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# Solid Oxide Fuel Cell System Control

## Modeling and Control Study of a Catalytic Partial Oxidation (CPOX) Reactor

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University of Akureyri

# SOLID OXIDE FUEL CELL SYSTEM CONTROL

Modeling and Control Study of a Catalytic Partial Oxidation
(CPOX) Reactor

Tomasz Szczęsny Miklis

A 30 credit units Master's thesis

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Dr. Tyrone Vincent (Project advisor)

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A Master's thesis done at

RES │ the School for Renewable Energy Science

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the University of Akureyri

Akureyri, February 2009

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# ABSTRACT

An advanced thermodynamic model of a *catalytic partial oxidation (CPOX)* reactor was developed. The dynamics of the reactor were simulated using *differential algebraic equations (DAEs)*. The aim of the project was to create a reliable and fast model that will be used, for control purposes, to maximize the hydrogen yield from the CPOX reaction. The composition of the output flow and species concentration is controlled by the input mass flows of fuel (Dodecane) and air. The state variables of the reactor considered in this model are *temperature* and *total internal energy* of the reactor. There are many options with which to customize the reactor model, from the geometry and materials used to build the reactor shell to different compositions of the gases fed to the reactor (fuel and air). The *Cantera* toolbox was used to simulate chemistry and the whole project was completed the in *MATLAB* programming environment.
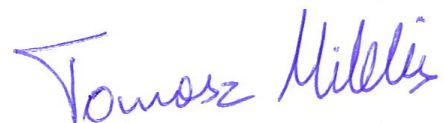
# PREFACE

The focus of this Master Thesis project for the *Fuel Cell Systems & Hydrogen* specialization at *RES | The School for Renewable Energy Science* is Solid Oxide Fuel Cell System Control. At my home university (*AGH University of Science and Technology in Kraków*) I am doing continuous M.Sc. studies in Automatics and Robotics specializing in Computer Science in Control and Management. My goal with this thesis is to study the control aspect of fuel cell systems and continue this research with my engineering M.Sc. thesis at my home university.

Ryan O'Hayre and Neal Sullivan, the Professors from the Colorado School of Mines, were lecturers at the RES | The School for Renewable Energy Science (*FC602 Fuel Cell Types & Technologies* course) in July 2008. During that time the idea of completing my M.Sc. project in Colorado was born. Thanks to the excellent cooperation between CSM and RES, I completed my thesis in the United States.

This project was developed during my work as a research associate at the Colorado School of Mines in Golden from 21$^{st}$ of October 2008 till 2$^{nd}$ of February 2009. My research was supervised Dr Tyrone Vincent. I was part of the Control Group of the Department of Energy (DOE) research grant.

I would like to give thanks for all the support I received during my work at CSM. There were many kind and helpful people I encountered during my work on this project. I would especially like to thank:

- **Mr. Tyrone Vincent** – for being my advisor and always finding time to answer my questions and guide me with my research;
- **Mr. Bob Kee** – for all the support with building the thermodynamic formulation of the CPOX reactor;
- **Mr. Huayang Zhu** – for his help with the chemistry behind the CPOX reactor and comparing results of this model with others;
- **Mr. Borhan Sanandaji** – for his cooperation and help with the control aspects of the project;
- **Mr. Kevin Moore** – for his willingness to host me at CSM and initializing my project;
- **Mr. Neal Sullivan** – for helping to organize the legal aspects of this project;
- **Mr. David Dvorak** – for **his** help with final revisions of the thesis report;
- **Mr. Thorsteinn Ingi Sigfusson** – for coordinating my specialization;
- **RES staff** – for organizing the stay in United Stated and help with many day-to-day problems;
- **RES teachers** – for preparing me to work on the M.Sc. project;
- **Fellow RES 2008/2009 students** – for a great year at the RES School.

Golden, 02.02.2009

# TABLE OF CONTENTS

## LIST OF FIGURES

# LIST OF TABLES

# 1    PROJECT OVERVIEW

This study focused on the modeling of the Catalytic Partial Oxidation (CPOX) reactor in the Solid Oxide Fuel Cell system. The overall aim of the *US Department of Energy* (DOE) research grant, of which this research is an important component, is to develop a flexible and fast model of a whole system containing fuel cell stack, CPOX reactor and balance-of-plant components. This research models the fuel processor element of the system. The output species composition is estimated based on the different mass flows of inlet streams (Dodecane and air). This information is necessary to develop control schemes that will maximize the yield of the hydrogen from CPOX reaction.

An advanced thermodynamic model was designed and formulated using differential algebraic equations. MATLAB software with the Cantera toolbox, to simulate the complicated chemistry, was used for numerical simulations.

## 1.1    Introduction
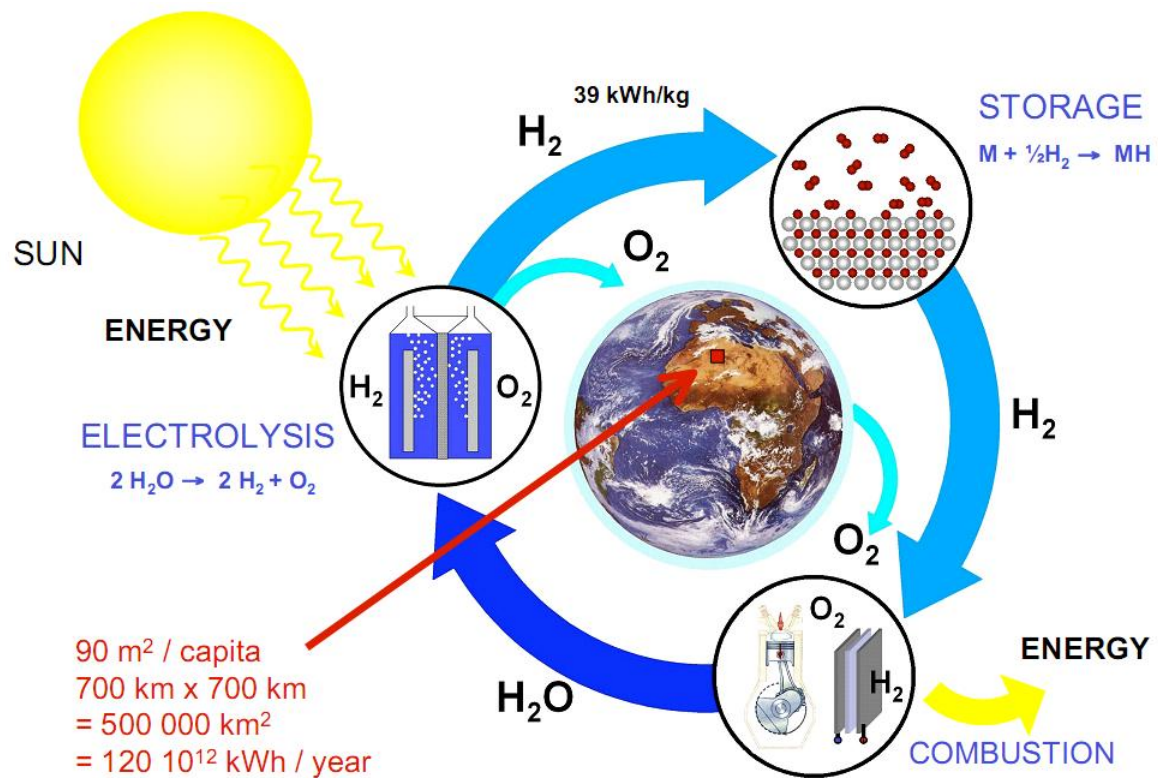


*Figure 1-1 Hydrogen cycle solution by Andreas Zuttel*

Today's world faces many environmental and economical hurdles. The growing gap between predicted energy production and consumption drives the search for the alternatives. As presented in *Figure 1-1* Hydrogen cycle solution by Andreas Zuttel a hydrogen economy might be the ultimate solution to those problems. There are many technical problems (hydrogen storage, infrastructure development etc.), however, which need to be overcome before the widespread implementation of the *hydrogen dream*.

The solid oxide fuel cell (SOFC) systems with CPOX reactors that can process hydrocarbon fuels to create hydrogen will be a very important intermediate step on the way to a hydrogen economy, from a short term perspective.

## 1.2    US Department of Energy (DOE) research project

This research was a part of the US Department of Energy (DOE) research grant:

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**"Renewable and Logistic Fuels for Fuel Cells at the Colorado School of Mines"**

Starting Date: 01.05.2008

Duration: 2 years

Budget: $1,476,000

*"The objective of this program is to advance the current state of technology of solid-oxide fuel cells (SOFCs) to improve performance when operating on renewable and logistics hydrocarbons fuel streams."*

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This project is aimed at answering some of the problems formulated in the *Task 3.0: Balance-of-Plant Development, System Optimization and Control.*

The goal of the Fuel Cell System Control task is the design of a control system to regulate the operation of a complete system based on an SOFC stack. The control system design is based on a dynamic model that can predict system behavior given perturbations in actuator settings, such as air and fuel flows and power loads. Ideally, these models are based on physical first principles. However, physically based models are often very complex and take considerable computational resources to compute. For some activities, computational complexity can become a limiting factor in the usefulness of the model, and it becomes necessary to capture the dominant behavior in a lower order model that can be run quickly. This is especially true when the models are used with a real-time, or on-line automated activity, such as process monitoring and control, but this can also be useful when building interconnected or hierarchical models that can be run in a reasonable amount of time. As part of this project, we have developed a model reduction that can capture both the linear and nonlinear behavior of physics based models. These reduced models are then utilized within a Model Predictive Control (MPC) implementation for integrated control of the fuel cell stack and associated balance of plant components.

## 1.3    Multimedia aspects of the project

There was a significant effort put into making the results of this project accessible and to develop a platform for international cooperation for the future development of this research.

### 1.3.1  Box.net data exchange space

All the MATLAB source codes, most of the references used in this report and installation files of the Cantera toolbox are available at the *box.net* server. The collaborator of the project can access all those files by using this address:

http://www.box.net/shared/86oa2k4d53

### 1.3.2  Control Wiki

The *Control Wiki* website was created to allow easy tracking of the current progress of the research. An outline of the research activities, some results, and important references are regularly published there. The collaborator of the project can access that information by using this address:

http://control.mines.edu/mediawiki/index.php/Control_of_Solid_Oxide_Fuel_Cells

# 2   REVIEW OF FUEL CELL CONTROL PUBLICATIONS

The control aspect of fuel cell systems is a relatively unexplored area of research. There is a limited amount of publications, most of which originate from the University of Michigan. A research group that focuses on the control of the fuel cell systems is led by Anna G. Stefanopoulou. Their research is connected to low-temperature *polymer exchange membrane (PEM)* fuel cells (Pukrushpan, Stefanopoulou, & Peng, 2004).

The current studies proved that the response of a fuel cell system depends on the air and hydrogen feed, flow and pressure regulation, and heat and water management. Dynamic models of PEM FC systems suitable for the control study were developed. The fuel cell stack temperature is treated as a parameter rather than state variable, which is a serious limitation (Pukrushpan, Peng, & Stefanopoulou, Control-Oriented Modeling and Analysis for Automotive Fuel Cell Systems, 2004).

# 3 SOLID OXIDE FUEL CELL SYSTEM

This chapter will introduce some basic knowledge about fuel cells. First, a brief history of this energy generating device will be presented, followed by a technical description of the working principles of Solid Oxide Fuel Cell System.

## 3.1 The promise of Fuel Cells

Although fuel cells (FC) seem like a twenty-first-century marvel, they are a nineteenth-century invention that predates the innovation of the internal combustion engine. The invention of fuel cells as an electrical energy conversion system is attributed to Sir William Grove (Carrette, Friedrich, & Stimming, 2001). For more than 150 years fuel cells have presented the promise of zero emission energy generation.

The hype about fuel cells gained momentum after the National Aeronautics and Space Administration (NASA) used them in the 60's with the Apollo program. The *alkaline fuel cells* did a good job in the sterile deep space environment. Unfortunately, 'back on Earth' they were easily poisoned with $CO_2$, which limited their commercial application. After the Oil Crisis hit the world in the 1973, fuel cells were again in the spotlight. The biggest problem for wide commercial application was, and still is, fuel storage. Because of its low *volumetric density,* energy-reach hydrogen storage is quite problematic. Rare and expensive Platinum, the catalyst that speeds up the reactions inside FC, is another difficulty. Even though recently scientists managed to reduce the amount of this precious metal used in FC systems by a factor of 10, it is a still limiting factor in wider applications.
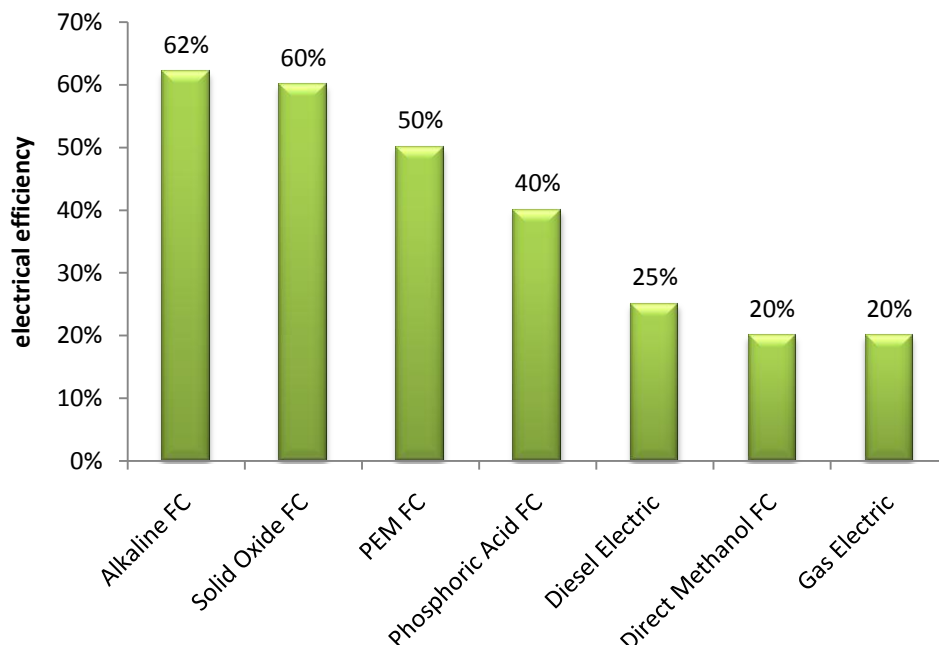
*Figure 3-1 Comparison of electrical systems efficiencies (Wikipedia, 2008)*

Fuel Cells were always '5 years ahead', but right now with the growing energy (we are probably past the *Hubbert's peak*) and environmental concerns (alarming $CO_2$ concentrations) it seems that this ultimate solution is just around the corner. Fuel cells offer

tremendous promise for solving a variety of energy needs, ranging from portable to automobile to stationary power. With their high efficiencies (see *Figure 3-1* Comparison of electrical systems efficiencies) and zero emissions, they will reduce our global dependence on oil and foster future energy security, prosperity, and a cleaner environment. Extensive government-funded research and the growing activity of the private sector build a much needed momentum for extensive fuel cell utilization.

