Numerical Analysis of Use of Syngas for Combustion Systems
and in Solid Oxide Fuel Cells

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THESIS
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This thesis is dedicated to my brother, Paolo.

The constant source of happiness in my life.
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SUMMARY

As the world energy demand and environmental concern continue to grow, there is increasing interest in developing renewable and cleaner energy sources. Syngas is a green fuel which can be produced from a variety of sources. It mainly consists of hydrogen and carbon monoxide, with small amounts of carbon dioxide and small traces of other species. These fuels present better characteristics than the elements they are obtained from, such as coal, biomass and municipal solid waste. This study is divided into two parts analyzing two different applications. In the first part a detailed numerical analysis of syngas combustion and emissions in different configurations has been performed, which include laminar premixed flames and laminar diffusion flames. Several studies can be found on combustion of syngas but in this thesis their use on solid oxide fuel cells has been investigated too. In particular, in the second part of this work a detailed numerical model has been developed and validated in order to evaluate the anode chemistry of a solid oxide fuel cell and use it for the optimal design of the cell. This can be a powerful tool for numerical investigation on the use of solid oxide fuel cells. The effects of syngas composition and other parameters have been investigated. At the end a comparison analysis of the two ways of producing energy has been performed.
CHAPTER 1

INTRODUCTION

1.1 Motivations and Aims

Nowadays the world energy demand continues to grow, the reserves of fossil fuel continue to decline and for the principle of supply and demand as the hydrocarbon supplies diminish the prices will rise. Furthermore emission laws imposed by the US environmental agency in addition to the Kyoto protocol restrictions are becoming more strict. So, as time progresses, renewable energy generally gets cheaper, while fossil fuels get more expensive. In this scenario, biomass and biomass derived fuels, like syngas, are becoming increasingly attractive alternatives for the power industries.

The main purpose of this work is to investigate how syngas may represent an attractive alternative to the conventional fossil fuels. In particular will be shown how syngas can be successfully be used for power generation in different scenarios, such as through conventional thermal machines (whose principle is based on combustion) and from innovative and promising electrochemical generators. Due to the potential in reducing greenhouse emissions, syngas seems to be a promising energy source in the future, even though they are significantly different one from each other.

This thesis is divided into two main parts. The first one aims to examine how syngas can be used in different types of thermal machines by performing a detailed simulation analysis
of different kinds of combustion processes. The effects of syngas compositions and other parameters that may have importance have been evaluated in order to understand how they can affect the flame structure, heat production and emissions of pollutant and figure out if syngas may be capable to guarantee performances which are close to the actual fuels but reducing the emissions too. Firstly has been performed an equilibrium analysis, then laminar premixed flames and diffusion flames have been deeply studied since they have a wide range of applications. A simulation study on syngas capable to show good performances and low emissions could represent a first important step towards a wider analysis upon the use of syngas in actual diesel generators.

The second part of this work shows how syngas can be successfully used directly in solid oxide fuel cells for the production of energy by electrochemical processes. In particular the main purpose has been to developed a detailed numerical model for SOFC simulation for the optimization and design of the cell. This model has been validated through several experimental results obtained in the laboratories of the Polytechnic University of Turin and will be used for a better design of solid oxide fuel cells. For a long time, experts have agreed that solid oxide fuel cells (SOFCs) hold the greatest potential of any fuel cell technology. The main advantage of SOFCs is that they do not present the need of being fed with pure hydrogen. The fastest reaction at the nickel anode is that of hydrogen, but other fuels can also react directly on the anode, depending on catalyst composition. Furthermore they have the capability to internally reform the fuel by mixing it either with carbon dioxide (dry reforming) or with water (steam reforming). SOFCs operate at extremely high temperature (typically above 800°C). This high temperature
gives them extremely high electrical efficiencies, and fuel flexibility, both of which contribute to better economics, but it also creates engineering challenges that inhibit the commercialization of this promising new technology.

Several studies on syngas combustion can be found in literature, but in this work their use on an electrochemical device has been investigated too, in order to make a comparison between the two ways of producing energy from a renewable source.

1.2 Syngas Background

Syngas is the abbreviation for Synthesis gas, it consists primarily of hydrogen, carbon monoxide, and very often some carbon dioxide, and has less than half the energy density of natural gas[3]. These fuels, presents better characteristics than the elements they are obtained from, such as coal, biomass and municipal solid wastes. Examples of production methods include steam reforming of natural gas or liquid hydrocarbons to produce hydrogen, the gasification of coal, biomass, and in some types of waste-to-energy gasification facilities. Syngas is combustible and often used as a fuel of internal combustion engines or as an intermediate for the production of other chemicals. It represents a viable energy source, particularly for stationary power generation, since it allows for a wide flexibility in fossil fuel sources, and since most of the harmful contaminants and pollutants can be removed in the post-gasification process prior to combustion. The main reaction that produces syngas, steam reforming, is endothermic with 206 kJ/mol methane needed for conversion[4].

Coal is actually the most abundant fossil source of any kind. All the resources are the equivalent to 83 % of all fossil fuel sources but its consumption represents only the 34% of the
total consumption of fossil fuels because of its solid state. In order to help to increase its use against petrol and natural gas it is necessary to change its state from solid to liquid or gaseous. Through gasification we can convert solid coal into a fuel gas.

