium constant of reaction (II)
	in Eqs.(3.17) and (3.38)
$\mathcal{K}_{CH_4}, \mathcal{K}_{CO}, \mathcal{K}_{H_2}$	Adsorption constant for CH_4 , CO , H_2 (1/Pa)
\mathcal{K}_{H_2O}	Adsorption constant for H_2O
k	Anode recirculation fraction
k_f	Fluid conductive heat transfer coefficient $(W/m/K)$
k_s	Solid conductive heat transfer coefficient $(W/m/K)$
L	Length(m)
Μ	Mass (kg)
MW	Molecular weight (kg/mol)
\dot{M}_{in}	Anode inlet mass flow rate (kg/sec)
\dot{M}_{o}	Anode exit mass flow rate (kg/sec)
Ν	Number of moles (moles)
Nu_D	Nusselt number
\mathcal{N}_{cell}	Number of cells in series
\dot{N}_{air}	Molar flow rate of air (moles/sec)
\dot{N}_{f}	Molar flow rate of fuel (moles/sec)
\dot{N}_{in}	Anode inlet flow rate (moles/sec)
Ňo	Anode exit flow rate (moles/sec)
n	Number of electrons participating in electro-
	chemical reaction $(=2)$
Р	Control volume pressure (N/m^2)
Pr	Prandtl number

p	Partial pressure (N/m^2)
\dot{Q}	Rate of heat transfer (W)
Re_D	Reynold's number along diameter
Re_L	Reynold's number along length
R_u	Universal gas constant (8.314J/mol/K)
${\cal R}$	Species rate of formation (moles/sec)
r_I, r_{II}, r_{III}	Rates of reactions (I), (II), (III)
	in Eqs.(3.17) and (3.38) (mol/kg cat./sec) $$
r_d	Rate of electro-chemical reaction (moles/sec)
S_T^0	Entropy of formation at temperature T $(J/K Mol)$
STCB	Steam-To-Carbon Balance (moles/sec)
STCR	Steam-To-Carbon Ratio
Т	Temperature (K)
T_{ref}	Reference temperature (K)
U	Utilization
V	Volume (m ³)
ν	Velocity of fluid through a control volume (m/sec)
\dot{W}_{net}	Net work done (W)
X	Species mole fraction
A	Reformer particle voidage
ε	Catalyst bed void fraction
ΔG_T^0	standard state Gibbs function for a unit reaction (J/mol)
ΔH	Enthalpy of reaction or adsorption (J/mol)
$\Delta h_{f,298}^0$	Enthalpy of formation at 298K and 1atm (J/mol)
κ_I, κ_{III}	Rate coefficient of reaction (I) and (III)
	(mol $Pa^{0.5}/kg cat/sec$)

κ_{II}	Rate coefficient of reaction (II)
	(mol/kg cat/sec/Pa)
$\dot{\eta}$	Molar flow rate (moles/sec)
σ	Stefan-Boltzmann constant (= 5.67e-8 (W/m^2K^4)

Subscripts

a	Anode control volume
air	Air supply
asp	Air supply pipe
с	Cathode control volume
cat	Catalyst
cb	Combustor control volume
cond	Conductive heat transfer
conv	convective heat transfer
des	Desired
elec	Electrolyte
ex	Exit condition of control volume
g	Gas control volume
in	Inlet condition of control volume
j	Values of 1 through 7 represent the species
	CH_4 , CO , CO_2 , H_2 , H_2O , N_2 , and O_2 respectively
pr	Preheater control volume
r	Reformate control volume
rad	Radiation
S	Solid volume
sep	Seperator volume
SS	Steady-state

CHAPTER 2

INTRODUCTION

Among different fuel cell technologies, Solid Oxide Fuel Cell (SOFC) systems have generated considerable interest in recent years. Fuel flexibility and tolerance to impurities are attractive attributes of SOFC systems. Their high operating temperatures (800° to 1000°C) are conducive to internal reforming of fuel. The exhaust gases are excellent means for sustaining on-board fuel reforming processes. SOFC systems are not only tolerant to carbon monoxide but can also use it as a fuel. They also serve as excellent combined heat and power (CHP) systems. However, the high operating temperatures have precluded automotive applications of SOFC systems due to the associated thermal stresses, material failure and significant start-up times.

In this thesis we perform model-based analysis of a steam reformer based SOFC system with anode recirculation and methane as fuel. Two types of SOFCs have typically been considered in the literature, namely the planar and the tubular configurations. Mathematical models of the planar version appear in [3], [5], [14] and [19], and those of the tubular type appear in [8], [10], [12], [13], [16] and [21]. We develop a lumped control-oriented model of a tubular SOFC system. The model serves as a powerful simulation tool in absence of an SOFC hardware. It enables risk-free experimentation and forms the basis of the analytical development presented in this thesis.

The model captures heat and mass transfer, chemical kinetics and electro-chemical phenomena of the system. The chemical kinetics of reforming are based on experimental results and observations presented in [2] and [20]. The model has similarities with the ones presented in [10] and [16].

The transient response of a fuel cell system directly impacts its load following capability. Hence, characterization of the transients will be helpful in control design for the cumulative system. One of the earlier works on transient analysis of SOFC systems appears in [1], where the author applied dimensional analysis to characterize voltage transients due to load changes. Transient simulations of an SOFC-Gas Turbine hybrid system with anode recirculation is presented in [6]. In [17], the authors simulate voltage response of a stand-alone SOFC plant to step changes in load and fuel. In [15], the authors study the detrimental effects of load transients due to differences in the response times of the SOFC, power electronics, and balance-of-plant components. To mitigate these effects, they further investigate the effectiveness of energy buffering devices such as battery.

In this thesis we specifically derive analytical expressions that characterize the transient and steady-state behavior of fuel utilization (U) and steam-to-carbon balance (STCB) of an SOFC system. To the best of our knowledge, such results have not appeared in the literature. Utilization is a critical variable in an SOFC system that indicates the ratio of hydrogen consumption to the net available hydrogen in the anode. While high utilization implies high efficiency, very high utilization leads to reduced partial pressure of hydrogen in the fuel cell anode which can cause irreversible damages due to anode oxidation [16]. Typically, 85% is the target utilization for SOFC systems. Steam-to-carbon ratio (STCR) is another critical variable in steam-reformer based SOFC systems. STCR indicates the availability of steam for fuel reforming at the inlet of the reformer. A minimum STCR, that allows stoichiometric combination of steam and carbon, is necessary. For steam reforming of methane, a stoichiometric

mixture has an STCR value of approximately 2. A mixture lean in steam causes catalyst deactivation through carbon deposition on the catalyst surfaces, [6], and therefore must be prevented. In this thesis, instead of STCR, we analyze the transient response of steam-to-carbon balance (STCB) due to its preferred mathematical form. This is justified since a positive STCB automatically implies a mixture rich in steam and hence results in a favorable value of STCR. Both U and STCR/STCB experience dramatic transients due to step changes in load and our study focuses on predicting these behaviors. These transients arise from the mass transfer and chemical kinetics phenomena. Temperature variation in SOFC systems occur at a significantly slower rate and simulations indicate that a quasi-steady thermal behavior can be assumed with minimal loss of accuracy.

This thesis is organized as follows: In section 3, we first describe the SOFC system under consideration. We then develop the mathematical model of the SOFC system in three subsections. We first present the equations for fundamental gas and solid control volumes. The following subsections elaborate on the steam reformer and SOFC system models respectively, with emphasis on the mass transfer phenomena and chemical kinetics. An open-loop simulation of the system model is provided next. Transient characterization of utilization U and STCB/STCR, due to load changes, are carried out in sections 4 and 5 respectively, and simulation results are provided. Based on these results, a steady-state fuel optimization problem is addressed and a minimum fuel operating condition is derived in section 6. Concluding remarks are provided in section 7.

CHAPTER 3

SOFC MODEL DEVELOPMENT

3.1 SOFC System Description

In this section, we describe a steam reformer based tubular SOFC system which forms the basis of our analysis. A schematic diagram of the SOFC system is presented in Fig.3.1. The system consists of three main components, namely,

- Steam reformer
- Solid oxide fuel cell
- Combustor

The steam reformer produces a hydrogen rich gas-mixture by reforming hydrocarbon fuels. The solid oxide fuel cell produces electricity from electro-chemical combination of hydrogen in the anode and oxygen in the cathode. The combustor oxidizes unused fuel to generate heat. For our system, methane is chosen as the fuel. The hydrogen-rich gas-mixture produced by the reformer is supplied to the anode of the fuel cell. Electro-chemical reactions occuring at the anode, due to current draw, results in a steam-rich gas-mixture at the anode exit. A fraction k of the anode efflux is recirculated into the reformer through a mixing chamber where fuel is added.



Figure 3.1. Schematic of the SOFC system

Steam reforming, which is an endothermic process, occurs as the fuel and steam mixture flows through the reformer catalyst bed. We have considered a Nickel-Alumina catalyst bed in our analysis. The energy required to sustain this endothermic process is supplied from two sources, namely, the combustor exhaust gas that is passed through the reformer, and the aforementioned recirculated flow. The recirculated flow is routed through the reformer before being injected into the mixing chamber, as shown in Fig.3.1. In addition to oxidizing the unused fuel, the combustor also serves to preheat the incoming air flow. The tubular construction of individual cells causes the preheated air to first enter the cell through the air supply tube and then reverse its direction to enter the cathode chamber. The cathode air serves as the source of oxygen for the fuel cell.

3.2 Fundamental Models

The thermal characteristics of the system is modeled using solid volume and gas control volume models described below.