## 3.2   Solid Oxide Fuel Cell – 'the heart'

*Solid oxide fuel cells (SOFCs)* use ceramic as the electrolyte. They operate at very high temperatures– up to 1000°C– and can operate with air and natural gas (or other fuels) as direct inputs. In contrast to *proton exchange membrane (PEM) fuel cells* (in which positively charged hydrogen ions travel through the polymer membrane), SOFCs use negatively charged oxygen ions that travel through a porous anode, where they combine with the hydrogen to form water (see *Figure 3-2* Solid Oxide Fuel Cell operation diagram). The solid ceramic electrolyte is a hermetic barrier between the chemical reactants, so no hydrogen or water can reach the air side of the fuel cell, which simplifies operation (Romm, 2005). One of the biggest advantages of these systems is that they can use relatively impure hydrocarbon fuels. The downside is the slow thermal response that causes long start-up times (Dvorak, Fuel Cell Operation, 2008).
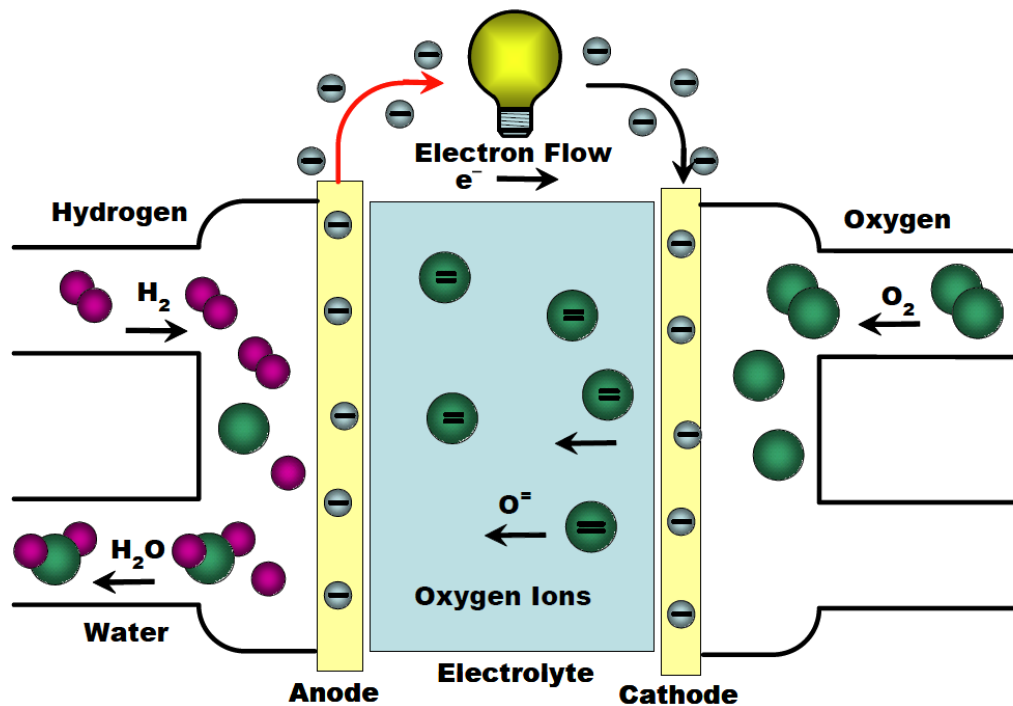


*Figure 3-2 Solid Oxide Fuel Cell operation diagram (Dvorak, 2008)*

There are two chemical equations that govern SOFC work. The anode reaction

$$H_2 + O^{\bar{=}} \rightarrow H_2O + 2e^-,$$
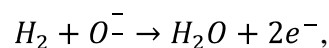
and the cathode reaction

$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{\overline{-}}.$$
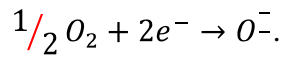
Those formulas sum up to the overall reaction

$$\boxed{H_2 + \frac{1}{2}O_2 \rightarrow H_2O}.$$
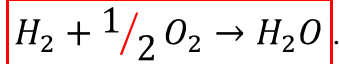
The SOFC stack can have either planar or tubular construction. In this project the SOFC system is equipped with tubular construction, as depicted in *Figure 3-3* Tubular concept pursued by Siemens-Westinghouse. This design has a self-sealing structure which improves thermal stability and eliminates the need for good thermal-resistant sealants. Due to the high temperature of the exhaust gases, a SOFC system in combination with other power generation systems (e.g., gas turbines) is a promising solution. It can provide a high overall electrical efficiency (up to 70% in a combined cycle system).
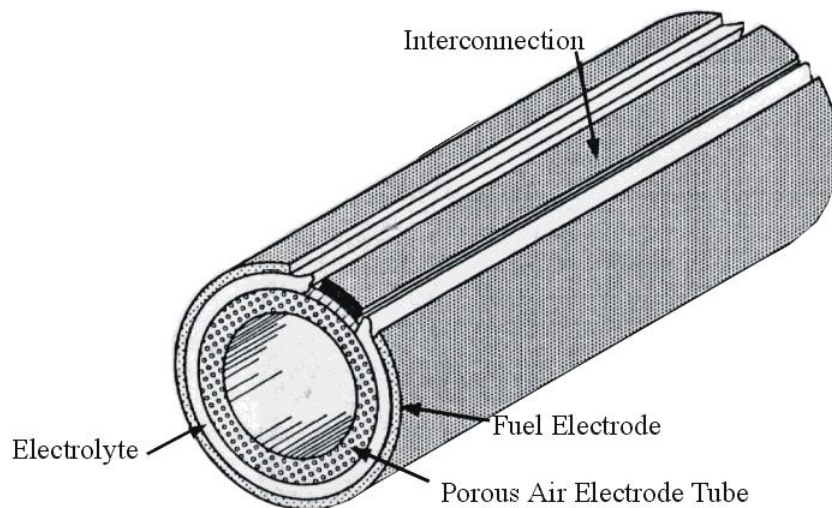


*Figure 3-3 Tubular concept pursued by Siemens-Westinghouse*

## 3.3    Balance-of-Plant components – 'the body'

A fuel cell power system requires the integration of many components beyond the fuel cell stack itself. All of these auxiliary components are collectively named Balance-of-Plant (BOP). The fuel cell will produce only DC power and utilize only certain processed fuel. Various system components are incorporated into a power system to allow operation with conventional fuels (in this case Dodecane), to tie into the AC power grid, and often to utilize rejected heat to achieve high efficiency. In an elementary form, fuel cell power systems consist of a fuel processor (reformer), fuel cell power section (fuel cell stack), power conditioner, and potentially a cogeneration or bottoming cycle to utilize the rejected heat (EG&G Technical Services, Inc., 2004). A simple schematic of these basic systems and their interconnections is presented in *Figure 3-4* Fuel Cell system schematic.
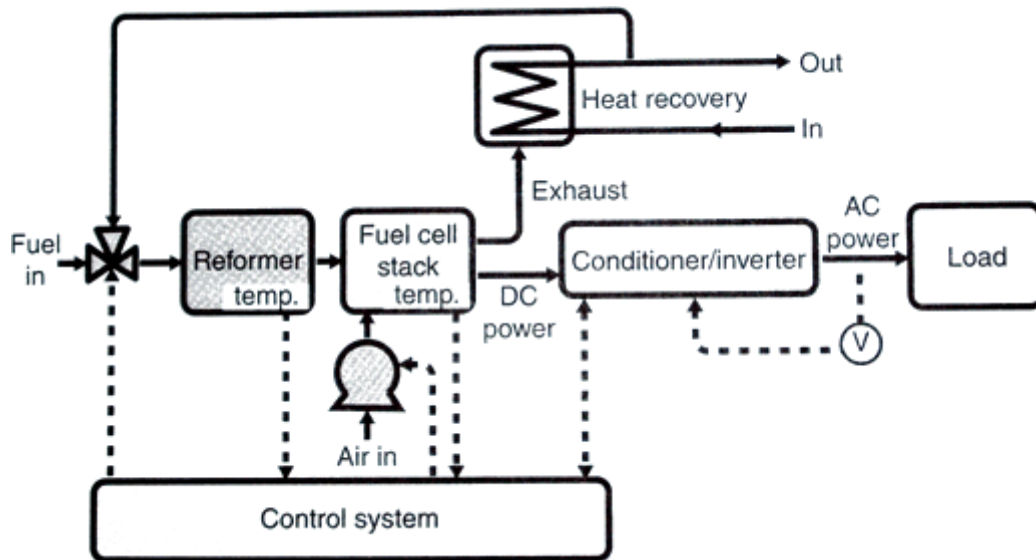
*Figure 3-4 Fuel Cell system schematic (O'Hayre et al., 2006)*

The overall aim of the project is the development of reliable control scenarios for the SOFC system. The focus of this research is modeling a reformer component of the Balance-Of-Plant.

## 3.4 Control Units – 'the brains'

The fuel cell control unit is the "brain" of the fuel cell system. The fuel cell system requires continuous feedback control in order to respond to variations in demand, thermal environment, fuel mixture and other disturbances. Control units use feedback loops between system-monitoring elements (sensors) and system actuation elements (valves, switches, fans) to maintain operation within a desired range (O'Hayre, Cha, Colella, & Prinz, 2006). A well designed control system guarantees good efficiencies and the extended lifetime of a fuel cell. Some of the control problems in the fuel cell systems include

- fuel-air coordination problems,
- load matching (thermal constrains vs. efficiency and utilization),
- minimizing the parasitic power of the air compressor,
- transient periods,
- optimal system air flow excess ratio.

This research is part of an effort aimed at solving the fuel-air coordination problem in the CPOX reactor.

# 4  CONTROL THEORY OVERVIEW

In this chapter, the question *"How are models created and used in control systems?"* will be answered. A brief introduction to the main ideas in the modern control theory will be presented (state space representation, system identification). This introductory knowledge is necessary to follow the concepts in the subsequent chapters.

## 4.1  Basics of Control Theory

Control engineering is based on the foundation of feedback theory and linear system analysis, and it integrates the concepts of network theory and communication theory (Dorf & Bishop, 2008). A *control system* is an interconnection of components forming a system configuration that will provide a desired system response. The basis for the analysis of a system is the foundation provided by linear system theory, which assumes a cause-effect relationship for the components of a system. This is why a component or *process* that will be controlled can be represented by a block (see *Figure 4-1* The concept of the feedback loop to control the dynamic behavior of the system). The input-output relationship represents the cause-and-effect relationship of the process, which in turn represents a processing of the input signal to provide an output signal variable. In this case, the process is defined as fuel reforming in the CPOX reactor. There are two main types of control systems:

- *open-loop control system* (utilizes an actuating device to control the process directly without using feedback),
- *closed-loop feedback control system* (uses a measurement of the output and feedback of this signal to compare it with the desired output – reference or command).
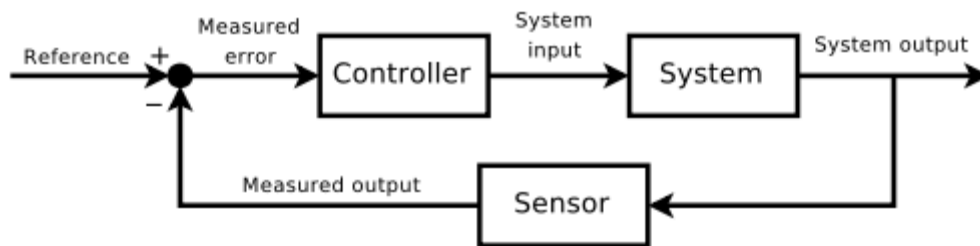


*Figure 4-1 The concept of the feedback loop to control the dynamic behavior of the system (Wikipedia, 2008)*

Mathematical models of physical systems are key elements in the design and analysis of control systems. It is necessary to analyze the relationship between the system variables to obtain a mathematical model. In most cases the systems are dynamic in nature; the descriptive equations are usually *differential equations* (see *Chapter 7*). Those equations are obtained by utilizing the physical laws of the process. This approach applies equally well to mechanical, electrical, fluid and the focus of this project – thermodynamic systems. If these equations can be *linearized,* then the *Laplace transform* can be used to simplify the method of solution. In practice, the complexity of systems and the limited computational power require the introduction of *assumptions* concerning the system operation.

## 4.2   State-space representation

State-space representation is a mathematical model of a physical system as a set of input, output and state variables related by first-order differential equations.

For a dynamic system, the state of a system is described in terms of a set of *state variables* $[x_1(t),\ x_2(t), \ldots, x_n(t)]$. The state variables describe the present configuration of a system and can be used to determine the future response, given the excitation inputs and the equations describing the dynamics. In the case of the CPOX reactor, the **state variables are total internal energy ($x_1(t) = U$) and temperature ($x_2(t) = T$)**.