Another fuel source for the production of syngas is biomass, which is the most important source of renewable energy based on organic materials. When talking about biomass we are referring to a varied set of materials that include mainly the forestry woods and leaves, the residues from agricultural harvesting and processing into alimentary and industrial products, as well as post consumers food and drink wastes and furniture waste. In some classifications a part of MSW (municipal solid waste) is included as a biomass source. Its composition includes recyclable material such as paper, glass, bottles, metals, plastics; construction wastes (bricks, debris); electronic wastes and medical wastes. Biomass cannot be used as a main source of energy. Otherwise the specific production of agricultural crops can produce a clash between the demand of food products and fuel products. As an example, in America the prices of the sugarcane and corn has risen in the last years due to their use to produce biofuels and that has caused the rise of alimentary products prices. Based on scenarios of a growing energy demand, the sustainable contribution of biomass is in a range between 20 and 50% of the future world primary energy\textsuperscript{[5]}. The highest value is done with a high dampening of the growth of the energy demand because of an increase in the energy efficiency. Considering this, a good manner to use biomass is to process it altogether with coal. If the co-gasification process of coal and biomass results to produce a convenient fuel that is usable in fuel cells, it may be considered the way to follow in the next years for the production of syngas fuel.
The gasification process consists to partially oxidize fuels that are difficult to work with because of their solid or liquid state. The process is composed by three main processes:

- Drying
- Pyrolysis
- Reduction
- Combustion

The drying process is realized with the energy received by heat transfer with other zones within the reactor that are at a higher temperature. The drying rate is determined by the temperature (between 100 and 200°C), the velocity and the moisture content of feedstock particles, as well as the type of feed used. Because that zone is mainly focused into reduce the moisture content of coal and/or biomass used, no chemical reactions take place during this process. The pyrolysis process is an endothermic reaction so it is able due to heat transferred from the reduction zone. Due to relatively large temperature differences between dried feedstock and hot gases the temperature rises very fast, hence feed material is decomposed into gases, condensable products (tars and oil) and char. The final distribution of each product is determined by the temperature of the process, the heating rate, and the catalysts structure and composition. The reduction process is composed by endothermic and exothermic reactions. Products from the combustion are reduced to obtain mainly $H_2$ and $CO$. The combustion process is realized between the char resulting from the pyrolysis and the gasification agent. The oxidation reactions
are highly exothermic; hence the temperature of this zone is the higher within the entire reactor and provides heat to the rest of the processes\[6\].

1.3 Syngas Current Research and Future Objectives

According to most of chemical and engineering research performed in recent years, syngas may become a promising energy source in the future alternative to conventional fuels in producing energy since they present better characteristics than the elements they are obtained from, such as coal, biomass and municipal solid waste. Syngas fuels are typically composed primarily of $H_2$ and $CO$ and may contain $N_2$, $CO_2$, $H_2O$, $CH_4$, and other higher-order hydrocarbons. The specific composition depends upon the fuel source and processing technique. These substantial variations in composition and heating value are among the largest barriers toward their usage and further investigations are needed.

Among the variety of applications that syngas can be used for, can become important their use for feeding internal combustion engines since they are one of the main cause of greenhouse emissions. For instance the use of syngas in diesel engines has become an up-and-coming issue, since this type of engine is known to present good characteristics to be modified for dual-fuel operation. Diesel dual-fuel engines have higher efficiencies than spark-ignition engines, and the main reason is in the higher compression ratio reached. A higher efficiency results in a decrease of the fuel consumption and the polluting emissions (i.e., nitrogen and carbon oxides), and less soot is released. Several experimental investigations have been performed so far for different types of diesel engines fed with syngas, with engine performances, exhaust emission characteristics, fuel consumption, and efficiency being the main fields to be investigated. All
different studies were able to point out how dual-fuel engines remain an interesting alternative for producing power, using gases of low energy content like syngas\textsuperscript{[7]}.  

Syngas can be used to feed solid oxide fuel cells as well in order to produce energy electrochemically. Fuel cells are the most efficient devices to convert chemical energy into usable electrical energy and they are capable to overcome the combustion limitations. The most common proton exchange membrane fuel cells require to be fed by pure hydrogen, in contrast SOFCs have the advantage of fuel flexibility (processes of internal reforming) that allows them to be used on the existing hydrocarbon fuel infrastructure while simultaneously providing efficiency gains (and corresponding CO2 emission reductions). Current research aims to model the chemical processes (heterogeneous reactions) occurring on the anode surface, the electrochemical reactions due to charge transfer\textsuperscript{[8]}\textsuperscript{[9]} and develop and validate a numerical model for predicting the final composition of the exhaust gases coming out of the fuel cell and the current-voltage curve associated to it. However the main issue for SOFCs is the high operating temperature (about 800°C) and the consequent limitations, high costs and operating complexities. In this scenario a future goal may be the reduction of the operating temperatures that will lead to an improvement of the performance and to a reduction of the operating costs.
CHAPTER 2

SYNGAS CHEMICAL EQUILIBRIUM

2.1 Introduction

All the concepts presented in this chapter are of fundamental importance to a study of combustion. In particular, the main thermodynamic properties can be evaluated to determine the goodness of the combustion process and an analysis of combustion products can provide a general overview about fuel emissions. The final intent in this chapter dealt with the variation of the combustion product mixture composition with equivalence ratio and the importance of dissociation.

All the numerical simulations performed in the first part of this work have been done using CHEMKIN 10101, a software produced by Reaction Design, Inc.

2.1.1 CHEMKIN Description

CHEMKIN is a software tool for solving complex chemical kinetics problems. It is used worldwide in the microelectronics, automotive, combustion, and chemical processing industries. It was originally developed at Sandia National Laboratories and is now developed at Reaction Design. It is a set of flexible and powerful tools for incorporating complex chemical kinetics into simulations of reacting flow. The software is a collection of programs and subroutine libraries, which work together to facilitate the formation, solution, and interpretation of problems involving gas-phase and heterogeneous (gas-surface) chemical kinetics. At its most
fundamental level, CHEMKIN software enables the simulation of complex chemical reactions. With the advanced capabilities now available, sophisticated Design-of-Experiments can be created to parametrically explore potential design solutions well before costly hardware is built. Using CHEMKIN, researchers are able to investigate thousands of reaction combinations to develop a comprehensive understanding of a particular process, which might involve multiple chemical species, concentration ranges, and gas temperatures. Since its origins nearly 30 years ago, CHEMKIN has enabled significant strides in the modeling of complex chemical processes, such as combustion. It has become the standard for anyone involved in chemistry modeling and chemically reacting flow modeling. It has also become an important educational tool in chemical engineering, mechanical engineering and chemistry curricula\cite{10}\cite{11}.