3.2.1 Solid Volume Model

The rate of change of temperature of a solid volume is dependant on the net rate of heat transfer into the volume through the following fundamental energy balance equation:

$$M_s C_s \dot{T}_s = \sum \dot{Q}_s \tag{3.1}$$

The conductive and the convective heat transfers into a solid volume is explained through the following schematic diagram. The conductive heat transfer between



individual solid volumes is modeled using the Fourier's law of conduction. In Fig.3.2, the conductive heat transfer from the $(m + 1)^{th}$ element into the m^{th} element is

$$\dot{Q}_{cond} = \frac{A_{cond} k_s \left(T_{s,m+1} - T_{s,m}\right)}{L_{cond}}$$
(3.2)

where, A_{cond} and L_{cond} are the cross-sectional area and length respectively for conductive heat transfer. Newton's law of cooling is used for modeling convective heat transfer between solid and gaseous control volumes. In Fig.3.2, the convective heat transfer within the m^{th} element from the gas control volume into the solid volume can be expressed as

$$\dot{Q}_{conv} = A_{conv} \mathcal{H} \left(T_{g,m} - T_{s,m} \right)$$
(3.3)

where A_{conv} is the area of convective heat transfer.

3.2.2 Gas Control Volume Model

The gas control volume model consists of energy and mass balance equations. Additionally, it captures the reaction kinetics arising from reforming of fuel and electrochemical reactions. The energy balance equation for a gaseous control volume is

$$N_g C_v \dot{T}_g = \dot{\eta}_{in} h_{in} - \dot{\eta}_{ex} h_{ex} + \sum \dot{Q}_g - \dot{W}_{net}$$
(3.4)

The mass balance equation for individual species is constructed as follows,

$$N_g \dot{\mathcal{X}}_{j,g} = \dot{\eta}_{in} \mathcal{X}_{j,in} - \dot{\eta}_{ex} \mathcal{X}_{j,g} + \mathcal{R}_{j,g}, \quad j = 1, 2, \cdots, 7$$
(3.5)

where specific values of subscripts $j, j = 1, 2, \dots, 7$, correspond to the species CH_4 , CO, CO_2, H_2, H_2O, N_2 , and O_2 respectively, as described in the nomenclature. From Eq.(3.5), we additionally have

$$\sum_{j=1}^{7} \mathcal{X}_{j,in} = \sum_{j=1}^{7} \mathcal{X}_{j,g} = 1 \implies \sum_{j=1}^{7} \dot{\mathcal{X}}_{j,g} = 0 \implies \dot{\eta}_{ex} = \dot{\eta}_{in} + \sum_{j=1}^{7} \mathcal{R}_{j,g}$$
(3.6)

From Eqs.(3.4) and (3.5) it is evident that, in our formulation, the states of the gaseous control volume are T_g and $\mathcal{X}_{j,g}$, $j = 1, 2, \dots, 7$. Flow is assumed to be governed by a nominal pressure drop across each module, [16], and hence pressure is not treated as a state variable. The gas mixture is assumed to satisfy ideal gas laws and hence N_g in Eqs.(3.4) and (3.5) is related to P_g and T_g through the equation $N_g = P_g V_g / R_u T_g$. In Eq.(3.4), C_v , h_{in} , and h_{ex} are related to the state variables through the following general equations:

$$C_{v}(T) = \sum_{j=1}^{7} \mathcal{X}_{j} C_{p,j}(T) - R_{u},$$

$$C_{p,j}(T)/R_{u} = a_{j} + b_{j}T + c_{j}T^{2} + d_{j}T^{3} + e_{j}T^{4},$$

$$h = h(T) = \sum_{j=1}^{7} \mathcal{X}_{j} \left(\int_{298}^{T} C_{p,j}(T) \, dT + \Delta h_{f,298}^{0} \right)$$
(3.7)

where the coefficients a_j , b_j , c_j , d_j , e_j , are given in [18]. The inlet and exite enthalpies, h_{in} and h_{ex} , are computed as $h_{in} = h(T_{in})$ and $h_{ex} = h(T_{ex})$. In the following two sections, details of the reformer and the fuel cell model are presented.

3.3 Reformer Model

In this section, we describe the model of a tubular steam reformer. The integrated steam reformer provides a hydrogen-rich gas-mixture to the fuel cell anode. A schematic diagram of the tubular steam reformer is shown in Fig.3.3. In sections 3.3.1 and 3.3.2, we present the details of a lumped steam reformer model. In section 3.3.3, we present an axially discretized version of this model.

3.3.1 Reformer Heat Transfer Model



Figure 3.3. Schematic of a tubular steam reformer

The steam reformer is modeled using three gas control volumes and one solid volume.

The exhaust, steam and reformate flows are modeled using gas control volumes and the catalyst bed is modeled as a solid volume. Three convective heat transfer phenomena, \dot{Q}_{conv1} , \dot{Q}_{conv2} , \dot{Q}_{conv3} , are captured in the model as shown in Fig.3.4. \dot{Q}_{conv1} is the convective heat transfer between exhaust gases and the catalyst bed. Similarly, \dot{Q}_{conv2} is the convective heat transfer between the recirculated flow section and the catalyst bed and \dot{Q}_{conv3} is the convective heat transfer between the reformate and the catalyst bed.



Figure 3.4. Convective heat transfer in a reformer model

The convective heat transfers between the annular catalyst bed and the exhaust flow and the recirculated flow are modeled using Eq.(3.3). Here, the convection coefficients \mathcal{H} are calculated using

$$\mathcal{H} = \frac{N u_D \, k_f}{D_H} \tag{3.8}$$

From [9] and Fig.3.4, the covective heat transfer area A_{conv} and the hydraulic diamter D_H for the catalyst bed to exhaust heat transfer are derived as

$$A_{conv} = 2\pi r_{r2}L_r, \qquad D_H = 2\left(r_{r3} - r_{r2}\right) \tag{3.9}$$

and those for the heat transfer between the catalyst bed and the recirculated flow are

$$A_{conv} = 2\pi r_{r1} L_r, \qquad D_H = 2r_{r1} \tag{3.10}$$

where r_{r1} and r_{r2} are the inner and outer diameters respectively of the catalyst bed, r_{r3} is the diameter of the cylindrical exhaust can and L_r is the reformer length. The catalyst bed to reformate convective heat transfer is modeled using Eq.(3.3). The corresponding convection coefficient is calculated using the following formula to account for geometric contour variations in the porous catalytic bed:

$$\mathcal{H} = \frac{2.06 Re_L Re_D^{-0.575} k_f}{\epsilon L_r P r^{-1/3}}$$
(3.11)

The Reynold's number Re_D is defined with respect to the catalyst ring equivalent diameter d_p , and is given by

$$Re_D = \frac{\mathcal{V} \, d_p}{\nu} \tag{3.12}$$

 Re_L is defined with respect to the length of the catalyst ring L_{cat} , and is given by

$$Re_L = \frac{\mathcal{V}L_{cat}}{\nu} \tag{3.13}$$

In Eqs.(3.12) and (3.13), the empty channel velocity \mathcal{V} is computed as

$$\mathcal{V} = \frac{\dot{N}_O V_r}{N_r \pi (r_{r2}^2 - r_{r1}^2)} = \frac{\dot{N}_O L_r}{N_r}$$
(3.14)

In Eqs.(3.12) and (3.13), the kinematic viscosity ν is computed as

$$\nu = \sum_{j=1}^{7} \mathcal{X}_{j} \nu_{j}(T_{g})$$
(3.15)

Similarly, the heat conduction coefficient k_f in Eqs.(3.11) and (3.8) is computed using

$$k_f = \sum_{j=1}^{7} \mathcal{X}_j \, k_{f,j}(T_g) \tag{3.16}$$

The prandtl number Pr is assumed to be a constant with an approximate value of 0.7.

3.3.2 Reformer Mass Transfer and Chemical Kinetics

In this section, we derive the mass transfer equations for the reformate control volume. The three main reactions that simultaneously occur during steam reforming of methane are, [10], [20]:

(I)
$$CH_4 + H_2O \leftrightarrow CO + 3H_2$$

(II) $CO + H_2O \leftrightarrow CO_2 + H_2$ (3.17)
(III) $CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$

From Fig.3.1, the mass balance equations for CH_4 , CO, CO_2 , H_2 and H_2O can be written using Eq.(3.5) as follows:

$$N_{r}\dot{\mathcal{X}}_{1,r} = k\dot{N}_{o}\mathcal{X}_{1,a} - \dot{N}_{in}\mathcal{X}_{1,r} + \mathcal{R}_{1,r} + \dot{N}_{f}$$

$$N_{r}\dot{\mathcal{X}}_{2,r} = k\dot{N}_{o}\mathcal{X}_{2,a} - \dot{N}_{in}\mathcal{X}_{2,r} + \mathcal{R}_{2,r}$$

$$N_{r}\dot{\mathcal{X}}_{3,r} = k\dot{N}_{o}\mathcal{X}_{3,a} - \dot{N}_{in}\mathcal{X}_{3,r} + \mathcal{R}_{3,r}$$

$$N_{r}\dot{\mathcal{X}}_{4,r} = k\dot{N}_{o}\mathcal{X}_{4,a} - \dot{N}_{in}\mathcal{X}_{4,r} + \mathcal{R}_{4,r}$$

$$N_{r}\dot{\mathcal{X}}_{5,r} = k\dot{N}_{o}\mathcal{X}_{5,a} - \dot{N}_{in}\mathcal{X}_{5,r} + \mathcal{R}_{5,r}$$
(3.18)

where $N_r = P_r V_r / R_u T_r$. Note that the reformer inlet and exit flows shown in Fig.3.1 do not contain O_2 and N_2 . Hence $\mathcal{X}_{6,r} = \mathcal{X}_{7,r} = 0$. From Eq.(3.17), we express $\mathcal{R}_{j,r}$, $j = 1, 2, \dots, 5$, in terms of the reaction rates r_I , r_{II} and r_{III} as follows

$$\mathbf{R}_{r} = \mathbf{G} \mathbf{r}, \ \mathbf{R}_{r} = \begin{bmatrix} \mathcal{R}_{1,r} \\ \mathcal{R}_{2,r} \\ \mathcal{R}_{3,r} \\ \mathcal{R}_{4,r} \\ \mathcal{R}_{5,r} \end{bmatrix}, \ \mathbf{r} = \begin{bmatrix} r_{I} \\ r_{II} \\ r_{III} \end{bmatrix}, \ \mathbf{G} = \begin{bmatrix} -1 & 0 & -1 \\ 1 & -1 & 0 \\ 0 & 1 & 1 \\ 3 & 1 & 4 \\ -1 & -1 & -2 \end{bmatrix}$$
(3.19)