The most general state space representation of a linear system with *r* inputs, *p* outputs and *n* state variables is written in the following form

$$\begin{cases} \dot{x}(t) = A(t)x(t) + B(t)u(t) \\ y(t) = C(t)x(t) + D(t)u(t) \end{cases}$$

where $x(t) \in \mathbb{R}^n$, $y(t) \in \mathbb{R}^p$, $u(t) \in \mathbb{R}^r$ and $\dot{x}(t) := \frac{dx(t)}{dt}$. The illustration of this representation can be seen in *Figure 4-2* Typical State Space model, where the matrixes are of the following dimensions $A^{n \times n}, B^{n \times r}, C^{p \times n}, D^{p \times r}$.
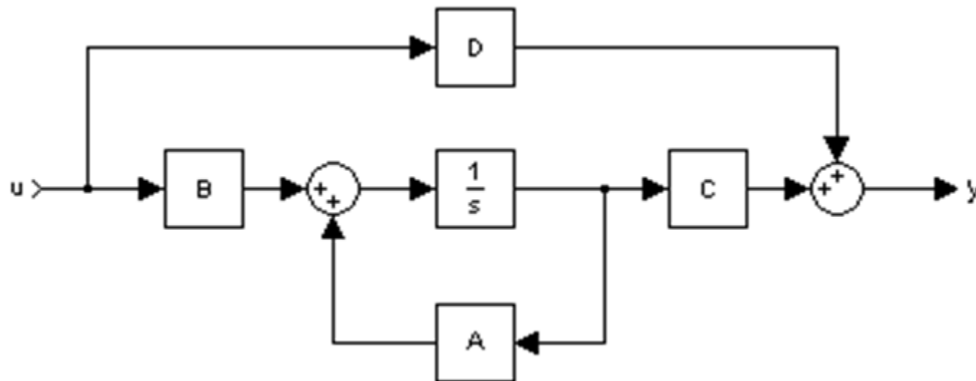


*Figure 4-2 Typical State Space model (Wikipedia, 2008)*

State-space representation (also known as the *time-domain approach*) provides a convenient and compact way to model and analyze systems with multiple inputs and outputs.

## 4.3   System Identification

Often it is impossible to accurately describe the system using basic physical laws. Modeling a problem using the *first principles* (e.g. for the physical process, the Newton equations), leads to an overly complex mathematical description that cannot be estimated in a reasonable time. This method of system description is called the *white-box* approach.

A more common approach is to start from measurements of the behavior of the system and the external influences (inputs to the system). It is important to correctly design the test signals so that the whole dynamics can be obtained from the test data. In this project, the PRBS (*Pseudo-Random-Binary-Sequence*) signals were used for the system identification of the SOFC stack. After obtaining the test data, a set of candidate models is created by specifying their common properties. The next step is to find the best model in this set (Yucai, 2001). For more information about this process see *APPENDIX C:* .

## 4.4   Model-Based Control Methods

System models are necessary for a variety of different control methods. One of them is *Linear Time-Invariant Controllers,* which is very popular in the electrical, mechanical and aerospace industries. Another example is *Model Predictive Control* (MPC), which has a long history in chemical plants and oil refineries. This multivariable control algorithm uses an internal dynamic model of the process and a history of past control moves for the optimization of the cost function. Generally, model-based control systems demonstrate better control results.

## 4.5   CPOX Reactor Model
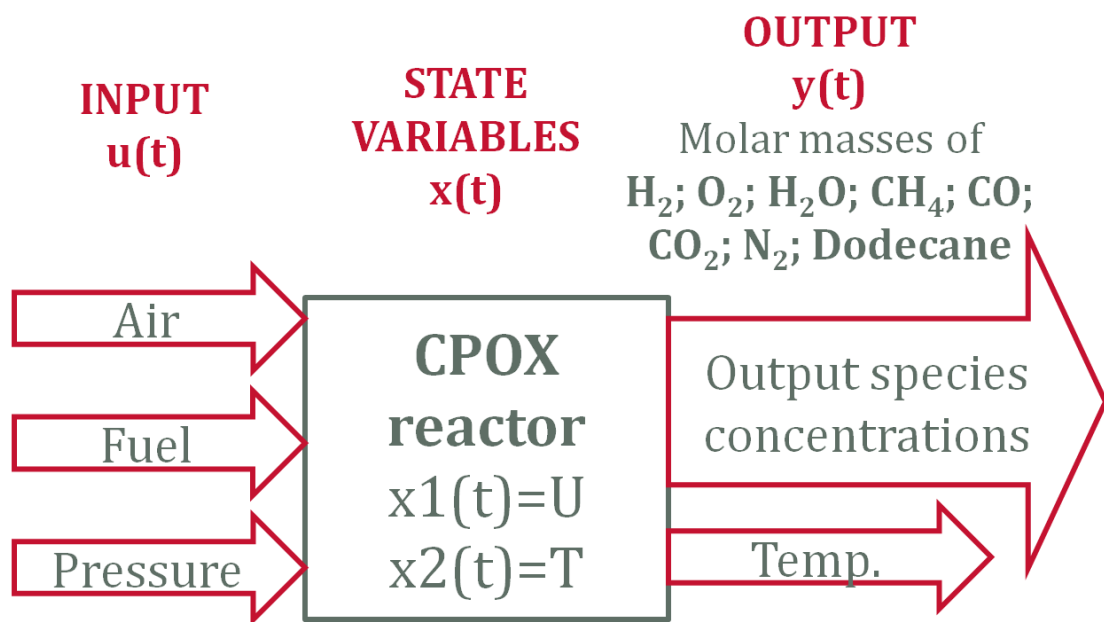


*Figure 4-3 Input/Output representation of the CPOX system model*

A visualization of the model can be observed in *Figure 4-3* Input/Output representation of the CPOX system model. This CPOX reactor DAE model has two state variables (it is a *second order system*) with three inputs and nine outputs. All outputs are dependent on the state variables and inputs.

# 5    CHEMICAL EQUILIBRIUM

Advanced chemistry simulation tools are needed to properly model a CPOX reactor. The main task of this project is to accurately estimate the chemical species that are coming out of the catalytic reactor. For control purposes it is necessary to know the *dynamics* of the system. The question that needs to be answered is: What will be the output of the reactor (species concentrations), to a given input (fuel and air flow)? The chemical equilibrium concept is introduced in detail in this chapter. It is a base for proper estimation of the output species concentration. The Cantera software is the main tool that had been used during reactor modeling in the MATLAB environment. The origins of this software trace back to the 80's and the STANJAN program that implemented the *Element-Potential Method* – a powerful tool for chemical equilibrium calculations.


## 5.1    Theory behind chemical equilibrium

In chemical processes the *chemical equilibrium* is defined as a state in which the chemical activities or concentrations of the products and reactants **do not have net change over time** (Wikipedia_Contributors, Chemical equilibrium, 2009). This basic chemistry principle states that the forward chemical processes proceed at the same rate as their reverse reaction. The *dynamic equilibrium* happens when the reaction rates for forward and reverse processes are not zero but, being equal, there are no net changes in any of the reactant or product concentrations. The concept of chemical equilibrium was developed after Berthollet (1803) found that some chemical reactions are reversible. Below, a few basic concepts connected to chemical equilibrium are introduced.

Law of Mass Action

Consider a thermodynamic system of the form

$$\alpha A + \beta B \rightleftharpoons \sigma S + \tau T,$$
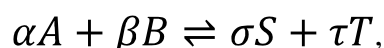
Where $\alpha$ is the number of moles of chemical species $A$ etc., such that $\alpha, \beta, \sigma$ and $\tau$ represent a balanced chemical equation.

Equilibrium Constant

Define equilibrium constant $K_c$ as follows

$$K_c = \frac{[S]^\sigma [T]^\tau}{[A]^\alpha [B]^\beta},$$

where $[A]$ is the *concentration* of species $A$ etc. For solids and pure liquids, in a concentration equal to one, and for solutions, it is in units of moles per liter. For ideal gasses the concentration is defined in terms of *partial pressures*.

LeChatelier's Principle

If the conditions of a system, originally at equilibrium, are changed, the system will, if possible, shift in a direction to restore the original equilibrium conditions (Dvorak, Introduction to Chemical Equilibrium, 2008).

LeChatelier's Principle accounts for

- changes in pressure,
- changes in temperature,
- changes in composition.

## 5.2   STANJAN and the Element-Potential Method

The solution of chemical equilibrium problems has posed a tough challenge for numerical computation. The problem may be formulated in several ways. If the concept of equilibrium constants is being used, then it is necessary to identify the set of reactions that take place and to determine the associated equilibrium constants. The next step is to solve a set of nonlinear algebraic equations for the mol numbers of each species. This might prove to be difficult if the system is large. Other methods based on the minimization of the Gibbs function (*Gibbs free energy*) adjust the mols of each species, consistent with atomic constraints, until the minimum Gibbs function state is found. Many variables are involved in this approach and great care must be take to be sure that all mols are non-negative (Reynolds, 1986).

The method of element potentials uses theory to relate the mol fractions of each species to quantities called element potentials. There is one element potential for each independent atom in the system and these element potentials, plus the total number of mols in each phase, are the only variables that must be adjusted for the solution. In large problems this is a much smaller number than the number of species, therefore far fewer variables need be adjusted.

STANJAN is the first software package to have implemented this method. In the mid 1980's it was a big step forward for the chemical science community. It is called STANJAN because of its roots at the Stanford University and its connection with the JANAF thermochemical data tables. The National Institute of Standards and Technology (NIST) regularly publish *NIST-JANAF Thermochemical Tables*. These tables cover the thermodynamic properties over a wide temperature range with single-phase and multiphase tables for the crystal, liquid, and ideal gas states (Journal of Physical and Chemical Reference Data, 2007).

STANJAN software provides an efficient algorithm for minimizing the free energy of the mixture to find the equilibrium state. It is also designed to handle multiple condensed phases using surface kinetics to identify non-gas phases. The assumption of ideal gases is made for gas phase mixture and condensed phases are treated as ideal solutions. Specific heats are temperature-dependent. The minimum Gibbs function is calculated using constraints on atom population state parameters. The Gibbs function of a system can be express as

$$G = \sum_{j=0}^{S} \bar{g}_j N_j,$$

where $\bar{g}_j$ is the partial molar Gibbs function, $N_j$ is the number of moles in species $j$, and $S$ is the total number of species in the system. Treating each phase as either a mixture of ideal gases or as an ideal solution, the partial molar Gibbs functions are given by

$$\bar{g}_j = g_j(T,p) + RT \ln x_j,$$

where, $g_j(T,p)$ is the Gibbs function of pure $j$ specie evaluated at the system temperature and pressure, $x_j$ is the mol fraction of species $j$ in its phase, and $R$ is the *ideal gas constant* ($8.314\,472(15)\,\mathrm{J\,K^{-1}\,mol^{-1}}$). Applying the Lagrange multipliers method, the mol fraction of each species can be found from

$$x_j = exp\left(-\frac{\bar{g}_j}{RT} + \sum_{i=1}^{a} \lambda_i n_{ij}\right),$$

where, $\lambda_i$ is the Lagrange multiplier for atom $i$ and $n_{ij}$ is the number of $i$ atoms in $j$ molecule and $a$ is the number of different elements (atom types) present in the system. This equation is the **main result of the theory of element potentials** for mixture of ideal gases or for ideal solution and is used to find the product's composition at the equilibrium state (Jangsawang, Klimanek, & Gupta, 2006). For more information about the STANJAN algorithms, theory behind the Lagrange multipliers etc., see the *References* section of this paper.

## 5.3   CHEMKIN EQUIL

CHEMKIN is a software tool for solving complex chemical kinetics problems. It solves thousands of reaction combinations to develop a comprehensive understanding of a particular process, which might involve multiple chemical species, concentration ranges, and gas temperatures. The computational capabilities of CHEMKIN allow for a complex chemical process to be studied in detail, including intermediate compounds and trace compounds (Wikipedia_Contributors, CHEMKIN, 2008).

EQUIL is an application that calculates the chemical equilibrium state for a system consisting of one or more phases. The program is a CHEMKIN implementation of the STANJAN software. The application provides an interface that accepts input in CHEMKIN format and calls routines in the STANJAN library to find the equilibrium state (Kee, Rupley, & Miller, 2000).

## 5.4   CANTERA

Cantera is software that allows advance chemistry simulations. It creates objects that represent gas mixtures. Every gas entity is characterized by multiple properties (pressure,

temperature, enthalpy etc.) that precisely simulate the real-life situation. The chemical equilibrium calculations are based on the CHEMKIN EQUIL package. Cantera's chemical equilibrium solver uses an element potential method.

Every object created in Cantera implements *GRI-Mech 3.0*. It is a 53-species, 325-reaction natural gas combustion mechanism which was developed through the cooperation of the University of California at Berkley, Stanford University and Sandia National Laboratory. GRI-Mech is essentially a list of elementary chemical reactions and associated rate constant expressions. Most of the reactions listed have been studied in the laboratory, so the rate constant parameters mostly have direct measurements behind them (Smith, Golden, Frenklach, Moriarty, & Eiteneer).

Cantera adopts the following convention: only one of the set (temperature, density, mass fractions) is altered by setting any single property. In particular:

- setting the temperature is done by holding density and composition fixed (the pressure changes),
- setting the pressure is done by holding temperature and composition fixed (the density changes),
- setting the composition is done by holding temperature and density fixed (the pressure changes).

For more information about the available options and conventions consult Cantera's tutorial files.

## 5.4.1  MATLAB Cantera toolbox

Cantera is available either in the Python or MATLAB environment. For detailed installation instructions follow the manual or consult the Control Wiki (see *APPENDIX C:* ).

Because of the control focus of the project the MATLAB Cantera toolbox was used.

# 6  CATALYTIC PARTIAL OXIDATION (CPOX) REACTOR MODEL

This chapter contains a detailed description of the model used in this project. The geometry and materials used to build the CPOX reactor will be introduced as well as a brief introduction to the theory behind fuel reforming and the algorithm used to calculate the C/O ratio.

## 6.1  Fuel reforming overview

Fuel cells can be powered by hydrogen produced either externally or internally in the fuel cell system. There are few ways to produce hydrogen by fuel reforming (see *Table 6-1 Different examples of fuel reforming reactions*):

- Steam reforming (the most commonly used way to manufacture hydrogen industrially, endothermic reaction),
- Partial oxidation (exothermic reaction),
- Auto Thermal Reforming (oxidation in first zone, steam reforming in second zone).