2.1.2 Davis Mechanism

In order to run CHEMKIN simulations, it is necessary for the user to choose a reaction mechanism which is considered our best guess at how a reaction proceeds. Therefore, even if a mechanism agrees with the experimental results of a reaction, it cannot be proven to be correct. A reaction mechanism is defined as a proposed set of elementary steps, which account for the overall features of the reaction. Each of the reactions that comprises the mechanism is called an elementary step. It is called elementary because it takes place in a single reactive encounter between the reactants involved. These elementary steps are the basic building blocks of a complex reaction and cannot be broken down any further. The elementary processes in a reaction mechanism describe the molecular reaction and the changes it undergoes during the reaction. Because a reaction mechanism is used to describe what occurs at each step of
a reaction, it also describes the transition state, or the state when the maximum of potential energy is reached, in a reaction. A mechanism must show the order that the bonds form or break and the rate of each elementary step. Also accounted for in a mechanism are the reaction intermediates, which are stable molecules that do not appear in the experimentally determined rate law because they are formed in one step and consumed in a subsequent step.

One of the most recent and advanced technology for high-efficiency gasification of fossil fuels or biomass is the Integrated Gasification Combined Cycle (IGCC) power generation systems. The process includes conversion of coal into a synthesis gas (syngas) in a gasifier. The gas is composed of primarily Hydrogen and carbon monoxide and smaller amount of carbon dioxide and steam. This technology includes the capturing of CO\textsubscript{2} by pre-combustion methods (Carbon capture and storage, CCS) combined with low emissions of other gases like NO\textsubscript{x}, and SO\textsubscript{x}. Since syngas can be considered as a mixture of hydrogen and carbon monoxide with little amounts of multiple contaminants, the mechanism chosen for the current study is the well-known Davis mechanism\textsuperscript{[12]}. The Davis et al. Mechanism contains 14 species and 38 reactions while the GRI 3.0 mechanism including the NO\textsubscript{x} chemistry model contains 53 species and 325 reactions. The Davis mechanism performed the best in terms of reproducing the experimental data\textsuperscript{[13]}. Consequently this mechanism was employed in this work in order to run the simulations of syngas flames under different conditions. In order to examine the structure and the NO\textsubscript{x} emissions characteristics of syngas laminar premixed flames and counterflow flames this model will be combined with a detailed NO\textsubscript{x} chemistry model. The NO\textsubscript{x} chemistry was taken from GRI 3.0 and incorporated
into the Davis mechanism, as the this $NO_x$ has been previously validated\textsuperscript{[14]}. The modified Davis mechanism contains 38 species and 144 reactions.

A kinetic mechanism has an important role in the development of this kind of advanced combustion technologies that aims to the production of hydrogen rich syngas fuel. Simulation of the reacting flows is the basis for designing the combustors. The kinetic mechanism is one of the key tools in predicting entities like flame speed and ignition delay for implementation in commercial CFD codes. Hence, it is of utmost importance to analyze the kinetics of each reaction, their behavior at different conditions of pressure, temperature and fuel/oxidizer composition and implication on the production of other species.

### 2.1.3 Syngas Composition

The syngas composition varies widely depending upon the fossil fuel source, gasification process, and post-gasification treatment. In addition, the type and amount of diluents present during syngas combustion can vary significantly. These variations are well illustrated in Table II taken from reference\textsuperscript{[13]}, which lists the composition of syngas fuel and the various diluents used in gas turbine power generation facilities in different regions of the world. Literature review indicates that while the combustion and emission characteristics of individual syngas components, such as hydrogen and methane, have been extensively investigated, the corresponding research dealing with the combustion of syngas mixtures has been relatively sparse. Consequently, there is a gap in the fundamental understanding of the combustion and emission characteristics of various syngas mixtures. Further experimental and numerical investigations are needed to characterize the detailed structure of syngas flames, and the effects of various
diluents on emissions from these flames. The syngas flames are simulated using three representative syngas mixtures containing $CO$, $H_2$, and $CO_2$, one containing 50% $H_2$ and 50% $CO$, the second one containing 95% $CO$ and 5% $H_2$ and the other 45% $H_2$, 45% $CO$, and 10% $CO_2$ (to evaluate the effect of dilution), Table I. A fourth composition was added in order to analyze the effect on the syngas behavior of the different percentage of hydrogen. The choice of these four reference mixtures is based on the composition of syngas mixtures used in various power generation systems listed in Table II. As indicated in this table, while the syngas composition may vary significantly, $CO$ and $H_2$ represent the dominant components of most syngas mixtures with varying amounts of diluents. Since most of the chemical elements contained and in particular $CH_4$ are not included in the Davis mechanism they will be neglected.