Since **G** has a rank of 2, therefore there are only two independent reaction rates among $\mathcal{R}_{j,r}$, $j = 1, 2, \dots, 5$. Considering the rate of formation of CH_4 and CO in the reformer to be independent variables, we can write

$$\mathcal{R}_{3,r} = -\mathcal{R}_{1,r} - \mathcal{R}_{2,r}$$

$$\mathcal{R}_{4,r} = -4\mathcal{R}_{1,r} - \mathcal{R}_{2,r}$$

$$\mathcal{R}_{5,r} = 2\mathcal{R}_{1,r} + \mathcal{R}_{2,r}$$
(3.20)

and rewrite Eq.(3.18) as follows:

$$N_{r}\dot{\mathcal{X}}_{1,r} = k\dot{N}_{o}\mathcal{X}_{1,a} - \dot{N}_{in}\mathcal{X}_{1,r} + \mathcal{R}_{1,r} + \dot{N}_{f}$$

$$N_{r}\dot{\mathcal{X}}_{2,r} = k\dot{N}_{o}\mathcal{X}_{2,a} - \dot{N}_{in}\mathcal{X}_{2,r} + \mathcal{R}_{2,r}$$

$$N_{r}\dot{\mathcal{X}}_{3,r} = k\dot{N}_{o}\mathcal{X}_{3,a} - \dot{N}_{in}\mathcal{X}_{3,r} - \mathcal{R}_{1,r} - \mathcal{R}_{2,r}$$

$$N_{r}\dot{\mathcal{X}}_{4,r} = k\dot{N}_{o}\mathcal{X}_{4,a} - \dot{N}_{in}\mathcal{X}_{4,r} - 4\mathcal{R}_{1,r} - \mathcal{R}_{2,r}$$

$$N_{r}\dot{\mathcal{X}}_{5,r} = k\dot{N}_{o}\mathcal{X}_{5,a} - \dot{N}_{in}\mathcal{X}_{5,r} + 2\mathcal{R}_{1,r} + \mathcal{R}_{2,r}$$
(3.21)

From Eqs.(3.6) and (3.21) we deduce

$$\dot{N}_{in} = k\dot{N}_o + \dot{N}_f + \sum_{j=1}^7 \mathcal{R}_{j,r} \quad \Rightarrow \quad \dot{N}_{in} = k\dot{N}_o + \dot{N}_f - 2\mathcal{R}_{1,r}$$
(3.22)

The mathematical functions representing the reaction rates r_I , r_{II} and r_{III} are provided in the Appendix. For the steam and exhaust control volumes which are non-reactive, the corresponding equations can be derived using Eq.(3.5) by setting $\mathcal{R}_{j,g} = 0, j = 1, 2, \cdots, 7$.

3.3.3 One Dimensional Discretized Reformer Model

The reformer model presented in sections 3.3.1 and 3.3.2 can be extended to develop a one dimensional discretized model. Since our objective is system characterization leading to control development, we refrain from modeling spatial dependence of the various physical phenomena. Instead, we limit our focus to axial variations only. A schematic diagram of a discretized reformer model is shown in Fig.3.5. The gas control volume energy balance equations can be derived using the basic structure given in



• Heat transfer into a solid volume

Figure 3.5. Schematic of a one dimensional discretized reformer model Eq.(3.4) and hence are not repeated here. The corresponding convective heat transfer coefficients can be derived using Eqs.(3.8) through (3.16). The corresponding areas of convective heat transfer are modified to Eqs.(3.9), (3.10) and (3.11).

$$\bar{A}_{conv} = \frac{A_{conv}}{u_r} \tag{3.23}$$

to account for the model discretization. The mass balance equations for each gaseous control volume can be derived from Eq.(3.5). For the reformate control volume, the reaction rates can be modeled using the development in section 3.3.2 and Appendix A. In the discretized model, the heat conduction in the catalytic bed between neighboring elements must be modeled. The overall heat transfer equation for the m^{th} catalytic

bed element is derived from Eqs.(3.1), (3.2) and (3.3) and Fig.3.5 as follows:

$$M_{s,m}C_{s,m}\dot{T}_{s,m} = \sum \dot{Q}_{conv}^{(m)} + \sum \dot{Q}_{cond}$$

= $\sum \dot{Q}_{conv}^{(m)} + \frac{A_{cond}k_s(T_{s,m+1} - T_{s,m})}{L_r/u_r} + \frac{A_{cond}k_s(T_{s,m-1} - T_{s,m})}{L_r/u_r}$

where, $\sum \dot{Q}_{conv}^{(m)} = \dot{Q}_{conv,1}^{(m)} + \dot{Q}_{conv,2}^{(m)} + \dot{Q}_{conv,3}^{(m)}$ and A_{cond} is derived from Fig.(3.3) as $A_{cond} = \pi (r_{r2}^2 - r_{r1}^2)$. The conductive heat transfer coefficient k_s is computed as follows [7]:

$$k_s = k_{eo} + k_{cv} + k_{rad} \tag{3.24}$$

In Eq.(3.24), k_{eo} is the stagnant bed conductivity given by

$$k_{eo} = k_f \left[1.814 \left(\frac{k_{cat}}{k_{cat} - k_f} \right)^2 \left(log \left(\frac{k_{cat}}{k_f} \right) - \frac{k_{cat} - k_f}{k_{cat}} \right) + 0.0931 \right]$$
(3.25)

where k_{cat} is the catalyst bed conduction coefficient assumed to be a constant and k_f is the fluid conduction coefficient computed as in Eq.(3.16). The convection coefficient k_{cv} is given by

$$k_{cv} = 0.75 k_f Pr Re_D \tag{3.26}$$

where the prandtl number Pr is assumed to be a constant and k_f and Re_D are computed using the formulaes in Eqs.(3.16) and (3.12). and k_{rad} is the radiation coefficient given by

$$k_{rad} = \frac{1 - \alpha}{\frac{1}{k_{cat}} + \frac{1}{k_{ro}}} + \alpha \, k_{ro} \qquad k_{ro} = \frac{0.229 \, E \, \alpha \, d_p \, T_{cat}^3}{10^6} \tag{3.27}$$

The definition of each term in Eq.(3.27) is given in the nomenclature.

3.4 SOFC Model

In sections 3.4.1 to 3.4.3, we present a lumped model of a unit tubular solid oxide fuel cell. The fuel cell system consists of a number of such fuel cell units connected electrically in series. In section 3.4.4, we present a discretized version of this model. A schematic diagram of a unit tubular fuel cell is shown in Fig.3.6. The hydrogen-rich reformate gas-mixture enters the anode control volume from left. It is separated from the cathode control volume by the electrolyte which serves as a conductor of O^{2-} ions at temperatures above 800°C. Air is supplied to the cathode control volume via the air feed tube (air supply pipe) as shown in Fig.3.6. The extended travel path of air in the fuel cell is utilized to remove heat generated by the fuel cell from electro chemical conversion of hydrogen to steam.



Figure 3.6. Schematic diagram of tubular SOFC unit

3.4.1 SOFC Heat Transfer Model

A tubular unit is shown in Fig.3.6. The anode, cathode and air flows are modeled as gas control volumes and the air feed tube and electrolyte are modeled as solid volumes. Four convective heat transfer phenomena \dot{Q}_{conv1} through \dot{Q}_{conv4} and one radiative heat transfer \dot{Q}_{rad} are captured in the model, as shown in Fig.3.7. The following list gives a description of the different modes of heat transfer mentioned above:

- \dot{Q}_{conv1} : Convective heat transfer between anode and electrolyte
- \dot{Q}_{conv2} : Convective heat transfer between cathode and electrolyte
- \dot{Q}_{conv3} : Convective heat transfer between cathode and air supply tube
- \dot{Q}_{conv4} : Convective heat transfer between air flow and air supply tube
- \dot{Q}_{rad} : Radiative heat transfer between air supply tube and electrolyte



Figure 3.7. Convective and radiative heat transfers in a unit SOFC model

The convective heat transfers \dot{Q}_{conv1} through \dot{Q}_{conv4} are modeled using Eq.(3.3). For each case, the heat transfer coefficient \mathcal{H} is assumed to be constant. The exposed area for convective heat transfers are computed as follows:-

$$Q_{conv1}: \quad A_{conv1} = 2\pi r_{fc2,o} L_{fc}$$

$$\dot{Q}_{conv2}: \quad A_{conv2} = 2\pi r_{fc2,i} L_{fc}$$

$$\dot{Q}_{conv3}: \quad A_{conv3} = 2\pi r_{fc1,o} L_{fc}$$

$$\dot{Q}_{conv4}: \quad A_{conv4} = 2\pi r_{fc1,i} L_{fc}$$
(3.28)