Because Solid Oxide Fuel Cells work in high temperatures, the internal CPOX (Catalytic Partial Oxidation) reactors are being used to produce hydrogen. In these systems, waste heat from the stack is channeled to the fuel processor to help with the reforming.
Partial oxidation reforming is an exothermic reaction that combines a hydrocarbon fuel with some oxygen to *partially oxidize* (or partially combust) the fuel into a mixture of CO and $H_2$, usually in the presence of a catalyst. In POX (or *partial* combustion), a hydrocarbon fuel combines with less than the stochiometric amount of $O_2$, such that *incomplete* combustion products CO and $H_2$ are formed (O'Hayre, Cha, Colella, & Prinz, 2006). Operating in these conditions is sometimes called operating *fuel rich* or $O_2$ *deficient*. For any hydrocarbon fuel, a general formula for POX is defined as

$$C_x H_y + \frac{1}{2} x O_2 \leftrightarrow x CO + \frac{1}{2} y H_2.$$
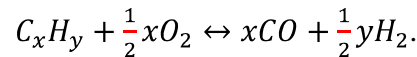
Similarly to Steam Reforming, the hydrogen yield from POX can be further increased by shifting the CO in the outlet to $H_2$ via the Water Gas Shift reaction.

*Table 6-1 Different examples of fuel reforming reactions (O'Hayre et al., 2006)*

| Reaction type | Stoichiometric formula | $\Delta \widehat{h}^0_{rxn}$(kJ/mol) |
|---|---|---|
| Steam Reforming | $CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$ | +165.2 |
| Water-Gas Shift | $CO + H_2O \rightarrow CO_2 + H_2$ | -41.2 |
| Partial Oxidation | $CH_4 + \dfrac{1}{2}O_2 \rightarrow CO + 2H_2$ | -35.7 |
| Partial Oxidation | $CH_4 + O_2 \rightarrow CO_2 + 2H_2$ | -319.1 |
| Methane Combustion | $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ | -880 |
| Hydrogen Combustion | $H_2 + \dfrac{1}{2}O_2 \rightarrow H_2O$ | -284 |

## 6.2 Calculating the C/O ratio

The CPOX reactor runs on oxygen from air and fuel. In this case it is a high hydrocarbon - Dodecane $C_{12}H_{26}$ ($CH_3(CH_2)_{10}CH_3$). The catalytic reactor gets a fuel mix at the input. Depending on the inlet stream flow of the air (input power of the blower) and fuel, different *carbon to oxygen ratios* (C/O ratios) can be reached.

*Table 6-2 Components of dry air, their volume percentages and molecular masses (Wikipedia, 2008)*

| Components in Dry Air | Volume percentage | Molecular Mass M [g/mol] |
|---|---|---|
| Nitrogen (N₂) | 78.09% | 28.02 |
| Oxygen (O₂) | 20.95% | 32.00 |
| Argon (Ar) | 0.93% | 39.94 |
| Carbon dioxide (CO₂) | 0.03% | 44.01 |

The air molar mass is calculated according to the formula

$$M_{AIR} = 0.7809 \cdot M_{N_2} + 0.2095 \cdot M_{O_2} + 0.0093 \cdot M_{Ar} + 0.0003 \cdot M_{CO_2}.$$

The fuel molar mass is the sum of molecular masses of carbon and hydrogen in the Dodecane compound:

$$M_{DODECANE} = 12 \cdot M_C + 24 \cdot M_H,$$

where $M_C = 12.011[\frac{g}{mol}]$ and $M_H = 1.008[\frac{g}{mol}]$.

The C/O ratio is defined as the ratio of mole flow rates of carbon and oxygen in the inlet streams:

$$C/O_{ratio} = \frac{\dot{M}_C}{\dot{M}_O} = \frac{12 \cdot \frac{\dot{m}_{C_{12}H_{26}}}{M_{C_{12}H_{26}}}}{2 \cdot \frac{\dot{m}_{AIR}}{M_{AIR}}},$$

where $\dot{m}_x$ is a mass flow rate in [g/s]. A few examples of C/O ratio calculation are given in *Table 6-3 Numerical examples of C/O ratio calculation*.

*Table 6-3 Numerical examples of C/O ratio calculation*

| Fuel flow rate [g/s] | Air flow rate [g/s] | $\dot{M}_C$ [mol/s] | $\dot{M}_O$ [mol/s] | C/O ratio |
|---|---|---|---|---|
| 0.2708 | 1.444 | $1.59 \times 10^{-3}$ | $4.98 \times 10^{-2}$ | 0.1914 |
| 0.2572 | 1.444 | $1.51 \times 10^{-3}$ | $4.98 \times 10^{-2}$ | 0.1818 |
| 0.2843 | 1.444 | $1.67 \times 10^{-3}$ | $4.98 \times 10^{-2}$ | 0.2009 |

The spreadsheet example of C/O ratio calculation is available in *APPENDIX B: Microsoft Excel Implementations*.

## 6.3   Model description



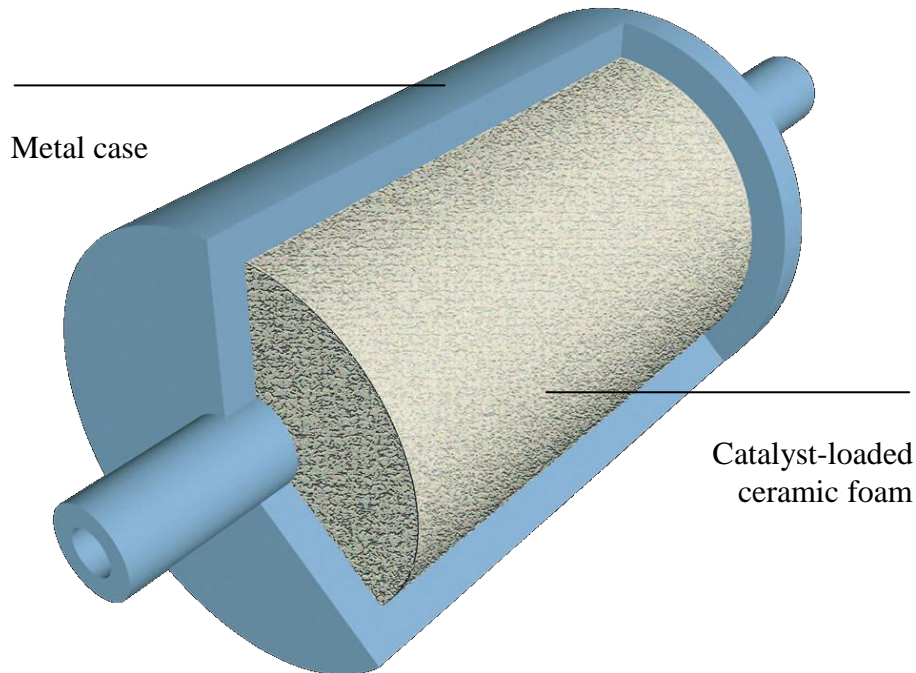Metal case

Catalyst-loaded ceramic foam

*Figure 6-1 Illustration of a catalytic reactor (Zhu et al., 2006)*

The model that was used for this control study is based on the research conducted at the Colorado School of Mines in 2006 for the InnovaTek Company (Zhu, Kee, & Harrold,

2006). Geometry and properties of this catalytic reactor are described in *Table 6-4 Geometry and parameters of the modeled CPOX reactor*.

*Table 6-4 Geometry and parameters of the modeled CPOX reactor*

| Symbol | Description | Default value | Unit |
|---|---|---|---|
| $\emptyset_{IN}$ | Outer diameter | 0.025 | m |
| $\emptyset_{OUT}$ | Inner diameter | 0.021 | m |
| $\overline{\overline{H}}$ | Outside height | 0.030 | m |
| $\overline{\overline{T}}$ | Wall thickness | 0.002 | m |
| $A_s$ | Outer surface area | 0.0033 | m$^2$ |
| $UA$ | Overall Convective Heat Transfer Coefficient | 0.0334 | W/K |
| $T_\infty$ | Environment temperature | 873 | K |

In this model the main focus is on the system dynamics in order to show that the thermal response depends on properties of the gas, foam and metal casing of the reactor. To create a reliable and reasonably fast model, a number of simplifying assumptions were applied:

- Chemistry remains in local equilibrium (gas within the reactor remains at chemical equilibrium at the reactor temperature and pressure);
- Thermal response of the solid materials is treated in lumped-capacity form;
- Gas within the pore spaces is treated as a perfectly stirred reactor at uniform pressure and volume;
- The gas and the solid materials are at the same temperature;
- Dodecane in a fuel stream is completely consumed within the CPOX reactor.

The model is formulated in terms of mass- and energy-conservation equations, which are solved computationally. The energy equation for the system is defined as

$$\frac{dH}{dt} = \dot{m}_{IN} h_{IN} - \dot{m}_{OUT} h_{GAS} - Q_{LOSS},$$

with variables described in *Table 6-5 Conservation equation symbols and units*.

*Table 6-5 Conservation equation symbols and units*

| Symbol | Description | Unit |
|---|---|---|
| $\dot{m}_{IN}$ | Fuel mix flow (mass flow rate) | kg/s |
| $h_{IN}$ | Fuel mix specific enthalpy | J/kg |
| $\dot{m}_{OUT}$ | Mass flow out | kg/s |
| $h_{GAS}$ | Gas specific enthalpy | J/kg |
| $Q_{LOSS}$ | Heat loss | W |

Heat loss ($Q_{loss}$) is defined as

$$Q_{loss} = UA_s(T - T_\infty),$$

where $U$ is an overall heat-transfer coefficient (10 W/m$^2$-K), $A_s$ is the effective surface area and $T_\infty$ is the external fluid temperature.

As the *Figure 6-1* Illustration of a catalytic reactorportrays it, the solid material of the CPOX reactor consists of a metal case and ceramic foam that supports the catalyst. The total enthalpy of the solids may be written as

$$H_{SOLID} = m_{STEEL}C_{pSTEEL}T + m_{FOAM}C_{pFOAM}T,$$

$$m_{STEEL} = \rho_{STEEL}V_{STEEL},$$

$$m_{FOAM} = \rho_{FOAM}V_{FOAM},$$

with variables described in *Table 6-6* Total enthalpy of solids symbols, default values and units.

*Table 6-6 Total enthalpy of solids symbols, default values and units*

| Symbol | Description | Default value | Unit |
|---|---|---|---|
| $m_{STEEL}$ | Mass of reactor steel walls | 0.0458 | kg |
| $\rho_{STEEL}$ | Density of stainless steel | 8000 | kg/m$^3$ |
| $V_{STEEL}$ | Volume of steel comprising chamber walls | 5.7208×10$^{-6}$ | m$^3$ |
| $C_{pSTEEL}$ | Specific heat capacity of stainless steel | 500 | J/kg-K |
| $k_{STEEL}$ | Thermal conductivity of stainless steel | 21 | W/m-K |
| $m_{FOAM}$ | Mass of foam | 0.0252 | kg |
| $\rho_{FOAM}$ | Density of foam (ceramic AL$_2$O$_3$) | 4000 | kg/m$^3$ |
| $V_{FOAM}$ | Volume of foam inside cavity | 6.3038×10$^{-6}$ | m$^3$ |
| $C_{pFOAM}$ | Specific heat capacity of foam (ceramic AL$_2$O$_3$) | 880 | J/kg-K |
| $\varphi$ | Porosity of catalytic foam | 0.30 | - |
| $T$ | Temperature of the reactor and gases | *state variable* | K |

The samples of the MATLAB code with the MATLAB variables names can be found in *APPENDIX A*: MATLAB Implementations in the CPOX reactor properties section.

# 7 DIFFERENTIAL ALGEBRAIC EQUATIONS

## 7.1 Theory behind DAEs

A differential equation is an equation that contains an unknown function and one or more of its derivatives (Steward, 2008). In a DAE formulation it is not necessary to formulate explicit equations for the time-derivatives of each state. Instead we can, for example, formulate the conservation of energy.

A first order DAE in its most general form is given by

$$F(t, x, x') = 0, \ t_0 \leq t \leq t_f,$$

where $x = x(t)$, the unknown function, and $F = F(t, u, v)$ have $N$ components, denoted by $x_i$ and $F_i, i = 1, 2, \ldots, N$, respectively (Campbell, 2008). DAEs are a generalization of ordinary differential equations (see *Table 7-1* Ordinary Differential Equations and Differential Algebraic Equations). While the standard-form ODE can be written as a DAE, the more general DAE form admits problems that can be quite different from a standard-form ODE.

*Table 7-1 Ordinary Differential Equations and Differential Algebraic Equations*

| ODE | DAE |
|---|---|
| Ordinary Differential Equations | Differential Algebraic Equations |
| $y' = f(t, y)$ | $M(t, y)y' = f(t, y)$ |
| $M(t, y) = 1$ | |

The systems of equations that govern certain phenomena (in electrical circuits, chemical kinetics, etc.) contain a combination of differential equations and algebraic equations. The differential equations are responsible for the dynamical evolution of the system, while the algebraic equations serve to constrain the solutions to certain manifolds. It is therefore of some interest to study the solutions of such *differential-algebraic equations* (DAEs).

When physical problems are simulated, the model often takes the form of a DAE depicting a collection of relationships between variables of interest and some of their derivatives. These relationships may even be generated automatically by a modeling or simulation program. The variables usually have a physical significance (Brenan, Cambell, & Petzold, 1996). Changing the model of a first order system in an ordinary differential equation (ODE) formulation

$$F\big(t, y(t), y'(t)\big) = 0,$$

where $F$ and $y$ are vector valued, to an *explicit* or *normal* form

$$y'(t) = f(t, y(t)),$$

may produce less meaningful variables. In the case of computer-generated or nonlinear models, it may be time consuming or impossible to obtain an explicit model. Parameters are present in many applications. Changing parameter values can alter the relationships between variables and require different explicit models with solution manifolds of different dimensions. If the original DAE can be solved directly, then it becomes easier for the scientist or engineer to explore the effect of modeling changes and parameter variation. It also becomes easier to interface modeling software directly with design software. These advantages enable researchers to focus their attention on the physical problem of interest. There are also numerical reasons for considering DAE'a. The change to explicit form, even if possible, can destroy sparsity and prevent the exploitation of system structure.