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>Syngas 1</th>
<th>Syngas 2</th>
<th>Syngas 3</th>
<th>Syngas 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CO$</td>
<td>50%</td>
<td>95%</td>
<td>45%</td>
<td>5%</td>
</tr>
<tr>
<td>$H_2$</td>
<td>50%</td>
<td>5%</td>
<td>45%</td>
<td>95%</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>0%</td>
<td>0%</td>
<td>10%</td>
<td>0%</td>
</tr>
</tbody>
</table>
TABLE II: MAJOR FUEL COMPONENTS AND DILUENTS (% vol) IN SYNGAS MIXTURES USED IN VARIOUS GAS TURBINE POWER GENERATION FACILITIES

<table>
<thead>
<tr>
<th>Syngas</th>
<th>PSI</th>
<th>Tampa</th>
<th>El Dorado</th>
<th>Pernis</th>
<th>Sierra Pacific</th>
<th>ILVA</th>
<th>Schwarze Pumpe</th>
<th>Sarlux</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>24.8</td>
<td>37.2</td>
<td>35.4</td>
<td>34.4</td>
<td>14.5</td>
<td>8.6</td>
<td>61.9</td>
<td>22.7</td>
</tr>
<tr>
<td>COPOLYM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TERPOLYM</td>
<td>39.5</td>
<td>46.6</td>
<td>45.0</td>
<td>35.1</td>
<td>23.6</td>
<td>26.2</td>
<td>26.2</td>
<td>30.6</td>
</tr>
<tr>
<td>$CH_4$</td>
<td>1.5</td>
<td>0.1</td>
<td>0.0</td>
<td>0.3</td>
<td>1.3</td>
<td>8.2</td>
<td>6.9</td>
<td>0.2</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>9.3</td>
<td>13.3</td>
<td>17.1</td>
<td>30.0</td>
<td>5.6</td>
<td>14.0</td>
<td>2.8</td>
<td>5.6</td>
</tr>
<tr>
<td>$N_2 + Ar$</td>
<td>2.3</td>
<td>2.5</td>
<td>2.1</td>
<td>0.2</td>
<td>49.3</td>
<td>42.5</td>
<td>1.8</td>
<td>1.1</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>22.7</td>
<td>0.3</td>
<td>0.4</td>
<td>5.7</td>
<td></td>
<td></td>
<td></td>
<td>39.8</td>
</tr>
<tr>
<td>LHV (Btu/ft³)</td>
<td>209</td>
<td>253</td>
<td>242</td>
<td>210</td>
<td>128</td>
<td>183</td>
<td>317</td>
<td>163</td>
</tr>
<tr>
<td>LHV (kJ/m³)</td>
<td>8224</td>
<td>9962</td>
<td>9528</td>
<td>8274</td>
<td>5024</td>
<td>7191</td>
<td>12492</td>
<td>6403</td>
</tr>
<tr>
<td>$T_{fuelF/C}$</td>
<td>570/300</td>
<td>700/371</td>
<td>250/121</td>
<td>200/98</td>
<td>1000/538</td>
<td>400/204</td>
<td>100/38</td>
<td>392/200</td>
</tr>
<tr>
<td>$H_2/CO$ ratio</td>
<td>0.63</td>
<td>0.8</td>
<td>0.79</td>
<td>0.98</td>
<td>0.61</td>
<td>0.33</td>
<td>2.36</td>
<td>0.74</td>
</tr>
<tr>
<td>Diluent</td>
<td>Steam</td>
<td>$N_2$</td>
<td>$N_2$/steam</td>
<td>Steam</td>
<td>Steam</td>
<td>Steam</td>
<td>Moisture</td>
<td></td>
</tr>
<tr>
<td>Equivalent LHV (Btu/ft³)</td>
<td>150</td>
<td>118</td>
<td>113</td>
<td>198</td>
<td>110</td>
<td></td>
<td></td>
<td>200</td>
</tr>
<tr>
<td>Equivalent LHV (kJ/m³)</td>
<td>5910</td>
<td>4649</td>
<td>4452</td>
<td>7801</td>
<td>4334</td>
<td></td>
<td></td>
<td>7880</td>
</tr>
</tbody>
</table>
2.2 Physical Considerations

In this section different thermodynamic concepts are introduced that can be useful in the study of combustion. Equilibrium is emphasized because in many applications a knowledge of equilibrium laws is enough to define many performance parameters. A system is said to be in equilibrium when there is no tendency for spontaneous change in its state with respect to time. In the post flame zone, many of the combustion products are in chemical equilibrium or possibly shifting equilibrium.

In all the combustion processes high temperature are reached and for this reason the combustion products are not a simply mixture of ideal elements as may be suggested by an atom-balance calculation to determine stoichiometry. On the contrary, the major species dissociate, producing a host of minor species. Under some conditions, what ordinarily might be considered a minor species is actually present in quite large quantities. For instance, the ideal combustion products for burning a hydrocarbon with air are \( \text{CO}_2, \text{H}_2\text{O}, \text{O}_2, \) and \( \text{N}_2 \). Dissociation of these species and reactions among the dissociation products yields the following species: \( \text{H}_2, \text{OH}, \) \( \text{CO}, \) \( \text{H}, \) \( \text{O}, \) \( \text{N}, \) \( \text{NO}; \) and possibly others.

The problems mainly analyzed in this section are the calculation of the adiabatic flame temperature and the computation of the mole fractions of all of the product species at a given pressure, subject to the constraint of conserving the number of moles of each of the elements present in the initial mixture. This constraint just says that the number of \( C, H, O, \) and \( N \) atoms is constant, regardless of how they are combined in the various species\(^2\).
There are two adiabatic flame temperatures: one for constant-pressure combustion and one for constant-volume. The first one is the most important in this work because it would be appropriate in dealing with a gas-turbine combustor, or a furnace. If a fuel-air mixture burns adiabatically at constant pressure, the absolute enthalpy of the reactants at the initial state (say, $T = 298$ K, $P = 1$ atm) equals the absolute enthalpy of the products at the final state ($T = T_{ad}$, $P = 1$ atm). Thus:

$$H_{\text{react}}(T_i, P) = H_{\text{prod}}(T_{ad}, P)$$ \hspace{1cm} (2.1)

or, equivalently, on a per-mass-of-mixture basis,

$$h_{\text{react}}(T_i, P) = h_{\text{prod}}(T_{ad}, P)$$ \hspace{1cm} (2.2)

This first-law statement defines what is called the constant-pressure adiabatic flame temperature. Conceptually, the adiabatic flame temperature is simple since it can be defined as the maximum temperature that the combustion process can reach in the absence of heat exchange; however, evaluating this quantity requires knowledge of the composition of the combustion products. At typical flame temperatures, the products dissociate and the mixture comprises many species. Flame temperatures are typically several thousand kelvins.