The radiative heat transfer \dot{Q}_{rad} and the corresponding exposed area for heat transfer is computed as follows [9]:

$$\dot{Q}_{rad} = \sigma A_{rad} L_{fc} \left(T_{asp}^4 - T_{elec}^4 \right) \left/ \left(\frac{1}{E_{asp}} + \frac{1 - E_{elec}}{E_{elec}} \left(\frac{r_{fc1,o}}{r_{fc2,i}} \right) \right), \quad A_{rad} = \pi r_{fc1,O}^2$$

$$(3.29)$$

3.4.2 Cell Voltage Model

The cell voltage is modeled by subtracting the activation, ohmic, and concentration potential from the open circuit voltage, i.e. Nernst potential. The effective cell voltage can therefore be expressed as:

$$V_{cell} = V_{Nernst} - V_{Act} - V_{Conc} - V_{Ohm}$$

$$(3.30)$$

The Nernst potential is computed as

$$V_{Nernst} = \frac{\Delta G_T^{\circ}}{nF} + \frac{R_u T_a}{nF} ln \left[\frac{p_{H_2} p_{O_2}^{1/2}}{p_{H_2 O}} \right]$$
(3.31)

Where ΔG_T° is the Gibb's free energy for the reaction

$$H_2 + \frac{1}{2}O_2 \to H_2O$$
 (3.32)

computed at the anode temperature T_a using Eqs.(8) and (9)given in appendix A. Noting that $p_{H_2} = P_a \mathcal{X}_{4,a}$, $p_{O_2} = P_c \mathcal{X}_{7,c}$ and $p_{H_2O} = P_a \mathcal{X}_{5,a}$, the Nernst potential in Eq.(3.31) can be expressed as

$$V_{Nernst} = \frac{\Delta G_T^{\circ}}{nF} + \frac{R_u T_a}{nF} ln \left[\frac{\mathcal{X}_{4,a} \mathcal{X}_{7,c}^{1/2}}{\mathcal{X}_{5,a}} P_c^{1/2} \right]$$
(3.33)

The activation polarization loss V_{Act} is given by [16]

$$V_{Act} = \frac{R_u T_c}{nF} ln\left(\frac{i/A_{cell}}{i_0(T_c)}\right), \qquad A_{cell} = 2\pi r_{fc2,o} L_{fc}$$
(3.34)

Where i_0 is the exchange current density assumed to be a constant. The concentration potential V_{conc} is computed using

$$V_{Conc} = -\frac{R_u T_a}{nF} ln \left(1 - \frac{i/A_{cell}}{i_{lim}} \right)$$
(3.35)

where i_{lim} is the fuel cell limiting current density. The ohmic voltage loss V_{Ohm} is given by

$$V_{Ohm} = iR_{int}A_{cell} \tag{3.36}$$

where R_{int} is the internal resistance of each cell and is assumed to be a constant [16]. The heat generated from the electrochemical combination of hydrogen and oxygen is expressed as the difference between the enthalpy of formation of water and the power generated. The model assumes this heat to be generated in the electrolyte solid and is given by the expression

$$\dot{Q}_{elec} = -\left(h_f(T_{elec})\frac{i}{nF} - iV_{cell}\right)$$
(3.37)

where $h_f(T_{elec}) = \Delta h_{f,298}^0 + h(T_{elec}) - h(298)$, presents the heat of formation of steam at the temperature of the electrolyte solid.

3.4.3 Fuel Cell Mass Transfer and Chemical Kinetics

In this section, we derive the mass transfer equations for the anode and cathode control volumes. For the air control volume, the corresponding equations can be derived using Eq.(3.5) by setting $\mathcal{R}_{j,g} = 0, j = 1, 2, \cdots, 7$. The three main reactions that simultaneously occur during steam reforming of methane are, [10], [20]: <u>Anode control volume</u>: The following chemical and electro-chemical reactions occur simultaneously in the anode control volume:

(I)
$$CH_4 + H_2O \leftrightarrow CO + 3H_2$$

(II) $CO + H_2O \leftrightarrow CO_2 + H_2$
(III) $CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$
(IV) $H_2 + O^{2-} \rightarrow H_2O + 2e$
(3.38)

Steam reforming, represented by reactions I, II and III, occur in the anode due to high temperatures and the presence of nickel catalyst. The primary electrochemical process is steam generation from H_2 , described by reaction IV. Simultaneous electrochemical conversion of CO to CO_2 in the anode is also possible. However, this electro-chemical reaction is ignored since its reaction rate is much slower in presence of reactions II and IV, as indicated in [4] and references therein. From Fig.3.1 and Eq.(3.5), the mass balance equations for CH_4 , CO, CO_2 , H_2 and H_2O can be written as

$$N_{a}\dot{\mathcal{X}}_{1,a} = -\dot{N}_{o}\mathcal{X}_{1,a} + \dot{N}_{in}\mathcal{X}_{1,r} + \mathcal{R}_{1,a}$$

$$N_{a}\dot{\mathcal{X}}_{2,a} = -\dot{N}_{o}\mathcal{X}_{2,a} + \dot{N}_{in}\mathcal{X}_{2,r} + \mathcal{R}_{2,a}$$

$$N_{a}\dot{\mathcal{X}}_{3,a} = -\dot{N}_{o}\mathcal{X}_{3,a} + \dot{N}_{in}\mathcal{X}_{3,r} + \mathcal{R}_{3,a}$$

$$N_{a}\dot{\mathcal{X}}_{4,a} = -\dot{N}_{o}\mathcal{X}_{4,a} + \dot{N}_{in}\mathcal{X}_{4,r} + \mathcal{R}_{4,a} - r_{e}$$

$$N_{a}\dot{\mathcal{X}}_{5,a} = -\dot{N}_{o}\mathcal{X}_{5,a} + \dot{N}_{in}\mathcal{X}_{5,r} + \mathcal{R}_{5,a} + r_{e}$$
(3.39)

where $N_a = P_a V_a / R_u T_a$ and r_e is the rate of electrochemical reaction given by

$$r_e = \frac{i\mathcal{N}_{cell}}{nF} \tag{3.40}$$

Since current *i* can be measured, the rate of electrochemical reaction r_e is known. As with the reformate control volume, the anode inlet and exit flows do not contain O_2 and N_2 . Therefore, $\mathcal{X}_{6,a} = \mathcal{X}_{7,a} = 0$. From Eq.(3.38), we express $\mathcal{R}_{j,a}$, $j = 1, 2, \dots, 5$, in terms of the reaction rates r_I , r_{II} and r_{III} as follows

$$\mathbf{R}_a = \mathbf{G} \,\mathbf{r} + r_e \begin{bmatrix} 0 & 0 & 0 & -1 & 1 \end{bmatrix}^T \tag{3.41}$$

where $\mathbf{R}_a = [\mathcal{R}_{1,a} \ \mathcal{R}_{2,a} \ \mathcal{R}_{3,a} \ \mathcal{R}_{4,a} \ \mathcal{R}_{5,a}]^T$, and **G** and **r** are given in Eq.(3.19). Since **G** has a rank of 2 and r_e is known, therefore there are only two independent reaction

rates among $\mathcal{R}_{j,a}$, $j = 1, 2, \dots, 5$. Considering $\mathcal{R}_{1,a}$ and $\mathcal{R}_{2,a}$ to be independent variables, we can write

$$\mathcal{R}_{3,a} = -\mathcal{R}_{1,a} - \mathcal{R}_{2,a},
\mathcal{R}_{4,a} = -4\mathcal{R}_{1,a} - \mathcal{R}_{2,a} - r_e,
\mathcal{R}_{5,a} = 2\mathcal{R}_{1,a} + \mathcal{R}_{2,a} + r_e$$
(3.42)

and rewrite Eq.(3.39) as

$$N_{a}\dot{\mathcal{X}}_{1,a} = -\dot{N}_{o}\mathcal{X}_{1,a} + \dot{N}_{in}\mathcal{X}_{1,r} + \mathcal{R}_{1,a}$$

$$N_{a}\dot{\mathcal{X}}_{2,a} = -\dot{N}_{o}\mathcal{X}_{2,a} + \dot{N}_{in}\mathcal{X}_{2,r} + \mathcal{R}_{2,a}$$

$$N_{a}\dot{\mathcal{X}}_{3,a} = -\dot{N}_{o}\mathcal{X}_{3,a} + \dot{N}_{in}\mathcal{X}_{3,r} - \mathcal{R}_{1,a} - \mathcal{R}_{2,a}$$

$$N_{a}\dot{\mathcal{X}}_{4,a} = -\dot{N}_{o}\mathcal{X}_{4,a} + \dot{N}_{in}\mathcal{X}_{4,r} - 4\mathcal{R}_{1,a} - \mathcal{R}_{2,a} - r_{e}$$

$$N_{a}\dot{\mathcal{X}}_{5,a} = -\dot{N}_{o}\mathcal{X}_{5,a} + \dot{N}_{in}\mathcal{X}_{5,r} + 2\mathcal{R}_{1,a} + \mathcal{R}_{2,a} + r_{e}$$
(3.43)

From Eqs.(3.6) and (3.43) we deduce that

$$\dot{N}_o = \dot{N}_{in} + \sum_{j=1}^{7} \mathcal{R}_{j,a} \quad \Rightarrow \quad \dot{N}_o = \dot{N}_{in} - 2\mathcal{R}_{1,a} \tag{3.44}$$

The models of internal reforming reaction rates r_I , r_{II} and r_{III} are shown in Appendix A.