## 7.2 CPOX reactor mathematical model

To solve the problem, the equations described in chapter 6.3 must be transformed into a DAE form accepted by the MATLAB programming environment. In this model the changes in total internal energy ($U_{total}$) and in temperature ($T$) are described. The problem statement is derived from the basic energy equation

$$\boxed{\frac{dU}{dt} = \frac{dQ}{dt} + \frac{dW}{dt}}.$$

The work done on the system is minimal so the term $\frac{dW}{dt}$ is ignored. The CPOX reactor system is described by a set of two equations representing the total internal energy and the change in this property. Total internal energy ($U_T$) derives as follow

$$U_{total} = m_s C_s T + u_g(T) m_g \,,$$

where $m_s$ and $m_g$ represent mass of solids and mass of gas; $C_s$ is a specific heat capacity of solid materials in the reactor (steel cover plus foam) and $u_g$ corresponds to specific internal energy of gas within the reactor. The change in the total internal energy is formulated as

$$\frac{dU_{total}}{dt} = \dot{m}_{in} h_{in} - \dot{m}_{out} h_g - Q_{loss},$$

where $\dot{m}_{in}$ and $\dot{m}_{out}$ correspond to inlet mass flow (fuel mix flow) and outlet mass flow (CPOX gas flow); $h_{in}$ and $h_{gas}$ are fuel mix specific enthalpy and gas specific enthalpy; $Q_{loss}$ stands for heat loss. Because $\dot{m}_{in} = \dot{m}_{out} = \dot{m}$ the formula is modified to

$$\frac{dU_{total}}{dt} = \dot{m}\left(h_{in} - h_g\right) - Q_{loss}.$$

The gas specific enthalpy is defined as $h_g = u_g(T) + P/\rho_g(T)$, where $P$ represents pressure and $\rho_g$ stands for density of the gas within the reactor. A perfect-gas equation of state is used to determine the gas density from temperature, pressure and composition. After a substitution the change in total internal energy is defined as follows

$$\frac{dU_{total}}{dt} = \dot{m}\left(h_{in} - u_g(T) - P/\rho_g(T)\right) - Q_{loss}.$$

Heat loss is defined as $Q_{loss} = UA(T - T_\infty)$, where $UA$ stands for overall convective transfer coefficient, $T_\infty$ represents environment temperature and $T$ is a temperature of the reactor and the gases. Change in total internal energy formula ends up as

$$\frac{dU_{total}}{dt} = \dot{m}\left(h_{in} - u_g(T) - P/\rho_g(T)\right) - UA(T - T_\infty).$$

In this DAE system the mass matrix is defined as $M = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}$. The **state velocity equation** for this system derives as follows

$$\boxed{\frac{dU_{total}}{dt} = \dot{m}\left(h_{in} - u_g(T) - P/\rho_g(T)\right) - UA(T - T_\infty)}.$$

The algebraic constrains for the system are identified by the total internal energy definition ($U_{total} = m_s C_s + u_g(T)m_g$). After substitution for the gas mass ($m_g = \rho_g(T)V_g$, where $V_g$ is a volume of the gas within reactor) and multiplication by the mass matrix, the **algebraic constrains** derive as follows

$$\boxed{0 = U_{total} - m_s C_s T - u_g(T)\rho_g(T)V_g}.$$

The MATLAB Cantera functions that were used to calculate parameters such as density are described in *MATLAB Cantera toolbox functionality*.

# 8 MODEL TESTING

This chapter will present the results from the model. The model could not be validated because the test-stand for this experiment is a work-in-progress at the *Colorado Fuel Cell Center*.

The CPOX reactor problem is solved as initial value problem with consistent initial conditions.

## Initial Value Problem

In mathematics, including the field of differential equations, an initial value problem is an ordinary differential equation together with the specified value, called the initial condition, of the unknown function at a given point in the domain of the solution. In physics or other sciences, modeling a system frequently amounts to solving an initial value problem; in this context, the differential equation is an evolution equation specifying how, given initial conditions, the system will evolve with time.

## Consistent Initial Conditions

For an accurate solution, the *consistent initial conditions* need to be found. This will guarantee that the solution to the initial value problem will be found.

## Error longitude reduction

To make the calculations more precise, adjustments of the algebraic constrains were applied. The solution for algebraic constrains is zero, so multiplying by any number will not affect the result.

## 8.1 Implicit problem formulation (MATLAB *fzero* solution)

The implicit formulation of the CPOX reactor problem was solved using the MATLAB `fzero` function (Zhu, Kee, & Harrold, 2006). An example of a heat-up transient can be observed in *Figure 8-1* Temperature history for an example CPOX heat-up transient.
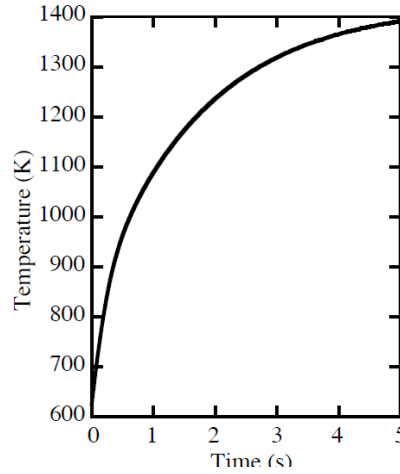
*Figure 8-1 Temperature history for an example CPOX heat-up transient (Zhu et al., 2006)*

## 8.2   DAE problem formulation (MATLAB *ode15s* solution)

The MATLAB `ode15s` is and efficient multistep solver designed for stiff type problems and provides medium order of accuracy. It uses the *backward differential formulas (BDF)* algorithm to estimate the solutions of DAEs.

Backward differential formulas

*Backward differential formulas (BDF)* are the most popular and hence best understood class of linear multistep methods for general DAE's (Brenan, Cambell, & Petzold, 1996). The simplest first order BDF method is the implicit Euler method, which consist of replacing the derivatives in

$$x' = f(x, y, t)$$
$$0 = g(x, y, t),$$

By backward difference

$$F\left(t_n, y_n, \frac{y_n - y_{n-1}}{t_n - t_{n-1}}\right) = 0.$$

The resulting system of nonlinear equations for $y_n$ at each time step is then usually solved by Newton's method. The Implicit Euler method is not accurate when the stepsize changes. Much of the success of BDF solver codes has undoubtedly been due to the extraordinary stability and accuracy properties of BDF applied to DAE's, including many higher index DAE's.

26

## 8.3    Model Results

### 8.3.1    Startup Transients

The system steady-state conditions are reached when the changes in the output signal are **less than 1% over 500 ms**. The data point when this state is reached is marked on the plot by a red cross.
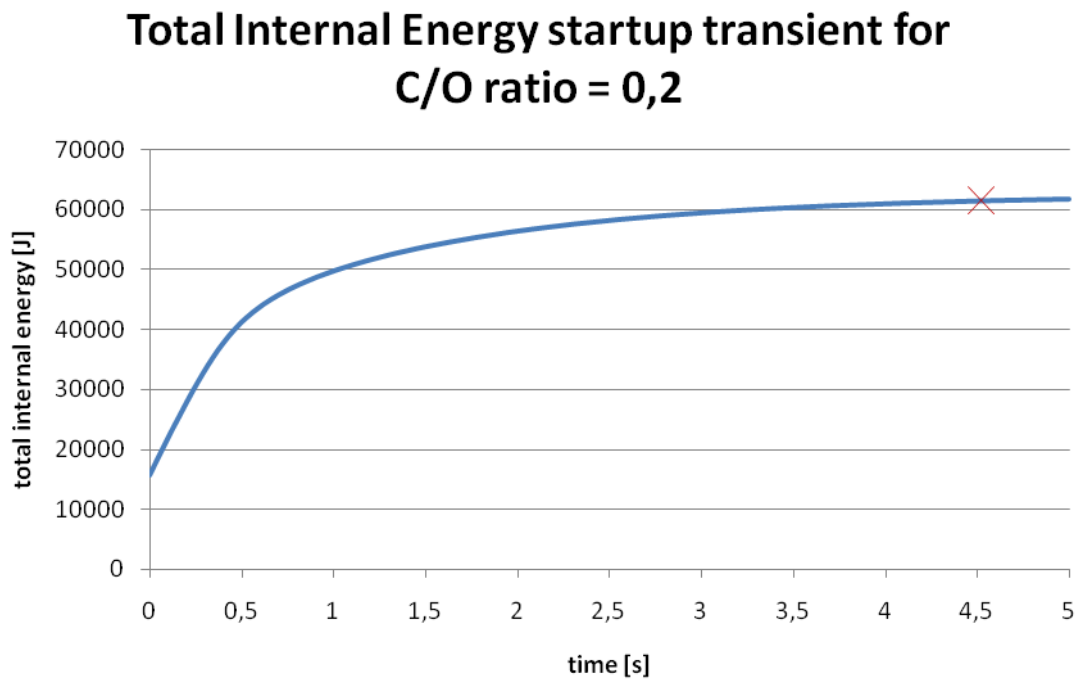


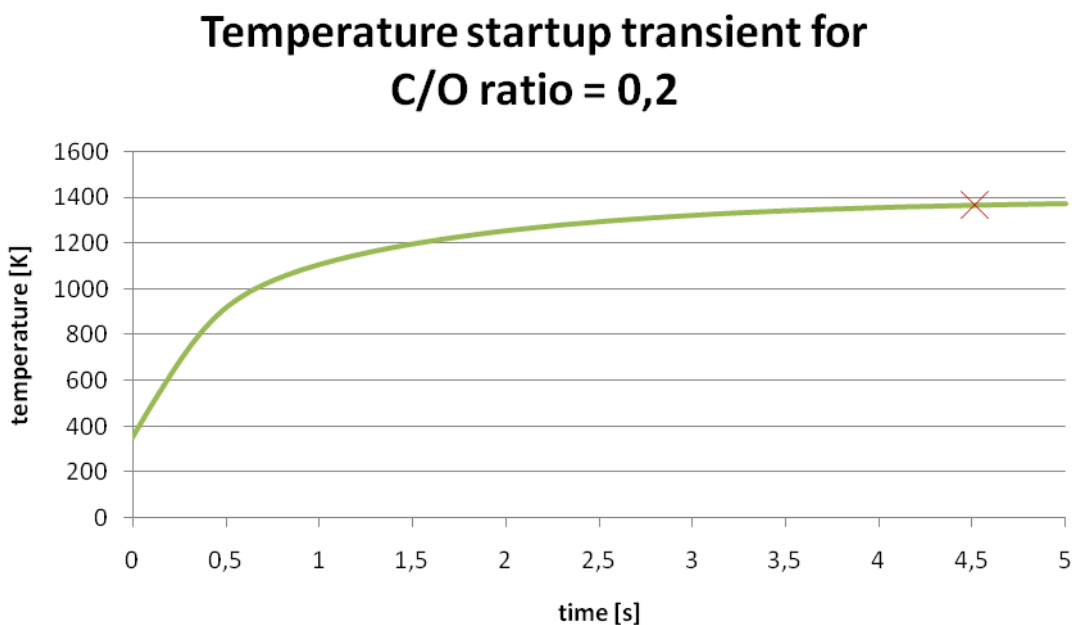*Figure 8-2 Total Internal Energy transient for 0.2 C/O ratio*



*Figure 8-3 Temperature transient for 0.2 C/O ratio*

For C/O ratio = 0,2 the model reaches the defined steady-state for total internal energy and temperature after 4,5 seconds. For C/O ratio = 0,1 the steady-state is attained after 3

seconds. With a bigger C/O ratio (less oxygen for the reactions), the time for the system to reach the steady-state is extended. *Table 8-1* Steady-state conditions for different CPOX reactor configurations presents steady-state conditions for different C/O ratios.

*Table 8-1 Steady-state conditions for different CPOX reactor configurations*

| C/O ratio | Fuel flow [kg/s] | Air flow [kg/s] | Time [s] | U [J] | T [K] |
|-----------|------------------|-----------------|----------|--------|-------|
| 0,1 | 4,02E-03 | 4,10E-02 | 3,17 | 110254 | 2446 |
| 0,2 | 4,02E-03 | 2,05E-02 | 4,51 | 61506 | 1364 |
| 0,4 | 4,02E-03 | 1,03E-02 | 7,14 | 61371 | 1361 |
| 0,8 | 4,02E-03 | 5,13E-03 | 10,36 | 48675 | 1079 |
| 1,6 | 4,02E-03 | 2,56E-03 | 11,38 | 35895 | 796 |

Graphs for different CPOX reactor configuration are available in *APPENDIX C: Graphs.*

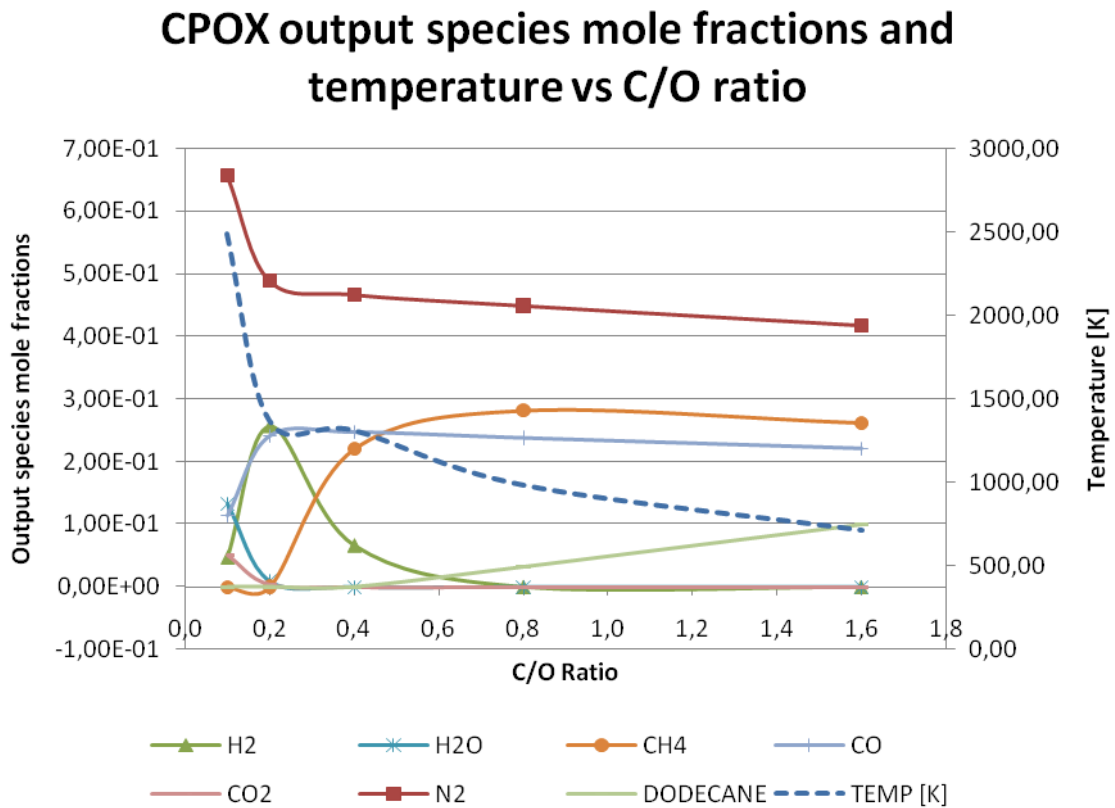### 8.3.2 Species concentrations



*Figure 8-4 CPOX output species mole fractions and temperature vs. C/O ratio (fuel rate 4,02E-03 kg/s)*

The desired C/O ratio of 0.2 gives the biggest yield of hydrogen. The concentration of output species for different C/O ratios and the steady-state temperature variations can be observed in *Figure 8-4* CPOX output species mole fractions and temperature vs. C/O ratio. Graphs for output species mole fractions and temperature vs. C/O ratio for different air and fuel rates are available in *APPENDIX C*: Graphs.