For what concerns the computation of the product mole fractions, it is well-known that there are several ways to approach the calculation of equilibrium composition. The solution of chemical equilibrium problems has posed a tough challenge for numerical computation. The
problem in determining the adiabatic flame temperature, $T_a d$ for known reactants, is that the product composition is itself a function of $T_a d$. This necessitates an iterative solution whereby one uses an initial temperature. This problem may be formulated in several ways. If one uses the concepts of equilibrium constants, then it is necessary to identify the set of reactions that take place and to determine the associated equilibrium constants. One then has to solve a set of nonlinear algebraic equations for the mole number of each species, a difficult task if the system is large.

The present analysis, and the program, assumes that the gas phase is a mixture of ideal gases and that condensed phases are ideal solutions. These are good approximations for many practical problems of interest.

2.3 **CHEMKIN Governing Equations for Chemical Equilibrium**[^1]

In addition to chemically reacting flow applications, *CHEMKIN* includes an Equilibrium Reactor model. This model allows users to determine the chemical state of a mixture under equilibrium conditions. Any number of gas-phase or condensed species can be included in an equilibrium calculation, while surface site species are ignored. In this way, the Equilibrium Reactor model can be used to determine phase equilibrium, between gas and condensed phases, as well as chemical equilibrium. All that is required is thermodynamic data for all species in each phase. An established method for evaluating chemical equilibrium is the element-potential method embodied in the Stanford software *STANJAN*. The *CHEMKIN* Equilibrium Reactor employs the *STANJAN* library of routines in its solution method. The equilibrium determines composition equilibrium and/or phase equilibrium. The results depend only on the
thermodynamic properties of the species in the users chemistry set, as well as the starting composition and conditions specified. The starting composition determines the relative amount of chemical elements in the system. An initial estimate of the equilibrium temperature can sometimes be used to select a burned equilibrium state from an unburned equilibrium state in the case where two equilibrium states are possible. Currently, the equilibrium program assumes that the gas-phase is a mixture of ideal gases and that condensed phases are ideal solutions. The user selects atomic populations through identity of initial species and their fraction in each phase, as well as the state parameters. The user may specify the state parameters in a number of different ways, including:

- temperature and pressure;
- pressure and entropy;
- enthalpy and pressure;
- volume and entropy.

The following paragraph is extracted from the CHEMKIN Theory Manual[1]. Species composition can be frozen in a given calculation, or the equilibrium composition can be determined. Calculations may be linked through continuations, such that the conditions calculated from a previous equilibrium case can be used as the starting point for a subsequent case with different constraints. In this way, the user can employ the Equilibrium Reactor Model to analyze stages in a thermodynamic cycle.
The Equilibrium Reactor Model is also commonly used to determine adiabatic flame temperatures for combustible gas mixtures. Such a simulation is performed by specifying an initial (reagent) gas mixture and constraining equilibrium for constant enthalpy (adiabatic) and constant pressure. The calculation can also be performed using constant internal energy and constant volume. An initial guess for the equilibrium temperature of \( \sim 1000 \text{ K} \) or above is usually needed to cause the equilibrium solver to find the burned-gas solution. For accurate adiabatic-flame temperature calculations, it is important to include all radical species that might occur in the flame, as well as stable reactants and products.

The following paragraph describes the equations solved and the methodology used for determining chemical and phase equilibrium of arbitrary systems.

### 2.3.1 Minimization of Gibb’s Free Energy

The basic theory for the element-potential method of determining equilibrium is based on the minimization of Gibbs free energy. The Gibbs function of a system is:

\[
G = \sum_{k=1}^{K} \bar{g}_k N_k
\]  

(2.3)

where \( \bar{g}_k \) is the partial molar Gibbs function and \( N_k \) is the number of moles of each species \( k \) in the system. \( K \) is the total number of species.

For ideal-gas mixtures or ideal solutions, the partial molal Gibbs functions are given by:

\[
\bar{g}_k = g_k(T, P) + RT \ln X_k
\]  

(2.4)
where $g_k$ is the Gibbs function for the pure species $k$, evaluated at the system temperature and pressure; $R$ is the universal gas constant; and $X_k$ is the mole fraction of the $k$th species. The equilibrium solution at a given temperature and pressure is the distribution of $N_k$ that minimizes the system Gibbs function, $G$, subject to atomic population constraints (and non-negative $N_k$). The atomic population constraints are:

$$\sum_{k=1}^{K} n_{jk} N_k = p_j \quad j = 1, \ldots, M$$  \hspace{1cm} (2.5)

where $n_{jk}$ is the number of the $j$th atoms that appear in the $k$th molecule, is the total population in moles of the $j$th atom in the system, and $M$ is the total number of different elements that are present in the system$^{[1]}$.

Details regarding the relationship between the partial molar Gibbs functions and the elemental potentials for the atoms, as well as the explicit form of the equations solved in the \textit{STANJAN} library, are described in the \textit{STANJAN} report$^{[15]}$.

2.4 \underline{Set Up an Equilibrium Simulation on CHEMKIN}

Since the software \textit{CHEMKIN} was new to me, I started using it to solve the ignition delay in different conditions. The ignition delay is important because it is the time period between the start of injection and the first identifiable pressure increase during combustion of the fuel. After this practical issue I started the equilibrium simulations.