<u>Cathode control volume</u>: Ionization of O_2 in the cathode control volume occurs through the reaction

$$\frac{1}{2}O_2 + 2e \to O^{2-} \tag{3.45}$$

with the reaction rate as given in Eq.(3.40). Considering the mole fractions of N_2 and O_2 in air to be 0.79 and 0.21 respectively, the mass balance equations of the cathode control volume can be written from Eqs.(3.40) and (3.45) as follows:

$$N_{c}\dot{\mathcal{X}}_{6,c} = 0.79\dot{N}_{air} - (\dot{N}_{air} - 0.5r_{e})\mathcal{X}_{6,c}$$

$$N_{c}\dot{\mathcal{X}}_{7,c} = 0.21\dot{N}_{air} - (\dot{N}_{air} - 0.5r_{e})\mathcal{X}_{7,c} - 0.5r_{e} \qquad (3.46)$$

$$\mathcal{X}_{j,c} = 0, \quad j = 1, 2, \cdots, 5$$

3.4.4 One Dimensional Discretized Fuel cell Model

The lumped fuel cell model presented in sections 3.4.1 through 3.4.3 can be extended to develop a one dimensional discretized model. As in section 3.3.3, we refrain from modeling spatial dependence of the various physical phenomena and we limit our focus on the axial variations only.



Figure 3.8. Schematic diagram of one dimensional discretized fuel cell model

A schematic diagram of a discretized fuel cell model is shown in Fig.3.8. The gas control volume energy balance equations can be derived using the basic structure given in Eq.(3.4) and hence are not repeated here. The areas of convective heat transfer given in Eq.(3.28) are modified to

$$\bar{A}_{conv1} = \frac{A_{conv1}}{u_{fc}}, \quad \bar{A}_{conv2} = \frac{A_{conv2}}{u_{fc}}, \quad \bar{A}_{conv3} = \frac{A_{conv3}}{u_{fc}}, \quad \bar{A}_{conv4} = \frac{A_{conv4}}{u_{fc}}$$
(3.47)

to account for model discretization. The mass balance equations for each gaseous control volume can be derived from Eq.(3.5). For the anode control volume, the reaction rates can be modeled using the development in section 3.4.3 and Appendix A. In the discretized model, the heat conduction between the neighboring elements of the electrolyte and the air supply tube must be modeled. For each elementary unit of the electrolyte and air supply pipe, in addition to the convective heat transfer, the radiative and conductive components must be accounted for. The radiative heat transfer between the m^{th} solid volume elements is deduced from Eq.(3.29) and Fig.3.8 as

$$\dot{Q}_{rad}^{(m)} = \sigma A_{rad} \frac{L_{fc}}{u_{fc}} \left(T_{asp,m}^4 - T_{elec,m}^4 \right) \left/ \left(\frac{1}{E_{asp}} + \frac{1 - E_{elec}}{E_{elec}} \left(\frac{r_{fc1,o}}{r_{fc2,i}} \right) \right), \quad A_{rad} = \pi r_{fc1,O}^2$$

$$(3.48)$$

The overall heat transfer equation for the m^{th} electrolyte element is desired from Eqs.(3.1),(3.2) and (3.48) as follows:

$$M_{elec,m}C_{elec,m}\dot{T}_{elec,m} = \sum \dot{Q}_{conv,elec}^{(m)} + \dot{Q}_{rad}^{(m)} + \sum \dot{Q}_{cond,elec}^{(m)}$$

$$= \sum \dot{Q}_{conv,elec}^{(m)} + \dot{Q}_{rad}^{(m)} + \cdots$$

$$\frac{A_{cond,elec}k_{elec} \left(T_{elec,m+1} - T_{elec,m}\right)}{L_{fc}/u_{fc}}$$

$$+ \frac{A_{cond,elec}k_{elec} \left(T_{elec,m-1} - T_{elec,m}\right)}{L_{fc}/u_{fc}}$$

where, $\sum \dot{Q}_{conv,elec}^{(m)} = \dot{Q}_{conv,1}^{(m)} + \dot{Q}_{conv,2}^{(m)}$, the cross-sectional area for conductive heat transfer in the electrolyte is given by $A_{cond,elec} = \pi (r_{fc2,O}^2 - r_{fc2,i}^2)$, and the conductive heat transfer coefficient k_{elec} is a constant. Similarly, the over all heat transfer

equation for the m^{th} air supply pipe element is given as

$$M_{asp,m}C_{asp,m}\dot{T}_{asp,m} = \sum \dot{Q}_{conv,asp}^{(m)} - \dot{Q}_{rad}^{(m)} + \sum \dot{Q}_{cond,asp}^{(m)}$$

$$= \sum \dot{Q}_{conv,asp}^{(m)} - \dot{Q}_{rad}^{(m)} + \cdots$$

$$\cdots \frac{A_{cond,asp}k_{asp} (T_{asp,m+1} - T_{asp,m})}{L_{fc}/u_{fc}}$$

$$+ \frac{A_{cond,asp}k_{asp} (T_{asp,m-1} - T_{asp,m})}{L_{fc}/u_{fc}}$$

where, $\sum \dot{Q}_{conv,asp}^{(m)} = \dot{Q}_{conv,3}^{(m)} + \dot{Q}_{conv,4}^{(m)}$, the cross-sectional area for conductive heat transfer in the air supply pipe is given by $A_{cond,asp} = \pi (r_{fc1,O}^2 - r_{fc1,i}^2)$ and the conductive heat transfer coefficient k_{asp} is a constant.

3.5 Gas mixing

The recirculated anode flow $k\dot{N}_O$ and the fuel flow \dot{N}_f are mixed and the mixture is pressurized in the gas mixture, shown in Fig.(3.1). The mixing and pressurization of the two fluid streams is achieved using an ejector or a recirculating pump [6], [11]. As with other component models, we consider a nominal pressure differential across the gas mixture and ignore the pressure dynamics in our model. The following energy conservation equation is implemented to model this component:

$$N_{mix}C_{v,mix}\dot{T}_{mix} = \dot{N}_f h_f(T_f) + k\dot{N}_O h_a(T_a) - (\dot{N}_f + k\dot{N}_O)h_{mix}(T_{mix})$$
(3.49)

with the enthalpy h computed as shown in Eq.(3.7) and the mole fractions of the mixture computed as

$$\mathcal{X}_{mix,j} = \frac{\dot{N}_f \mathcal{X}_{f,j} + k \dot{N}_O \mathcal{X}_{a,j}}{(\dot{N}_f + k \dot{N}_O)}, \quad j = 1, 2, ..., 5$$
(3.50)

3.6 Combustor Model

The combustor is modeled as a lumped unit with three control volumes, namely

- A mixing and combustion chamber where the anode and cathode exhaust gases combine followed by combustion of unused fuel. This is modeled as a gas control volume.
- An air preheater control volume which models the preheating of cathode air using the heat of combustion.
- A solid volume that acts as a separator and heat conductor between the gas mixture in the combustion chamber and the air control volume.

A schematic diagram of the combustor is given in Fig.3.9 The reactions that occur



Figure 3.9. Schematic diagram of combustor

in the combustion chamber are

(a)
$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O$$

(b) $CO + \frac{1}{2}O_2 \leftrightarrow CO_2$ (3.51)
(c) $H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O$

We assume that each of the combustible species, namely CH_4 , CO and H_2 , have the same selectivity for combustion. From Fig.3.9 and Eq.(3.51), we have the following

mass balance equations for the combustor control volume:-

$$N_{cb}\dot{\mathcal{X}}_{1,cb} = (1-k)\dot{N}_{O}\mathcal{X}_{1,a} - \dot{\eta}_{ex,cb}\mathcal{X}_{1,cb} + \mathcal{R}_{1,cb}$$

$$N_{cb}\dot{\mathcal{X}}_{2,cb} = (1-k)\dot{N}_{O}\mathcal{X}_{2,a} - \dot{\eta}_{ex,cb}\mathcal{X}_{2,cb} + \mathcal{R}_{2,cb}$$

$$N_{cb}\dot{\mathcal{X}}_{3,cb} = (1-k)\dot{N}_{O}\mathcal{X}_{3,a} - \dot{\eta}_{ex,cb}\mathcal{X}_{3,cb} + \mathcal{R}_{3,cb}$$

$$N_{cb}\dot{\mathcal{X}}_{4,cb} = (1-k)\dot{N}_{O}\mathcal{X}_{4,a} - \dot{\eta}_{ex,cb}\mathcal{X}_{4,cb} + \mathcal{R}_{4,cb}$$

$$N_{cb}\dot{\mathcal{X}}_{5,cb} = (1-k)\dot{N}_{O}\mathcal{X}_{5,a} - \dot{\eta}_{ex,cb}\mathcal{X}_{5,cb} + \mathcal{R}_{5,cb}$$

$$N_{cb}\dot{\mathcal{X}}_{6,cb} = (\dot{N}_{air} - 0.5r_{e})\mathcal{X}_{6,c} - \dot{\eta}_{ex,cb}\mathcal{X}_{6,cb} + \mathcal{R}_{6,cb}$$

$$N_{cb}\dot{\mathcal{X}}_{7,cb} = (\dot{N}_{air} - 0.5r_{e})\mathcal{X}_{7,c} - \dot{\eta}_{ex,cb}\mathcal{X}_{7,cb} + \mathcal{R}_{7,cb}$$
(3.52)