*Figure 8-5* CPOX Output Species concentrations in startup transient (C/O ratio = 0,2)Figure *8-6* Nitrogen concentrations in startup transient (C/O ratio = 0,2) present the change in species mole fractions vs. time. The maximum yield of hydrogen is reached after about 2 seconds.
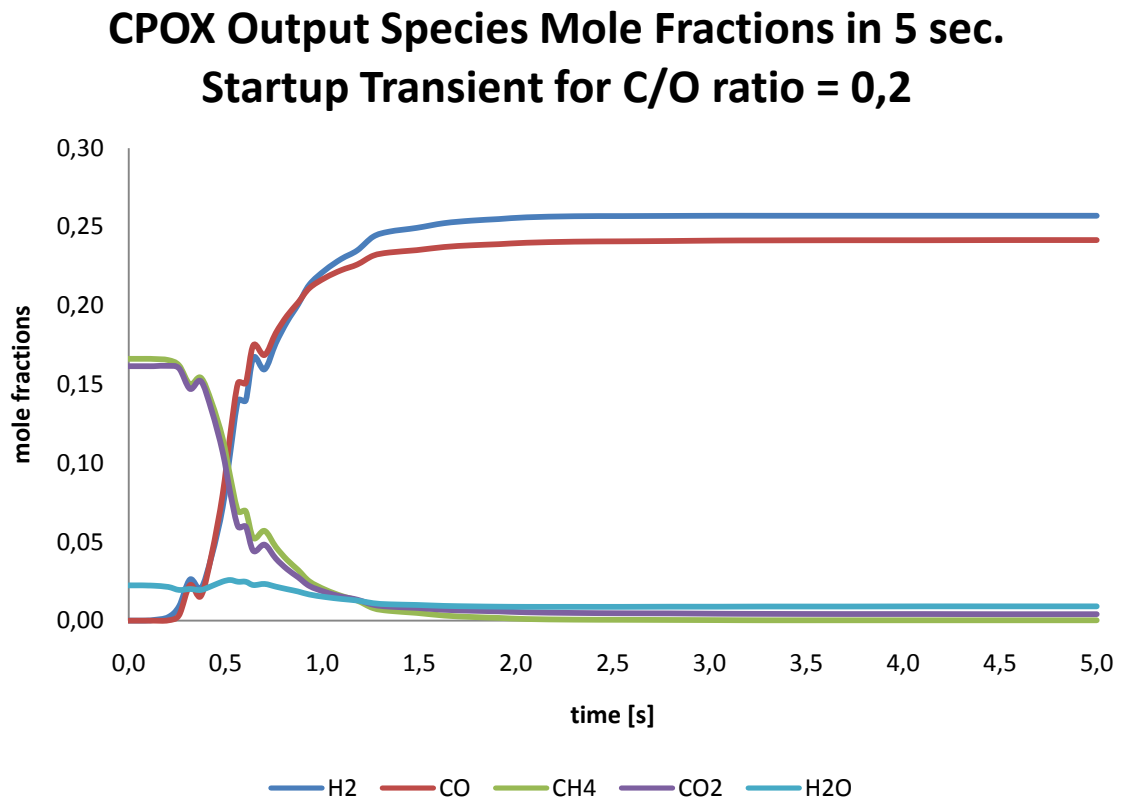
## CPOX Output Species Mole Fractions in 5 sec. Startup Transient for C/O ratio = 0,2



*Figure 8-5 CPOX Output Species concentrations in startup transient (C/O ratio = 0,2)*
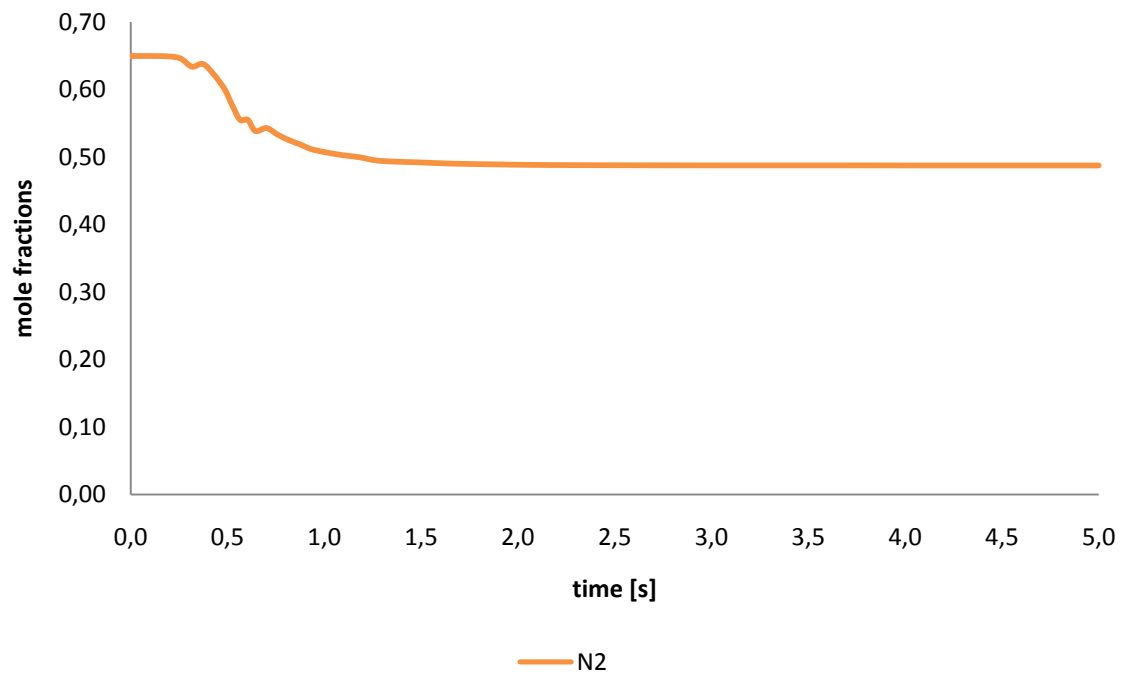
*Figure 8-6 Nitrogen concentrations in startup transient (C/O ratio = 0,2)*

# 9 FUTURE PROJECT DEVELOPMENT

*Figure 9-1* Multivariable, model-based control architecturedepicts the final formulation of the whole SOFC model for control purposes.
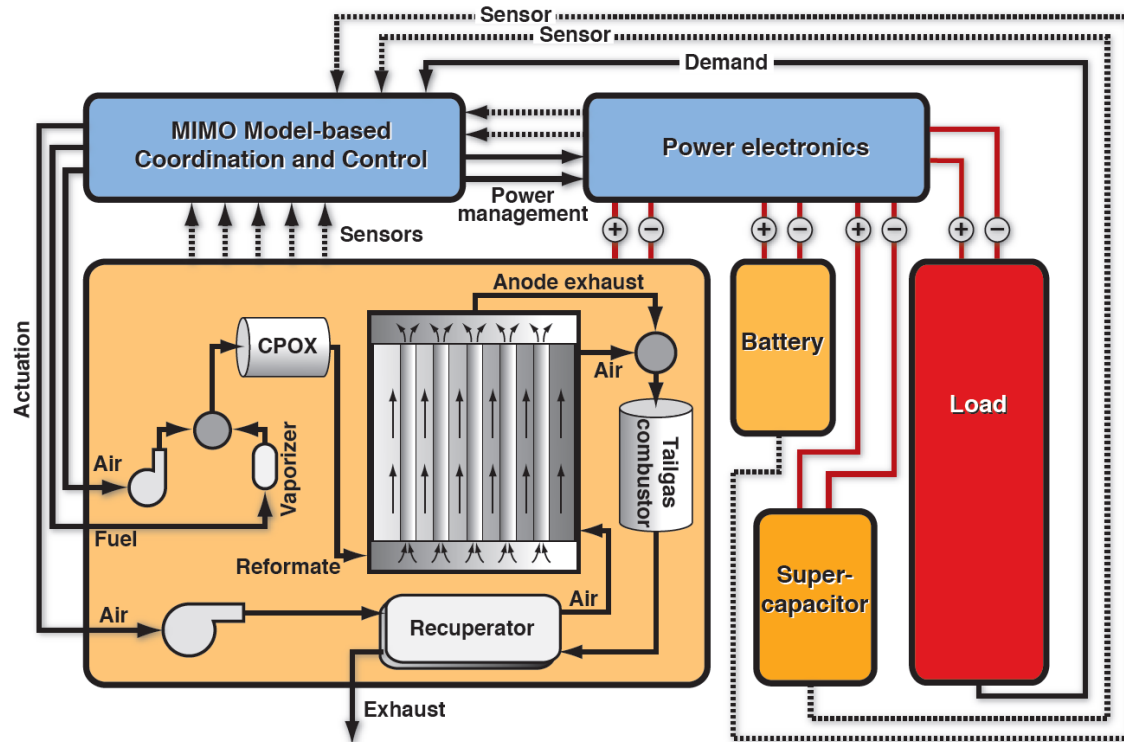


*Figure 9-1 Multivariable, model-based control architecture (Moore, 2006)*

This project will be continued in cooperation with the *AGH University of Science and Technology*. The future work will include:

- Further development of the DAE based CPOX reactor model

  This work will allow a control study of the CPOX model. The linearization of the model using *pseudorandom binary sequence (PRBS)* persistent excitation will be conducted. Different result data representation methods will be implemented and an application with a user friendly interface will be developed (*MATLAB GUIDE tools*).

- MATLAB Simulink implementation

  The DAE based catalytic reactor model will be implemented in the graphical block diagramming Simulink environment. This will be achieved by using the Level-1 and Level-2 S - functions. Simulink formulation will allow a more advanced control study of the system using varying inputs (air, fuel flow; C/O ratio control).

- Solid carbon species formation at low temperatures

  There are two routes to carbon formation. One, called coking, is the formation of graphitic carbon structures, which are catalyzed by Nickel. The other is gas-phase molecular weight growth, which usually leads to polyaromatic deposits. The

kinetics of both are complicated. However, it is at least reasonable to predict the onset of carbon formation by including solid carbon (graphite) in the equilibrium computations (Kee, 2009).
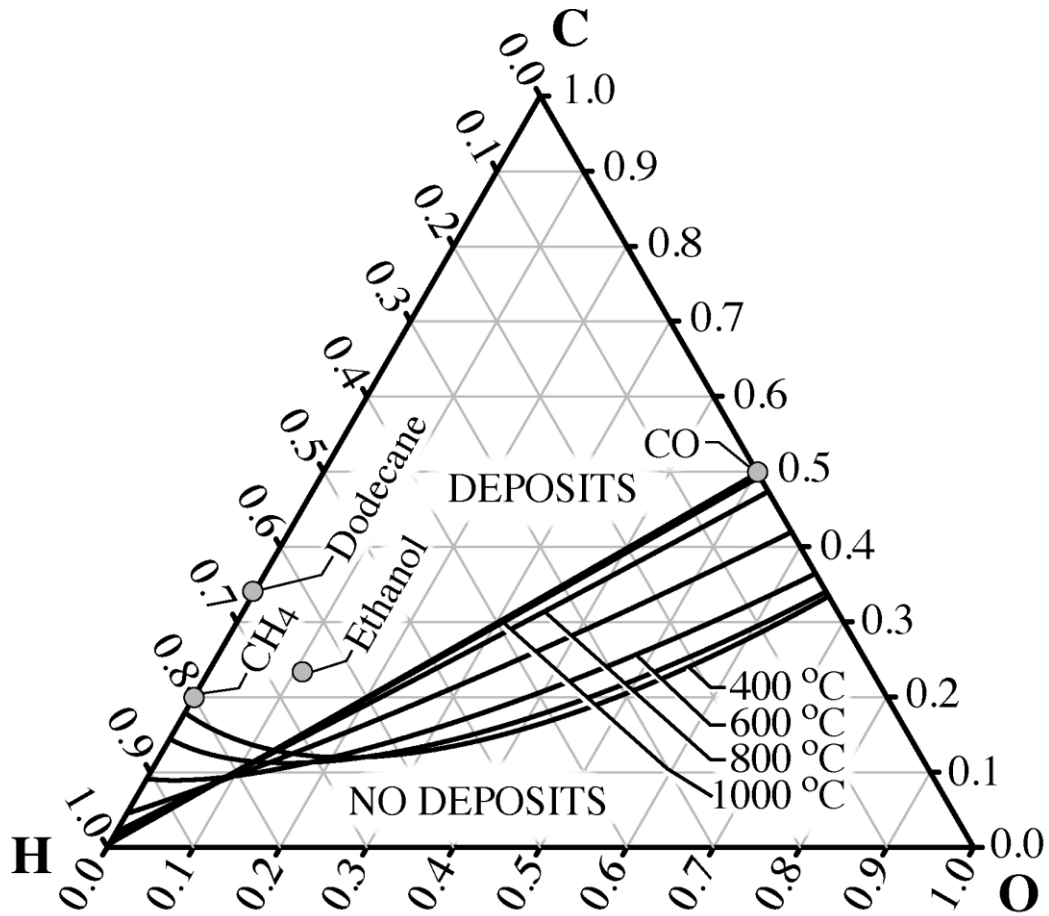


*Figure 9-2 Equilibrium solid-carbon formation in a ternary plot (Kee, 2008)*

- Balance-of-Plant components model development

    BOP components of the SOFC system (air blower, manifold and vaporizer) will be constructed in MATLAB Simulink. The air blower and manifold design will be based on available literature (Pukrushpan, Stefanopoulou, & Peng, Control of Fuel Cell Power Systems: Principles, Modeling, Analysis and Feedback Design, 2004). The vaporizer model development will be done in cooperation with the project industry partner - Protonex[1]. This is crucial for the whole model (CPOX reactor and BOP components) validation in the experiment. The experimental setup is being prepared at the *Colorado Fuel Cell Center (CFCC)*[2].