An important advantage of \textit{CHEMKIN} is represented by the fact that the software has its own interface that makes it a very user friendly software. It is very simple to set up a simulation
since there is no need to programming anything. In particular, when opening CHEMKIN, the user can decide whether to start their study from taking a sample file or to create a new file so that everything can be set according to their own needs. If the user decide to start a new simulation creating a new file, first of all he has to select in the model window the icon of Equilibrium Reactor Model. Once selected the type of simulation to perform the user can create a new chemistry or use an exisiting one in the pre-processing window. Here the user must select the working directory and enter the Gas-Phase Kinetics File and the Thermodynamics Data File have to be entered. The Gas Transport Data File is useless in the equilibrium analysis but will be useful in the following chapters. Those files used to study syngas combustion processes are taken from the Davis mechanism. After setting all fields in the pre-processing window, the user can open the main window and set all the inputs such as physical properties, reactant species, and possible constrained species. For what concerns the reactor physical properties must be defined the type of problem and, as said in the theory part, in this work has been chosen the Constant Pressure Enthalpy to get pressure fixed. Then the user must set the initial conditions like temperature and pressure and estimate the equilibrium temperature (it is not mandatory but often makes the computation faster). After that, the user can define the reactant species by expressing them on a mole-fraction or mass-fraction base and by specifying the equivalence ratio. In particular, mole fractions of the fuel-mixture species, mole fractions of the oxidizer-mixture species, and complete combustion products must be entered but the last two can be automatically computed by CHEMKIN. Constrained species can be also specified in the same way if any. The last option present that the user can use is the continuations. It is the
possibility to set up a simple parameter study or a series of continuations run that are executed all within a single batch job for a single simulation. At this point the simulation can be run.

When the simulation is completed the user can examine all quantities and properties of interest since they are collected in the output file. Furthermore CHEMKIN has also a post-processor with the possibility to make plots, see the data or export them to an Excel sheet.

2.5 Simulation Results

In Table III is listed a general summary about the equilibrium-composition mole fractions of all chemical species involved in the Davis mechanism. The simulation has been performed in stoichiometric conditions ($\phi = 1$), while initial temperature is 300 K and pressure is 1 atm. The asterisk is referred to the mole fractions of complete-combustion products: the initial

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>Syngas 1</th>
<th>Syngas 2</th>
<th>Syngas 3</th>
<th>Syngas 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>0.004573</td>
<td>3.70 $\cdot 10^{-4}$</td>
<td>3.31 $\cdot 10^{-3}$</td>
<td>0.012767</td>
</tr>
<tr>
<td>$N_2^*$</td>
<td>0.64172</td>
<td>0.6388</td>
<td>0.6197</td>
<td>0.6453</td>
</tr>
<tr>
<td>$O$</td>
<td>0.000848</td>
<td>0.00111</td>
<td>5.44 $\cdot 10^{-4}$</td>
<td>6.188 $\cdot 10^{-4}$</td>
</tr>
<tr>
<td>$OH$</td>
<td>0.00661</td>
<td>0.0023448</td>
<td>0.004987</td>
<td>0.007816</td>
</tr>
<tr>
<td>$H_2O^*$</td>
<td>0.16222</td>
<td>0.015295</td>
<td>0.15864</td>
<td>0.30844</td>
</tr>
<tr>
<td>$CO$</td>
<td>0.02407</td>
<td>0.04005</td>
<td>0.02118</td>
<td>0.003343</td>
</tr>
<tr>
<td>$O_2$</td>
<td>0.1249</td>
<td>0.01913</td>
<td>0.01087</td>
<td>0.006202</td>
</tr>
<tr>
<td>$CO_2^*$</td>
<td>0.14651</td>
<td>0.28258</td>
<td>0.1801667</td>
<td>0.01381</td>
</tr>
<tr>
<td>$H$</td>
<td>9.56 $\cdot 10^{-4}$</td>
<td>2.87 $\cdot 10^{-4}$</td>
<td>5.83 $\cdot 10^{-4}$</td>
<td>0.001648</td>
</tr>
</tbody>
</table>
content of nitrogen is the same in all syngas types so it is possible to gather that its different final content in the products has to deal with other chemical species containing nitrogen (in particular, it is well-known how the $NO_x$ play a fundamental role). Water vapor content is almost similar between Syngas 1 and Syngas 3 because of the initial content of $H_2$ is almost the same. In the second composition there is a very low mole fraction of $H_2O$ due to the small initial percentage of $H_2$ otherwise in Syngas 4 the water vapor percentage is the highest, while, the more the fuel contains carbon oxide in its initial composition, the more carbon-dioxide production is increased (it is not really correct about production since it is very difficult to estimate how much carbon dioxide is really produced or consumed during the combustion process, but, since we are examining an initial and a final state, we can refer to the latter state as the condition in which every chemical species has been produced or consumed). Furthermore in Syngas 3 there is an increase in the final carbon dioxide content but this is due to the 10% of $CO_2$ dilution in its initial composition. Making a preliminary comparison between

\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{Chemical Species} & \text{Syngas 1} & \text{Syngas 2} & \text{Syngas 3} & \text{Syngas 4} \\
\hline
N_2 & 0.64172 & 0.6388 & 0.6197 & 0.6453 \\
CO & 0.02407 & 0.04005 & 0.02118 & 0.003343 \\
CO_2 & 0.14651 & 0.28258 & 0.1801667 & 0.01381 \\
\hline
\end{array}
\]

TABLE IV: MAIN-CHEMICAL SPECIES COMPARISON ($\phi = 1$, $T_{IN} = 300K$, $P = 1ATM$)
the four syngas types by considering the the main chemical species responsible of emissions of main pollutants (Table IV where conditions are the same as above) is possible to state that the fourth composition guarantees the less final content of carbon monoxide and carbon dioxide. This is mainly due to the lower CO presence in the initial composition and to the absence of CO₂ dilution. But for what concern NOₓ emissions it is important to say that with the fourth syngas compositions higher temperature are reached, so there may be an increment in NOₓ emissions. Hence it is easy to state that, from a preliminary emission study based on the equilibrium composition, Syngas 1 seems to present lower emissions than composition 1 and 2 (Syngas 4 is simulated just to evaluate the effect of different Hydrogen mole fractions) in combustion processes, considering that carbon dioxide contained in the fuel of Syngas 2 can have a strong effect on final products.