Where, $N_{cb} = P_{cb}V_{cb}/R_uT_{cb}$ From reactions (a), (b), (c) in Eq.(3.52), it is clear that one molecule of CH_4 , CO and H_2 require 2, 0.5 and 0.5 molecules of O_2 for complete combustion respectively. With uniform selectivity for combustion, the oxygen available will be proportionally distributed for each reaction. Since the flow rates of CH_4 , CO, and H_2 into the combustion chamber are $(1 - k)\dot{N}_O\mathcal{X}_{1,a}$, $(1 - k)\dot{N}_O\mathcal{X}_{2,a}$ and $(1 - k)\dot{N}_O\mathcal{X}_{4,a}$, from Eq.(3.52) we deduce that for complete combustion, the minimum oxygen molar flow rate is

$$mf_{O_2,des} = 2(1-k)\dot{N}_O\mathcal{X}_{1,a} + 0.5(1-k)\dot{N}_O\mathcal{X}_{2,a} + 0.5(1-k)\dot{N}_O\mathcal{X}_{4,a}$$
(3.53)

In the combustor model, we consider two scenarios, namely, a mixture deficient in oxygen and one with excess oxygen. For the former case, considering uniform selectivity of all combustion reactions and noting that the molar flow rate of O_2 at the

inlet of the combustion chamber is $(\dot{N}_{air} - 0.5 r_e) \mathcal{X}_{7,c}$, we have

$$\begin{aligned} \mathcal{R}_{1,cb} &= -\frac{(1-k)\dot{N}_{O}\mathcal{X}_{1,a}}{mf_{O_{2},des}} \cdot (\dot{N}_{air} - 0.5r_{e})\mathcal{X}_{7,c} \\ \mathcal{R}_{2,cb} &= -\frac{(1-k)N_{O}\mathcal{X}_{2,a}}{mf_{O_{2},des}} \cdot (\dot{N}_{air} - 0.5r_{e})\mathcal{X}_{7,c} \\ \mathcal{R}_{4,cb} &= -\frac{(1-k)N_{O}\mathcal{X}_{4,a}}{mf_{O_{2},des}} \cdot (\dot{N}_{air} - 0.5r_{e})\mathcal{X}_{7,c} \\ \mathcal{R}_{3,cb} &= -\mathcal{R}_{1,cb} - \mathcal{R}_{2,cb} \\ \mathcal{R}_{5,cb} &= -2\mathcal{R}_{1,cb} - \mathcal{R}_{4,cb} \\ \mathcal{R}_{6,cb} &= 0 \\ \mathcal{R}_{7,cb} &= -(\dot{N}_{air} - 0.5r_{e})\mathcal{X}_{7,c} \end{aligned}$$
(3.54)

with $mf_{O_2,des} < (\dot{N}_{air} - 0.5r_e)\mathcal{X}_{7,c}$. When the inlet combustion mixture contains excess oxygen, i.e.

$$(N_{air} - 0.5r_e)\mathcal{X}_{7,c} \ge mf_{O_2,des} \tag{3.55}$$

then we have the following reaction rates

$$\begin{aligned} \mathcal{R}_{1,cb} &= -(1-k)\dot{N}_{O}\mathcal{X}_{1,a} \\ \mathcal{R}_{2,cb} &= -(1-k)\dot{N}_{O}\mathcal{X}_{2,a} \\ \mathcal{R}_{3,cb} &= -\mathcal{R}_{1,cb} - \mathcal{R}_{2,cb} \\ \mathcal{R}_{4,cb} &= -(1-k)\dot{N}_{O}\mathcal{X}_{4,a} \\ \mathcal{R}_{5,cb} &= -2\mathcal{R}_{1,cb} - \mathcal{R}_{4,cb} \\ \mathcal{R}_{6,cb} &= 0 \\ \mathcal{R}_{7,cb} &= -mf_{O_2,des} = -[2(1-k)\dot{N}_{O}\mathcal{X}_{1,a} + 0.5(1-k)\dot{N}_{O}\mathcal{X}_{2,a} + 0.5\dot{N}_{O}\mathcal{X}_{4,a}] \end{aligned}$$
(3.56)

Further more, from Eq.(3.56), we have

$$\dot{\eta}_{ex} = (1-k)\dot{N}_O + (\dot{N}_{air} - 0.5r_e) + \sum_{j=1}^7 \mathcal{R}_{j,cb}$$
(3.57)

The thermal behaviour of the combustion chamber is modeled using Eq.(3.42) as follows:-

$$N_{cb}C_v \dot{T}_{cb} = \left[(1-k)\dot{N}_O + (\dot{N}_{air} - 0.5r_e) \right] h_{in,cb} - \dot{\eta}_{ex} h_{ex,cb} + \dot{Q}_{conv,1}$$
(3.58)

where $\dot{Q}_{conv,1}$ is the convective heat transfer from the separator solid to the combustion chamber, expressed as

$$Q_{conv,1} = A_{conv,1} \mathcal{H}_{conv,1} (T_{sep} - T_{cb})$$
(3.59)

 $A_{conv,1}$, $\mathcal{H}_{conv,1}$ are the area and heat transfer coefficient respectively and T_{sep} is the temperature of the separator solid. Since the air preheater is a non-reactive control volume, there is no net change of mole fraction or molar flow rate. Therefore, the mass transfer equations are trivial. The thermal behaviour of the air preheater volume is given as

$$N_{pr}C_v \dot{T}_{pr} = \dot{N}_{air}h_{in,pr} - \dot{N}_{air}h_{ex,pr} + \dot{Q}_{conv,2}$$
(3.60)

where, $N_{pr} = P_{pr}V_{pr}/R_uT_{pr}$ and $\dot{Q}_{conv,2} = A_{conv,2}\mathcal{H}_{conv,2}(T_{sep} - T_{pr})$. Finally, the thermodynamics of the separator solid is modeled using the following energy balance equation:-

$$M_{sep}C_{sep}\dot{T}_{sep} = -\dot{Q}_{conv,1} - \dot{Q}_{conv,2}$$
(3.61)

CHAPTER 4

CHARACTERIZATION OF UTILIZATION

4.1 Steady-State and Transient Characteristics

To gain understanding of the dynamics of utilization, we perform an analysis based on the state-space models derived in previous sections. Based on the state variable definitions in Eqs.(3.21) and (3.43), fuel utilization can be written as follows:

$$U = 1 - \frac{\dot{N}_o \left(4\chi_{1,a} + \chi_{2,a} + \chi_{4,a} \right)}{\dot{N}_{in} \left(4\chi_{1,r} + \chi_{2,r} + \chi_{4,r} \right)}$$
(4.1)

Eq.(4.1) is based on the internal reforming capability of the fuel cell anode where a CH_4 and a CO molecule can yield four and one molecules of H_2 respectively, as indicated by reaction (I), (II) and (III) in Eq.(3.38). We rewrite Eq.(4.1) with the coordinate transformations as shown below:

$$U = 1 - \frac{\dot{N}_o \zeta_a}{\dot{N}_{in} \zeta_r}, \qquad \begin{aligned} \zeta_r &= 4\mathcal{X}_{1,r} + \mathcal{X}_{2,r} + \mathcal{X}_{4,r} \\ \zeta_a &= 4\mathcal{X}_{1,a} + \mathcal{X}_{2,a} + \mathcal{X}_{4,a} \end{aligned}$$
(4.2)

Using Eqs.(4.2), (3.21) and (3.43) the following state variable descriptions for ζ_r and ζ_a can be obtained:

$$\dot{\mathbf{Z}} = \mathbf{A}_{1}\mathbf{Z} + \mathbf{B}_{1}, \ \mathbf{Z} = \begin{bmatrix} \zeta_{r} \\ \zeta_{a} \end{bmatrix}, \ \mathbf{A}_{1} = \begin{bmatrix} -\frac{\dot{N}_{in}}{N_{r}} & \frac{k\dot{N}_{o}}{N_{r}} \\ \frac{\dot{N}_{in}}{N_{a}} & -\frac{\dot{N}_{o}}{N_{a}} \end{bmatrix}, \ \mathbf{B}_{1} = \begin{bmatrix} \frac{4\dot{N}_{f}}{N_{r}} \\ \frac{-iN_{c}}{nFN_{a}} \end{bmatrix}$$
(4.3)

It is interesting to note here that Eq.(4.3) is devoid of the reaction rates $\mathcal{R}_{1,r}$, $\mathcal{R}_{2,r}$, $\mathcal{R}_{1,a}$, and $\mathcal{R}_{2,a}$. This removes the nonlinearities associated with the reaction rates as given in Eqs.(1) through (3). Nevertheless, \dot{N}_{in} , \dot{N}_o , N_r , N_a are nonlinear functions of the states, temperatures and pressures given by

$$\dot{N}_{in} = \frac{\dot{M}_{in}}{\sum_{i=1}^{5} \mathcal{X}_{i,r} M W_i}, \ \dot{N}_o = \frac{\dot{M}_o}{\sum_{i=1}^{5} \mathcal{X}_{i,a} M W_i}, \ N_r = \frac{P_r V_r}{R_u T_r}, \ N_a = \frac{P_a V_a}{R_u T_a}$$
(4.4)

From Eq.(4.3), we obtain the following expression relating U, k, i and \dot{N}_{f} at steadystate

$$U_{ss} = \frac{1-k}{\frac{4nF\dot{N}_f}{iN_c} - k} \tag{4.5}$$

Eq.(4.5) is independent of the nonlinear variables given in Eq.(4.4). Furthermore, since k, i and \dot{N}_f are measurable and known quantities, Eq.(4.5) can be used to exactly predict the steady-state fuel utilization for any given set of inputs.