- Assistance in control strategies development

    Along with model development the different control strategies like *Model Predictive Control (MPC)* will be implemented.

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[1] http://www.protonex.com/
[2] http://www.coloradofuelcellcenter.org/

# 10 CONCLUSIONS

The correct C/O ratio is crucial for establishing optimal efficiency of a CPOX reactor and the whole fuel cell system. As observed in *Figure 8-4* CPOX output species mole fractions and temperature vs. C/O ratio*, control of this parameter will allow maximum hydrogen yield at the C/O ratio of 0,2.

The results of this model are comparable to the work done by other research groups, as presented in *Section 8.1*.

The analysis of the startup transient graphs proves that the speed of the transients is mostly dependent on the input flow rates (the thermal mass of the reactor also has some significance). This is an illustration of the non-linear behavior of the system. In a linear system, the speed of the transients does not depend on the input magnitude (Vincent, 2009).

One reason for some inconsistencies might be the error handling mechanism in Cantera and MATLAB. If error handling in those two environments do not match (one is coarse, the other is fine) it might seriously influence the calculations. The error handling mechanism in MATLAB is easy to check and adjust. Cantera is implemented in Python and there is no direct error handling mechanism control from the MATLAB environment. It is possible that an artifact of Cantera's error control can be observed at the *Figure 8-5* CPOX Output Species concentrations in startup transient (C/O ratio = 0,2) in the small signal disturbances at the beginning of the transient.

The next step of the project will focus on building the controller for the CPOX reactor. Initial control will be on temperature. Thermal limitations of the CPOX reactor will be considered. Because of carbonation issues the reactor is never operated at low temperatures (below 1000°C).

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# APPENDIX A: MATLAB IMPLEMENTATIONS

MATLAB code listing is available as a PDF printout in the *references* directory (references\ APPENDIX A - MATLAB code.pdf).

To get proper results with this DAE formulation, the *vectorized* option in the `ode15s` solver needs to be turned off.

## MATLAB Cantera toolbox functionality

A few of the functions available in MATLAB Cantera toolbox that were used to develop the solution for this problem are described below. Brief help on each of those functions can be displayed by typing

`help (`*`name of the function`*`)`

in the MATLAB environment.

### Calculating the gas density

`density(`*`phase name`*`)`

### Equilibrating

`equilibrate(`*`phase name`*`, `*`option`*`)`

There are few different ways the gas can be equilibrated:

`'TP'` - holding temperature and pressure fixed;

`'UV'` - fixed specific internal energy and specific volume;

`'SV'` - fixed specific entropy and specific volume;

`'SP'` - fixed specific entropy and pressure.

### Obtaining the specific internal energy

`intEnergy_mass(`*`phase name`*`)`

### Obtaining specific enthalpy

`enthalpy_mass(`*`phase name`*`)`

### Displaying the molar concentrations of the species

`moleFractions(`*`phase name`*`)`

# APPENDIX B: Microsoft Excel Implementations

The C/O ratio calculations and the graphs depicting the output species concentration were developed in Microsoft Excel worksheet.

The PDF printout of this worksheet is available in *references* directory:

references\APPENDIX B - 8 Hz CPOX Mdot Fuel Variation - C-O ratio.pdf


The MS Excel worksheets with the code to plot graphs for the startup transients and output species concentrations are available in the *references* directory.
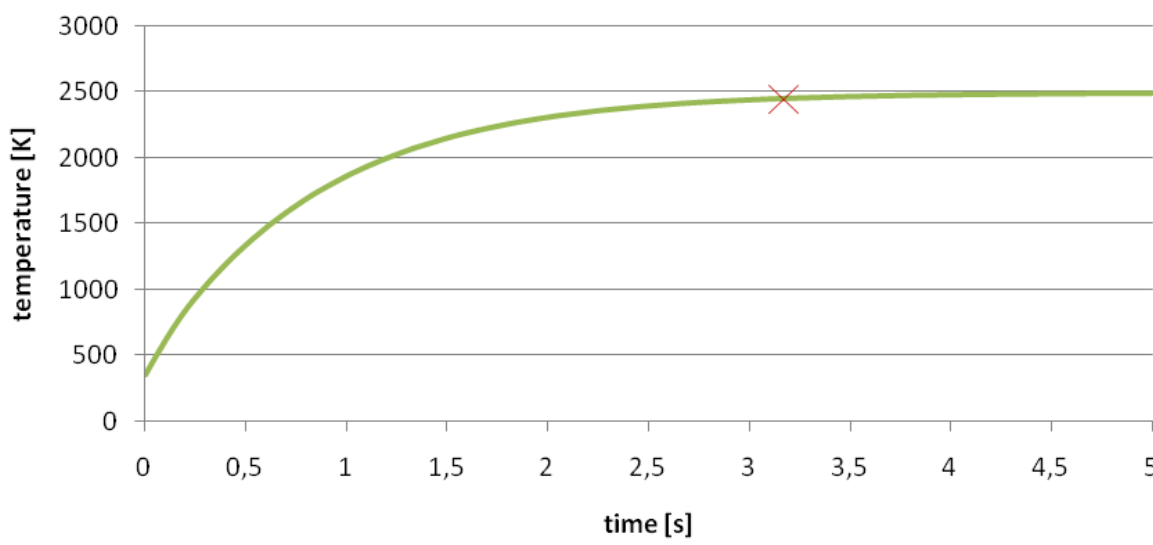
## APPENDIX C: GRAPHS

Graphs for Initial Problem Solutions



Total Internal Energy startup transient for C/O ratio = 0,1
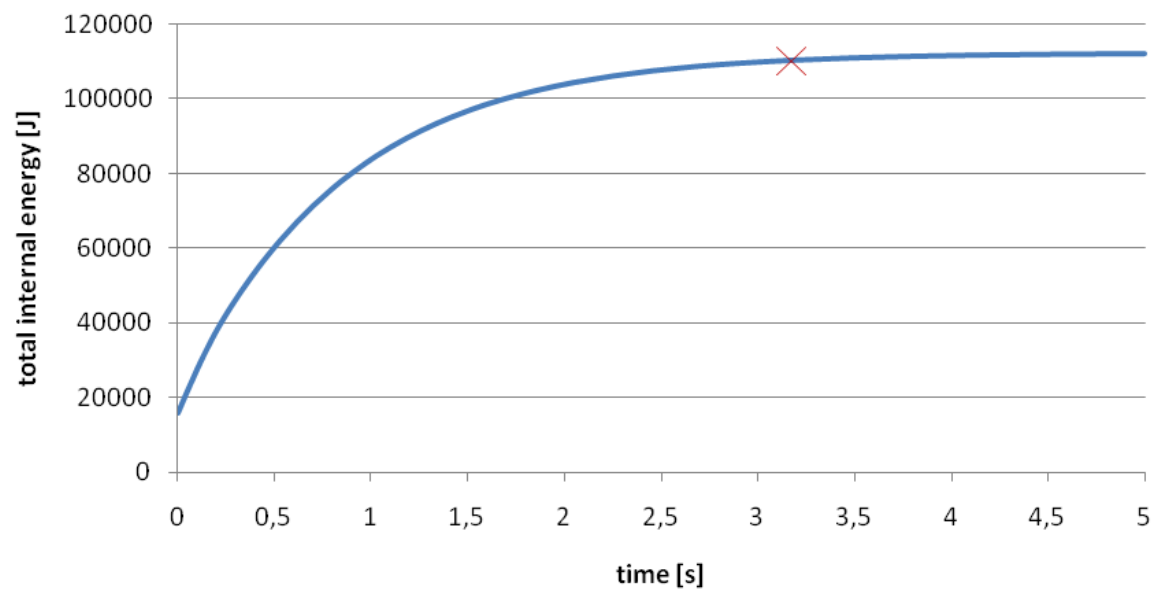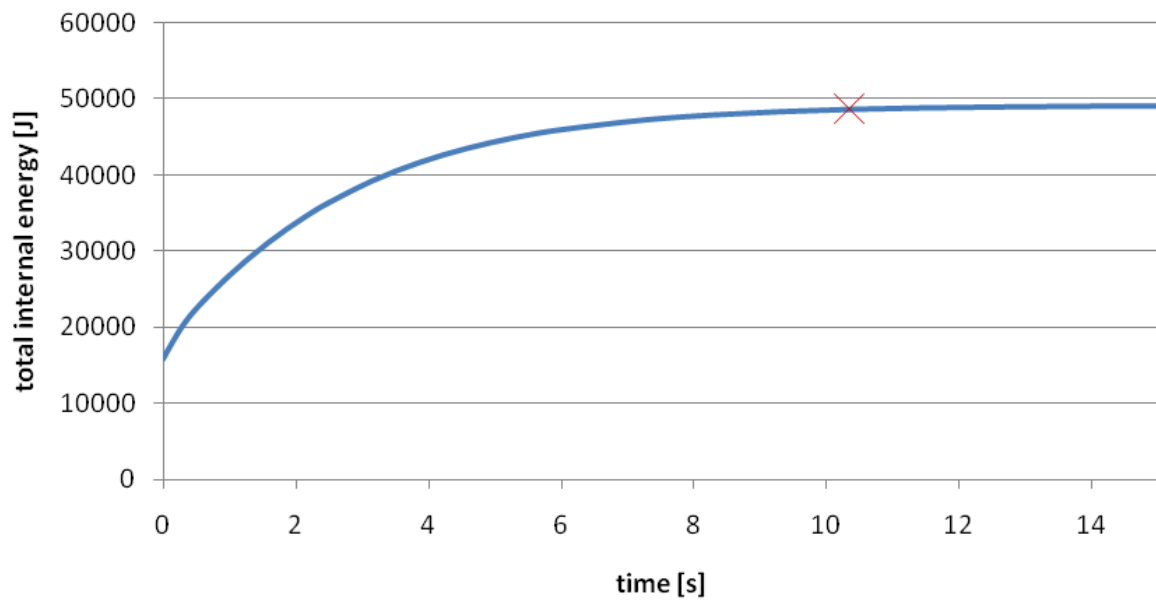