2.5.1 Influence of Equivalence Ratio on Adiabatic Flame Temperature

In this section is simulated and analyzed how adiabatic flame temperature varies with respect to the equivalence ratio of the air-fuel mixture. In order to make this the combustion process is considered to start from a temperature of 298 K, while pressure is kept constant and is set to 1 atm. In Figure 2 are shown the results. The global trend is practically the same for all the mixtures, so it is easy to generalize their behavior: adiabatic flame temperature increases for equivalence ratios lower than 1, while it decreases for values which are higher than 1.1, with the slope of the ascending branch being higher than the decreasing one. The peak temperature is different for all fuels and it is contained between the values of 1.1-1.2 of equivalence ratio. So the composition of the mixture affects both the maximum adiabatic temperature and the
equivalence ratio in which it is reached. That the maximum temperature is a slightly rich equivalence ratio is a consequence of both the heat of combustion and heat capacity of the products \( N_{prod} \cdot \bar{c}_{p,prod} \) declining beyond \( \phi = 1 \). For equivalence ratios between \( \phi = 1 \) and \( \phi(T_{max}) \), the heat capacity decrease more rapidly with \( \phi \) than \( \Delta H_c \); while beyond \( \phi(T_{max}) \), \( \Delta H_c \) falls more rapidly than does the heat capacity. The decrease in heat capacity is dominated by the decrease in number of product moles formed per mole of fuel burned, with the decrease in the mean specific heat being less significant. Note that dissociation cause a lowering of \( T_{ad} \) since more energy is tied up in chemical bonds (enthalpies of formation) at the expenses of the sensible energy. The curves of the Syngas 1 and Syngas 4 compositions are almost the same, so the different \( H_2 \) initial mole fraction doesn’t affect the adiabatic flame temperature. The difference
between the first two compositions is small: the adiabatic flame temperature difference is less than 50 K but is shifted by an equivalence ratio of 0.1. This temperature difference can be understood looking at the following reactions: $CO + \frac{1}{2}O_2 \leftrightarrow CO_2$ and $H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O$, the first one has more enthalpy $\Delta H_c$ than the second one. On the contrary the main different is in Syngas 3 where the maximum adiabatic flame temperature is much lower than the other two compositions and the difference between them increases with the increase of the equivalence ratio. This is probably due to the presence of $CO_2$ dilution which has lower enthalpy of formation and greater specific heat than the other two components. The decrease in heat
capacity is dominated by the decrease in number of product moles formed per mole of fuel burned, while the decrease in the mean specific heat being less significant.

2.5.2 Equivalence Ratio, Pressure and Temperature Effects on CO and CO$_2$

Figure 3(a) shows how carbon-monoxide production rapidly increases for richer air-fuel mixtures, with the rise of the second composition is faster than the others two because of the biggest percentage of carbon monoxide in the initial composition. CO is a major species in rich combustion products; thus, substantial CO will be produced whenever rich mixture are used. In normal operation of most devices, rich conditions are generally avoided; however spark-ignition engines employ rich mixtures during startup to prevent stalling, and at wide-open-throttle conditions to provide maximum power. For stoichiometric and slightly lean mixtures, CO is found in substantial quantities at typical combustion temperatures as a result of the dissociation of CO$_2$. This is shown in figure 3(b) where is possible to note that the production of carbon dioxide rapidly drop with the increase of the equivalence ratio.

In the following figure 4 is shown the relation between the pressure and the equilibrium CO mole fraction. Is evident in (figure 4) that the increase in pressure decreases the CO mole fraction and this can be explained analyzing the reaction $CO_2 \leftrightarrow CO + \frac{1}{2}O_2$. If this reaction is shifted on the right hand side the pressure increase (because the number of moles augment), otherwise it decreases, so this is the reason why there is a drop in the CO mole fraction with the pressure rise. Looking at the four different compositions is evident that the more the initial composition contains carbon monoxide, the more carbon monoxide at equilibrium there is. In the second one (figure 5) there is a comparison between four different temperatures and is
Figure 3: Influence of equivalence ratio on carbon-monoxide and carbon-dioxide production

\[ T_{in} = 300\, K, p = 1\, atm \]

easy to note that carbon monoxide production rise with the initial temperature. It possible to generalize what is in those two tables. First, at any fixed temperature, increasing the pressure suppresses the dissociation of \( CO_2 \) into \( CO \) and \( O_2 \); second, increasing the temperature at a fixed pressure promotes the dissociation. Both of these trends are consistent with the principle of Le Chatelier that states that any system initially in a state of equilibrium when subjected to a change (increasing pressure or temperature) will shift in composition in such a way as to minimize the change. For an increase in pressure, this translate to equilibrium shifting in the direction to produce fewer moles. For the reaction written above this means a shift to the left, to the \( CO_2 \) side. For equimolar reactions, pressure has no effect. When the temperature is increased, the composition shifts in the endothermic direction. Since heat is adsorbed when \( CO_2 \)
breaks down into $CO$ and $O_2$, increasing the temperature produces a shift to the right$^{[2][16]}$. 