From Eqs.(4.2) and (4.3) we note that the transient behavior of U can be predicted from the transient response of ζ_r , ζ_a , \dot{N}_o and \dot{N}_{in} . We specifically consider the transient response of U due to step changes in i, when k and \dot{N}_f are constant. In predicting the transient characteristics we assume that, in the process of a step change in i, the variables \dot{N}_{in} and \dot{N}_o can be treated as constants without significant loss of accuracy. With this assumption, Eq.(4.3) reduces to a Linear Time Invariant (LTI) system with eigenvalues of \mathbf{A}_1 as:

$$\lambda_{1,2} = 0.5 \left[-\left(\frac{\dot{N}_{in}}{N_r} + \frac{\dot{N}_o}{N_a} \right) \pm \left(\left| \frac{\dot{N}_{in}}{N_r} - \frac{\dot{N}_o}{N_a} \right| + \alpha \right) \right],$$

$$\alpha = \left[\left(\frac{\dot{N}_{in}}{N_r} - \frac{\dot{N}_o}{N_a} \right)^2 + 4k \frac{\dot{N}_{in}}{N_r} \frac{\dot{N}_o}{N_a} \right]^{1/2} - \left| \frac{\dot{N}_{in}}{N_r} - \frac{\dot{N}_o}{N_a} \right|, \quad \alpha \ge 0$$
(4.6)

Since $k \in (0, 1)$, the eigenvalues of \mathbf{A}_1 are real and negative. The time constant for ζ_r , ζ_a , and hence that for U due to a step change in i will be determined by the maximum eigenvalue of \mathbf{A}_1 . From Eq.(4.6),

$$\frac{N_{in}}{N_r} \ge \frac{\dot{N}_o}{N_a} \longrightarrow \lambda_{max} = -\frac{\dot{N}_o}{N_a} + 0.5\alpha$$

$$\frac{\dot{N}_{in}}{N_r} < \frac{\dot{N}_o}{N_a} \longrightarrow \lambda_{max} = -\frac{\dot{N}_{in}}{N_r} + 0.5\alpha$$
(4.7)

4.2 Simulations

In this section we provide simulation results in support of our analysis in the previous section. We run multiple simulations of the SOFC system with step changes in current applied at t = 50s, as shown in Fig.4.1. The step changes in current are from 25A



Figure 4.1. Transient and steady-state utilization

to 33, 38, 43 and 48A as shown in Fig.4.1(a). For all four simulations, the following settings were used

$$\dot{N}_f = 0.0068 \text{ moles/s}, \quad \dot{N}_{air} = 0.0692 \text{ moles/s}, \quad k = 70\%$$

In Fig.4.1(b) the transient response of utilization is plotted for the four simulations. The estimated utilization are obtained by simulating Eqs.(4.2) and (4.3) as an LTI system with A_1 evaluated at the instant t = 50s. The following values were observed at t = 50s

$$\begin{split} \dot{N}_{in} &= 0.0624 \text{ moles/s} \\ \dot{N}_o &= 0.0681 \text{ moles/s} \\ N_r &= 0.0263 \text{ mole} \\ N_a &= 0.1105 \text{ mole} \end{split} \qquad \begin{array}{l} \lambda_1 &= -2.8347 \\ \lambda_2 &= -0.1543 \\ \lambda_2 &= -0.1543 \\ \end{array}$$

Both the transient response as well as the steady-state value of estimated utilization match very closely with the non-linear model based calculation, as shown in Fig.4.1(b). The settling time computed based on 2% error is $T_s = 4/|\lambda_2| = 25.9235$ s which matches well with the simulations.

CHAPTER 5

CHARACTERIZATION OF STEAM-TO-CARBON BALANCE

5.1 Steady-State and Transient Characteristics

The Steam-To-Carbon-Ratio (STCR) is defined for the inlet flow of the steam reformer and can be mathematically expressed using Fig.3.1 as

$$STCR = \frac{kN_o\mathcal{X}_{5,a}}{\dot{N}_f + k\dot{N}_o\mathcal{X}_{1,a} + k\dot{N}_o\mathcal{X}_{2,a}}$$
(5.1)

As the name suggests and is indicated by Eq.(5.1), STCR is the ratio of the concentration of steam molecules to that of carbon atoms at the inlet of the reformer. The reactions (b) and (c) of Eq.(3.17) indicate that the stoichiometric quantity of steam required for reforming is two moles and one mole of steam for each mole of CH_4 and CO respectively. With this understanding, we define a new variable, namely the Steam-To-Carbon-Balance (STCB), which is mathematically expressed as

$$STCB = k\dot{N}_{o}\mathcal{X}_{5,a} - \left(2\dot{N}_{f} + 2k\dot{N}_{o}\mathcal{X}_{1,a} + k\dot{N}_{o}\mathcal{X}_{2,a}\right)$$

$$= k\dot{N}_{o}\left(\mathcal{X}_{5,a} - 2\mathcal{X}_{1,a} - \mathcal{X}_{2,a}\right) - 2\dot{N}_{f}$$
(5.2)

A positive value of STCB is an indication of sufficient steam at the reformer inlet for steam reforming and hence it is an indication of a favorable STCR. We rewrite Eq.(5.2) with the coordinate transformations as shown below:

$$STCB = k\dot{N}_{o}\xi_{a} - 2\dot{N}_{f}, \qquad \begin{aligned} \xi_{r} &= \mathcal{X}_{5,r} - 2\mathcal{X}_{1,r} - \mathcal{X}_{2,r} \\ \xi_{a} &= \mathcal{X}_{5,a} - 2\mathcal{X}_{1,a} - \mathcal{X}_{2,a} \end{aligned}$$
(5.3)

Using Eqs.(5.3), (3.21) and (3.43) the state variable descriptions for ξ_r and ξ_a can be written as

$$\dot{\mathbf{S}} = \mathbf{A}_2 \mathbf{S} + \mathbf{B}_2, \ \mathbf{S} = \begin{bmatrix} \xi_r \\ \xi_a \end{bmatrix}, \ \mathbf{A}_2 = \begin{bmatrix} -\frac{\dot{N}_{in}}{N_r} & \frac{k\dot{N}_o}{N_r} \\ \frac{\dot{N}_{in}}{N_a} & -\frac{\dot{N}_o}{N_a} \end{bmatrix}, \ \mathbf{B}_2 = \begin{bmatrix} \frac{-2\dot{N}_f}{N_r} \\ \frac{iN_c}{nFN_a} \end{bmatrix}$$
(5.4)

Note that, as in Eq.(4.3), the variables ξ_r and ξ_a in Eq.(5.4) are independent of $\mathcal{R}_{1,r}$, $\mathcal{R}_{2,r}$, $\mathcal{R}_{1,a}$, and $\mathcal{R}_{2,a}$. \dot{N}_{in} , \dot{N}_o , N_r , N_a are nonlinear functions of the states, temperatures and pressures given by Eq.(4.4). From Eq.(5.4), the following steady-state expression for STCB is obtained

$$STCB_{ss} = \frac{1}{k-1} \left(2\dot{N}_f - \frac{kiN_c}{nF} \right)$$
(5.5)

Note, from Eqs.(4.3) and (5.4), that $\mathbf{A}_2 = \mathbf{A}_1$. Hence, the time constant in the transient response of STCB due to step changes in the current demand can be estimated using the eigenvalues $\lambda_{1,2}$ of \mathbf{A}_1 given in Eq.(4.6). The discussion around Eqs.(4.6) and (4.7) is also applicable for transient response of STCB.

5.2 Simulations

The simulation results provided here are continuation of those provided above for step response of utilization in Figs.4.1(a) and (b). In Figs.5.1(a) and (b), STCR and STCB are plotted for the four simulations described in Fig.4.1(a). In Fig.5.1(b) the transient response of STCB are plotted. The estimated STCB are computed by considering the system given in Eqs.(5.3) and (5.4) as an LTI system with A_2 evaluated at the instant t = 50s. Both the transient response as well as the steady-state value of estimated STCB match very closely with the non-linear model based calculation, as shown in Fig.5.1(b).



Figure 5.1. Transient and steady-state STCR and STCB

CHAPTER 6

STEADY-STATE FUEL OPTIMIZATION

6.1 **Problem Statement**

Using the above derived results, we address a steady-state constrained fuel optimization problem which is stated as follows: Given that utilization and anode recirculation must be constrained within ranges $U_{ss} \in [U_{ss1}, U_{ss2}]$, $0 < U_{ss1}, U_{ss2} < 1$ and $k \in [k_a, k_b]$, $0 < k_a, k_b < 1$ respectively, and given a current i

- 1. Determine condition(s) under which there exists a range of solutions for N_f that satisfies the constraints above and maintains STCB ≥ 0 .
- 2. If a range of solutions exists, determine the minimum fuel operating conditions.