Temperature startup transient for C/O ratio = 0,1

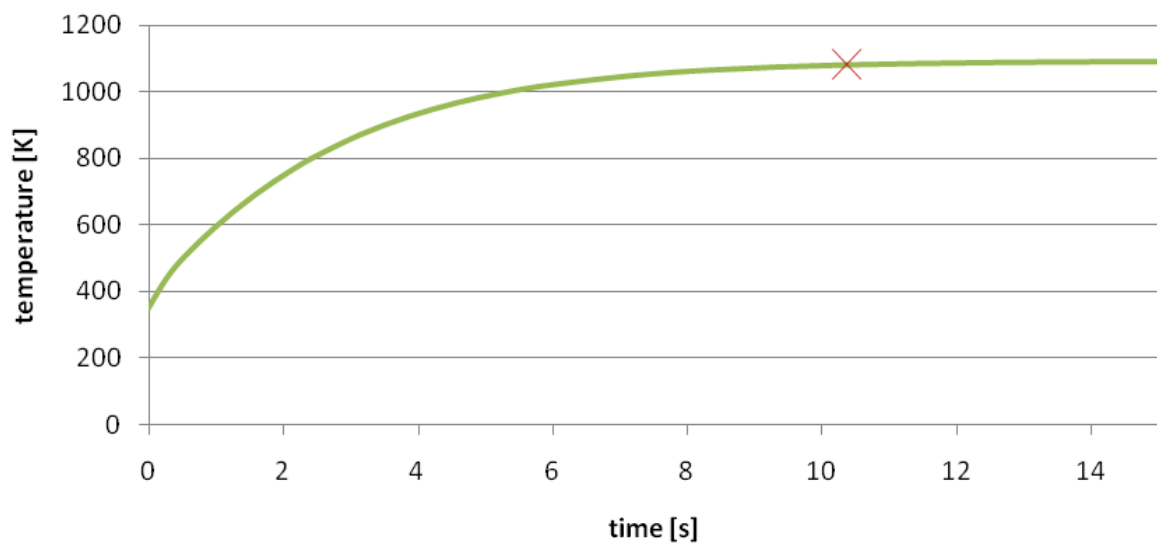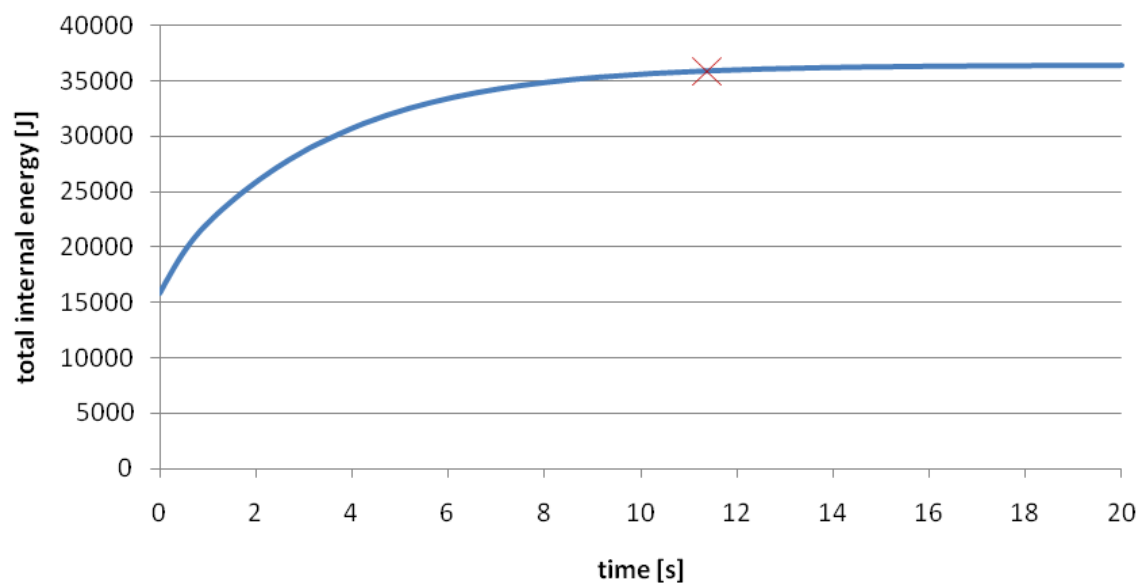## Total Internal Energy startup transient for C/O ratio = 0,4
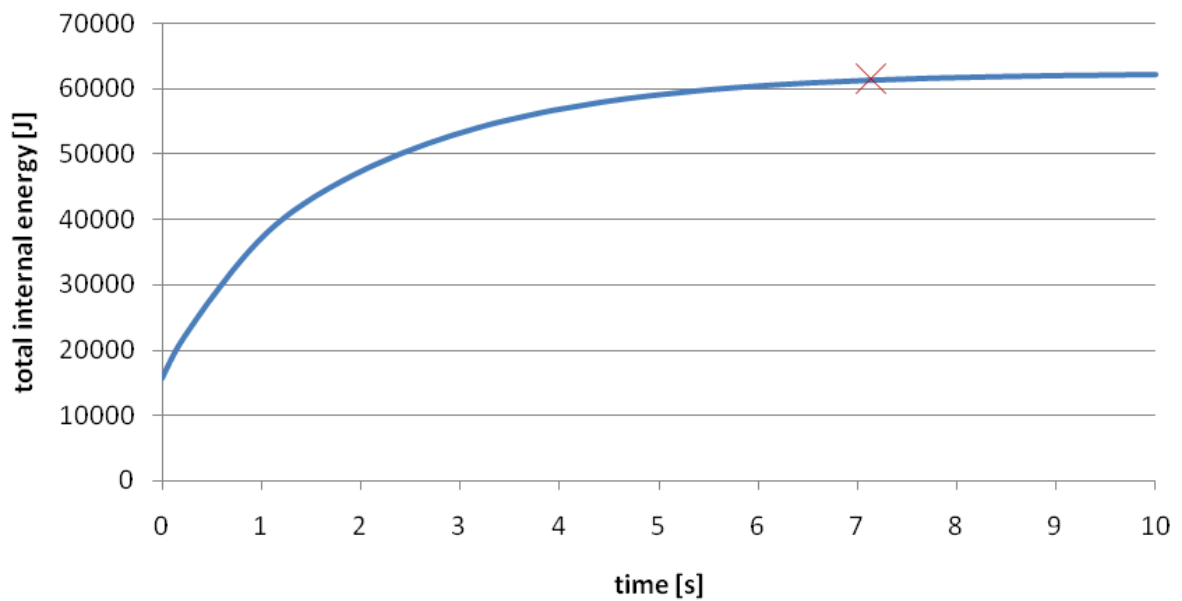


## Temperature startup transient for C/O ratio = 0,4
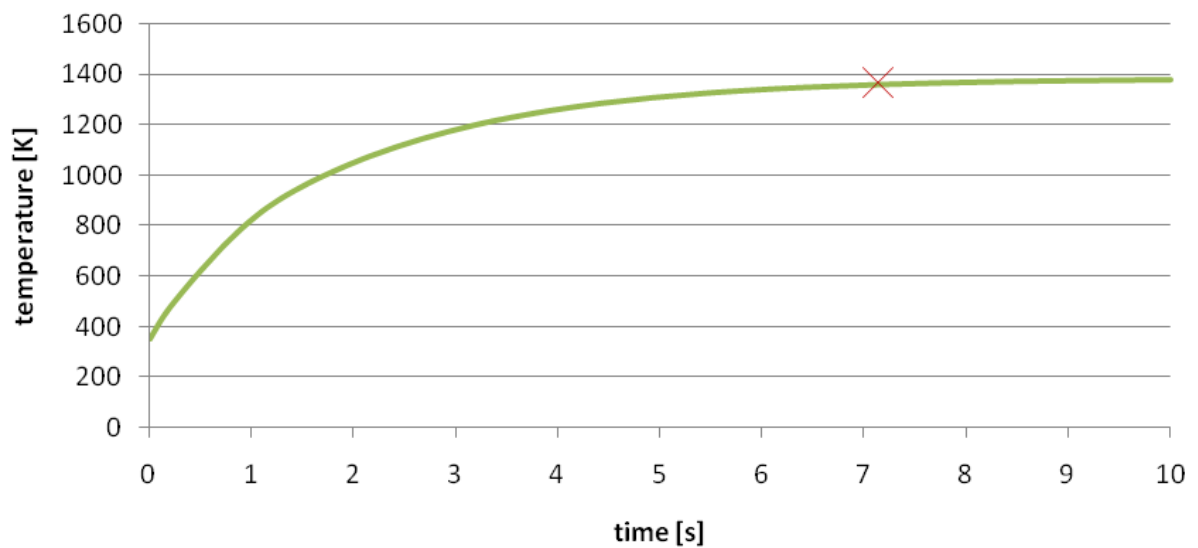
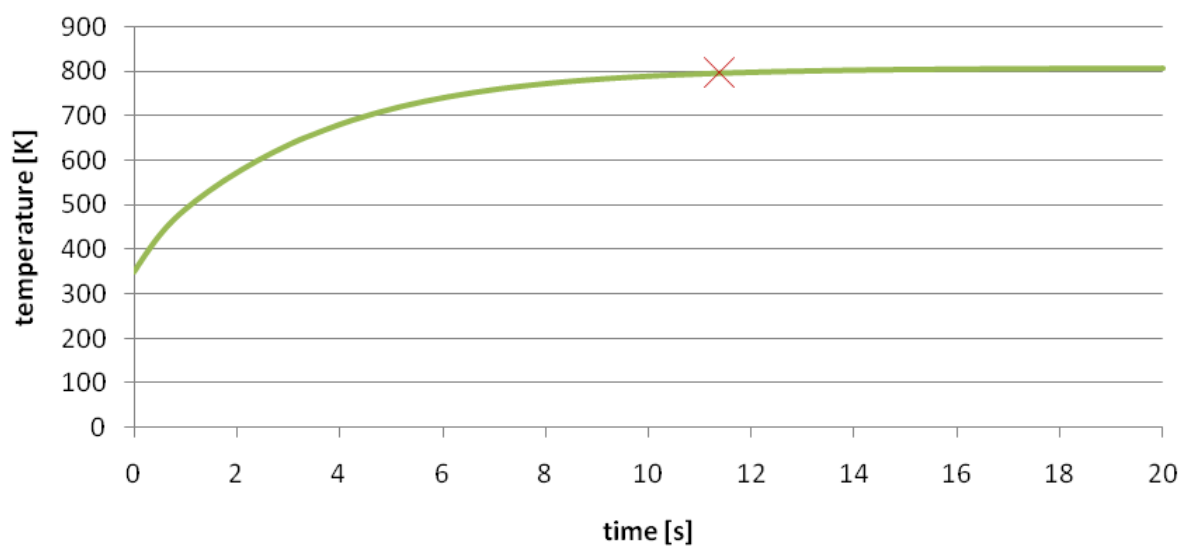# Total Internal Energy startup transient for C/O ratio = 0,8



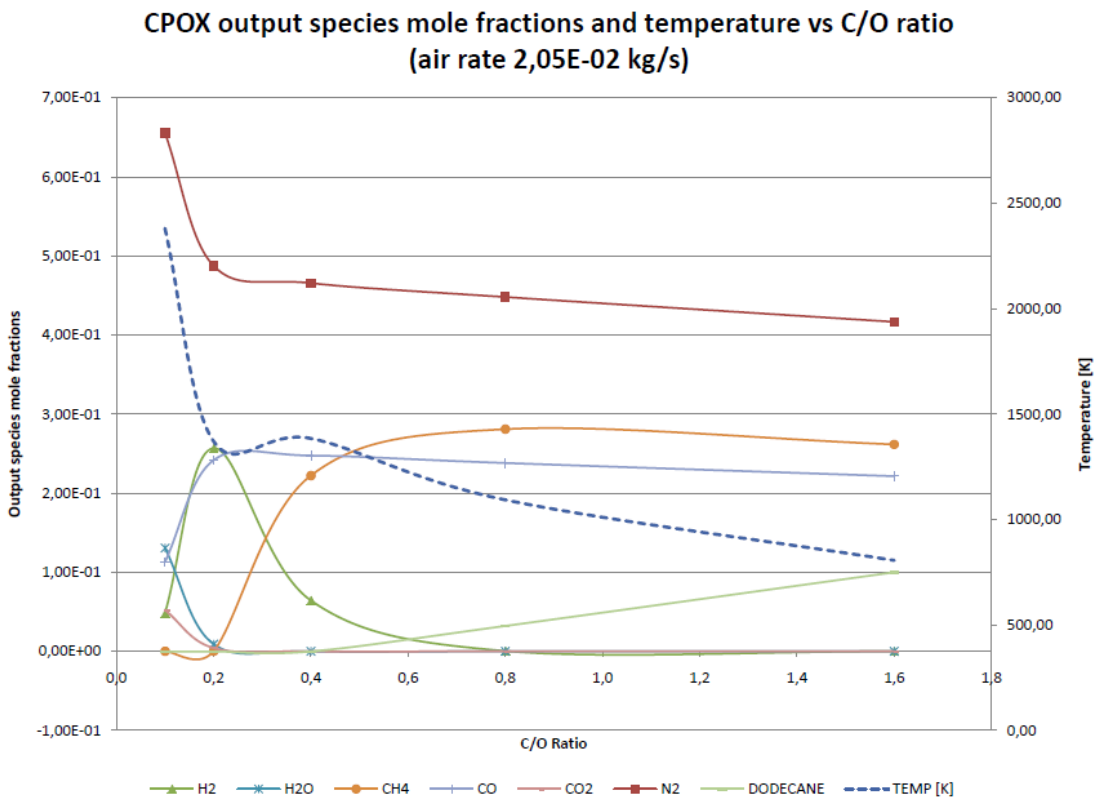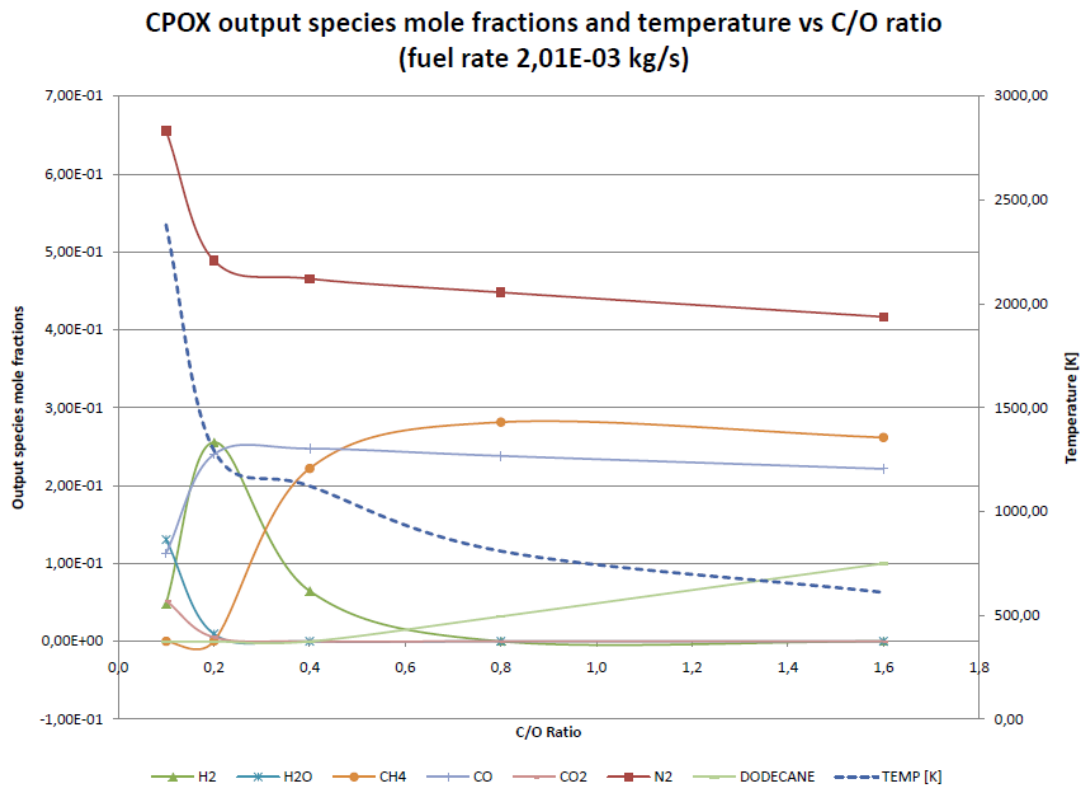# Temperature startup transient for C/O ratio = 0,8

# Total Internal Energy startup transient for C/O ratio = 1,6



# Temperature startup transient for C/O ratio = 1,6

Graphs for Output Species Concentrations



CPOX output species mole fractions and temperature vs C/O ratio
(fuel rate 2,01E-03 kg/s)



CPOX output species mole fractions and temperature vs C/O ratio
(air rate 2,05E-02 kg/s)

CPOX output species mole fractions and temperature vs C/O ratio
(air rate 1,03E-02 kg/s)