6.2 Optimum Fuel Operation

From Eq.(5.5), we note that for ensuring a steam rich inlet flow into the reformer, we must have

$$\text{STCB}_{ss} \ge 0 \to \dot{N}_f \le k \left(\frac{iN_c}{2nF}\right)$$
(6.1)



Figure 6.1. Steady-state fuel optimization

From Eq.(4.5) we have

$$U_{ss} \ge 0 \to \dot{N}_f \ge k \left(\frac{iN_c}{4nF}\right)$$
 (6.2)

and the constraints $0 < U_{ss1} \leq U_{ss} \leq U_{ss2} < 1$ are expressed as

$$\dot{N}_f\left(\frac{4nFU_{ss1}}{iN_c}\right) + (1 - U_{ss1})k \leq 1$$
(6.3)

$$\dot{N}_f\left(\frac{4nFU_{ss2}}{iN_c}\right) + (1 - U_{ss2})k \ge 1$$
(6.4)

Eqs.(6.1), (6.2), (6.3) and (6.4) are all linear in N_f and k and are denoted in Fig.6.1 by lr_1 , lr_2 , lu_1 and lu_2 respectively, along with the lines $k = k_a$ and $k = k_b$. Steadystate constrained fuel optimization for the steam reformer based SOFC system has thus been transformed to a problem in linear programming. From Fig.6.1 and from Eqs.(6.1) through (6.4), we can easily deduce that a solution region exists if $k_b \ge k^*$, where k^* is the value of k at the intersection between the lines lr_1 and lu_2 . Hence, from Eqs.(6.1) and (6.4) we have:

$$k^* = \frac{1}{1 + U_{ss2}} \rightarrow k_b \ge \frac{1}{1 + U_{ss2}}$$
 (6.5)

From Fig.6.1 it is also evident that if Eq.(6.5) is satisfied, then the steady-state minimum fuel operating point is at the intersection of lu_2 and $k = k_b$, given by

$$k = k_b, \quad U = U_{ss2}, \quad \dot{N}_{f,min} = \frac{iN_c}{4nFU_{ss2}} \left[1 - (1 - U_{ss2})k_b\right]$$
 (6.6)

6.3 Simulations

Steady-state minimum fuel operation is demonstrated using the following simulation results. We consider a system with 100 cells in series and i = 50A. It is desired to attain the steady state minimum fuel operating point under the constraints, $U_{ss1} = 0.6$, $U_{ss2} = 0.85$, $k_a = 0.6$, $k_b = 0.8$ and $STCB_{ss} \ge 0$. We choose the initial operating conditions k = 0.65 and $\dot{N}_f = 0.01$ moles/s, and set the air flow rate at $\dot{N}_a = 10\dot{N}_f$ for the entire simulation. The simulation results are shown below in Fig.6.2. In Fig.6.2(a),



Figure 6.2. Fuel optimization simulation

the lines lr_1 , lr_2 , lu_1 and lu_2 , representing Eqs.(6.1), (6.2), (6.3) and (6.4), are plotted and the trajectory of the operating point in $(\dot{N}_f \text{ vs. } k)$ space is superimposed. The initial conditon corresponds to point A in Fig.6.2(a). At this operating point, the model is first simulated in open loop mode up to $t_1 = 40$ s. Note that at A, the conditions $U_{ss1} \leq U_{ss} \leq U_{ss2}$ and $\text{STCB}_{ss} \geq 0$ are not satisfied. Specifically, at A, $U_{ss} \approx 0.4$ and STCB_{ss} ≈ -0.01 moles/s, as shown in Figs.6.2(b) and (e) respectively. At t_1 , a proportional-integral control is invoked to control utilization by varying N_f . Simultaneously, the target utilization is ramped from 0.45 at t_1 to 0.85 at $t_3 = 240$ s, as shown in Fig.6.2(b). This leads to reduction of \dot{N}_f , depicted in Fig.6.2(c), from 0.01 moles/s to 6.878×10^{-3} moles/s. During this interval k is maintained at 0.65, as shown in Fig.6.2(d), and the operating point in Fig.6.2(a) shifts from point A to B. Also note from Fig.6.2(e), that STCB > 0 for $t > t_2$. At $t_4 = 300$ s, k is ramped from 0.65 to $k_b = 0.8$ at $t_5 = 450$ s. This leads to further reduction of N_f to 6.705×10^{-3} moles/s, as shown in Fig.6.2(c). The corresponding shift in the operating point from B to C is shown in Fig.6.2(a). The minimum fuel operating point as computed using Eq.(6.6) is 6.706×10^{-3} moles/s which matches very closely with that obtained through simulation. It must be noted that the proportional-integral control implemented here is not a proposed control strategy. It is used to automatically arrive at the minimum fuel operating point and thus it serves to validate Eq.(6.6).

CHAPTER 7

CONCLUSION

In this thesis we have presented an analytical study of steady-state and transient behaviors of an SOFC system due to changes in current demand. For the analysis we considered a steam-reformer based tubular SOFC system with anode recirculation and with methane as fuel. We developed a detailed control-oriented model for the SOFC system and expressed the mass transfer and chemical kinetics phenomena of the reformer and anode control volumes in state-space form. We derived closed-form expressions that characterizes the steady-state and transient behaviors of utilization (U) and steam-to-carbon balance (STCB). Our analysis was facilitated by key coordinate transformations that led to elimination of non-linear reaction rate terms from the coupled dynamic equations of the reformer and anode volumes. For predicting the transient response we treated the molar flow rates \dot{N}_{in} and \dot{N}_o , and the molar contents N_r and N_a , as constants. This step was effective as it simplified the nonlinear state-space system to a Linear-Time-Invariant form with minimal loss of accuracy. The estimates of time constants and the steady-state values of U and STCB matched very closely with those generated by the plant model. The results were applied to address a steady-state fuel optimization problem for the SOFC system using the linear-programming approach. The constrained optimization problem yielded a minimum fuel operating point. The analytical results were confirmed through simulations.

APPENDIX A

APPENDIX A

Formulaes to Compute Reaction Rates

We use the following reaction rate expressions, given in [20], to model the kinetics of steam reforming reactions in Eqs.(3.17) and (3.38). The equations below are written for a generic gas control volume. For the SOFC system, these equations apply for the reforming reactions in the reformate control volume as well as the anode control volume.

$$r_{I} = \frac{M_{cat}\kappa_{I}}{p_{H_{2}}^{2.5}} \left(p_{CH_{4}} p_{H_{2}O} - \frac{p_{H_{2}}^{3} p_{CO}}{\mathcal{K}_{I}} \right) / \delta^{2}$$
(1)

$$r_{II} = \frac{M_{cat}\kappa_{II}}{p_{H_2}} \left(p_{CO}p_{H_2O} - \frac{p_{H_2}p_{CO_2}}{\mathcal{K}_{II}} \right) / \delta^2$$
(2)

$$r_{III} = \frac{M_{cat}\kappa_{III}}{p_{H_2}^{3.5}} \left(p_{CH_4} p_{H_2O}^2 - \frac{p_{H_2}^4 p_{CO_2}}{\kappa_{III}} \right) / \delta^2$$
(3)

where

$$\delta = 1 + \mathcal{K}_{CO} p_{CO} + \mathcal{K}_{H_2} p_{H_2} + \mathcal{K}_{CH_4} p_{CH_4} + \mathcal{K}_{H_2O} p_{H_2O} p_{H_2},$$

$$p_j = \mathcal{X}_j P_g, \ j = 1, 2, \cdots, 5$$
(4)

In Eqs.(1), (2) and (3), the rate coefficients κ_I , κ_{II} , and κ_{III} are given by

$$\kappa_b = \kappa_{b,T_{ref}} \exp\left[-\frac{E_b}{R_u} \left(\frac{1}{T_g} - \frac{1}{T_{ref,b}}\right)\right], \quad b = I, II, III,$$
(5)

and the adsorption constants \mathcal{K}_{CO} , \mathcal{K}_{H_2} , \mathcal{K}_{CH_4} , \mathcal{K}_{H_2O} are given as follows

$$\mathcal{K}_q = \mathcal{K}_{q,T_{ref}} \exp\left[-\frac{\Delta H_q}{R_u} \left(\frac{1}{T_g} - \frac{1}{T_{ref,q}}\right)\right], \quad q = CO, H_2, CH_4, H_2O \quad (6)$$

where the values of E_b , $T_{ref,b}$, $\kappa_{b,T_{ref}}$, with b = I, II, III, and ΔH_q , $T_{ref,q}$, $\mathcal{K}_{q,T_{ref}}$, with $q = CO, H_2, CH_4, H_2O$, are given in [20]. The equilibrium constants $\mathcal{K}_I, \mathcal{K}_{II}$ and \mathcal{K}_{III} in Eqs.(1),(2)and (3) are given by

$$\mathcal{K}_{b} = \exp\left(-\frac{\Delta G_{T,b}^{0}}{R_{u}T}\right), \quad b = I, II, III$$
(7)

In Eq.(7), ΔG_T^0 represents the net Gibb's free energy ([18]) of a reaction given by

$$\Delta G_T^{\circ} = \sum_{prod} \mathcal{Z}_w (\Delta h_{f,298}^0 + h(T) - h(298) - T S_T^0)_w - \sum_{reac} \mathcal{Z}_w (\Delta h_{f,298}^0 + h(T) - h(298) - T S_T^0)_w$$
(8)

where S_T^0 is computed using the following equation:

$$S_T^0 = R_u \left[a_w ln(T) + b_w T + \frac{c_w T^2}{2} + \frac{d_w T^3}{3} + \frac{e_w T^4}{4} \right]_{298}^T + S_{298}^0$$
(9)

APPENDIX B

APPENDIX B

Data

Gas properties:

Refer to [18], [9]

Reformer specific constants for heat transfer calculations:

Refer to [7], [16]

Parameters for computing the rates of reforming reactions:

Refer to [20]

Tubular stack parameters:

Refer to [7], [16]

Combustor parameters:

$$L_{cb} = 0.5 \text{ (m)}$$

$$Nu_{D,cb} = 8$$

$$D_{H,cb} = 0.12 \text{ (m)}$$

$$A_{conv1} = 0.314 \text{ (m}^2)$$

$$Nu_{D,pr} = 8$$

$$D_{H,pr} = 0.079 \text{ (m)}$$

$$A_{conv2} = 0.314 \text{ (m}^2)$$

$$M_{sep} = 0.376 \text{ Kg}$$

$$C_s = 765(\text{J/kg K)}$$

$$V_{cb} = 5.62\text{e-3}(\text{m}^3)$$

$$V_{pr} = 9.953\text{e-3}(\text{m}^3)$$

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