Figure 4: Influence of pressure on carbon-monoxide $T_{in} = 300K, \phi = 1$
Figure 5: Influence of pressure and temperature on carbon-monoxide for Syngas 1 $\phi = 1$
CHAPTER 3

SYNGAS LAMINAR PREMIXED FLAMES

3.1 Introduction

Understanding laminar premixed flames requires to utilize the concepts of mass transfer and chemical kinetics, linked together by thermodynamic and heat transfer knowledge.

The tasks of combustion flow analysis are to increase the fundamentals of combustion and to improve the performance of those devices that utilize it. Many practical combustion problems can be examined most conveniently under the well-defined, controlled conditions which the laminar premixed flame provides and frequently in conjunction with diffusion flames that will be discussed in the following chapter. Applications are many residential, commercial, and industrial devices and processes. Examples include gas ranges and ovens, heating appliances, and Bunsen burners. Laminar flame speed is a fundamental characteristic of the combustion processes. Many important flame properties such as, stability, extinction and flashback are all related to the flame speed. As suggested by the examples given above, laminar premixed flames are by themselves important; but more importantly, understanding laminar flames is a necessary prerequisite to the study of turbulent flames. In both laminar and turbulent flows, the same physical processes are active, and many turbulent flame theories are based on an underlying laminar flame structure. In this chapter will be qualitatively described the essential characteristics of laminar premixed flames and developed a simplified analysis of these flames.
that allows to see what factors influence the laminar flame speed and the flame thickness, which are the main parameters in understanding flame structure. We will focus on how equivalence ratio, temperature, pressure, and fuel type affect these fundamental quantities. Laminar flame speed is a fundamental characteristic to the combustion process as it contains fundamental information on reactivity, diffusivity, and exothermicity. Moreover in premixed flames, the laminar burning velocity and flame structure data can be extremely useful in the analysis of fundamental processes such as ignition, \( NO_x \), and soot formation, and flame quenching. In previous studies, several researchers have investigated the laminar flame speed of \( H_2/CO \) mixtures. In recent years, there has been more and more interest in the actual syngas compositions since detailed information describing the laminar burning velocity, flame thickness, ignition temperature and heat release on various system parameters can be a valuable design aid.

\[ 3.2 \text{ Physical Considerations} \]

A flame may be described as a reaction zone that moves with respect to the gas supporting it and it is a self-sustaining propagation of a localized combustion zone at subsonic velocities. Premixed flames means that the reactants are mixed before approaching the flame region. These flames can only be obtained if the initial fuel and oxidant mixture lies between certain composition limits called the composition limits of flammability. There are several key words in the previous definition. First we require a flame to be localized; that is, the flame occupies only a small portion of the combustible mixture at any one time. The second key word is subsonic. A discrete combustion wave that travels subsonically is called deflagration. It is also possible for combustion waves to propagate at supersonic velocities and in this cases we have a detonation.
The fundamental propagation mechanisms are different in deflagrations and detonations, and, because of this, these are distinct phenomena. A flame may be freely propagating, as occurs when a flame is initiated in a tube containing a combustible gas mixture. The appropriate coordinate system would be fixed to the propagation combustion wave. An observer riding with the flame would see the unburned mixture approaching at the flame speed, $S_L$. This is equivalent to a flat flame stabilized on a burner. In this situation the flame is stationary to the laboratory reference frame, and, once again, the reactants approach the flame with a velocity equal to the flame propagation velocity, $S_L$. In both examples, an important assumption is that the flame is one dimensional and that the unburned gas enters the flame in a direction normal to the flame sheet. Since a flame heats the products, the product density is less than the reactant density. Continuity thus requires the burned gas velocity to be greater than the velocity of the unburned gas as explained in the following equation:

$$\rho_u S_L A \equiv \rho_u U_u A \equiv \rho_b U_b A$$

(3.1)

where the subscripts u and b refer to the unburned and burned gases, respectively. For a typical hydrocarbon-air flame at atmospheric pressure, the density ratio is approximately seven. Thus, there is a considerable acceleration of the gas flow across the flame.

The propagation mode of laminar flame is expected to govern many properties in the flames. The flame, as said before, is the of a self-sustaining chemical reactions occurring within a region of space called the flame front where unburned mixture is heated and converted into products.
Generally, it is convenient to divide the flame front into two regions: a preheat zone and a reaction zone. In the preheat zone, the temperature of the unburned mixture is raised by conductive heat and radicals diffuse from the reaction zone, and there is no significant reaction or energy release occurring in this zone, until reaching a critical temperature, whereas exothermic chemical reaction begins. The region between the temperature where exothermic chemical reaction begins and the hot boundary at the downstream equilibrium burned gas temperature is called the reaction zone. It is useful to divide the reaction zone further into a thin region of very fast chemistry followed by a much wider region of slow chemistry. The destruction of the fuel molecules and the creation of many intermediate species occur in the fast-chemistry region. This region is dominated by bimolecular reactions. At atmospheric pressure, the fast-reaction zone is quite thin, typically less than a millimeter. Because this zone is thin, temperature gradients and species concentration gradients are very large. These gradients provide the driving forces that cause the flame to be self-sustaining, i.e., the diffusion of heat and radical species from the reaction zone to the preheat zone. In the secondary reaction zone, the chemistry is dominated by three-body radical recombination reactions, which are much slower than typical bimolecular reactions, and the final burnout of CO via $CO + OH \rightarrow CO_2 + H$. This secondary reaction zone may extend several millimeters in a 1-atm flame.

Hydrocarbon flames are also characterized by their visible radiation. Within an excess of air, the fast-reaction zone appears blue. This blue radiation results from excited $CH$ radicals in the high-temperature zone. When the air is decreased to less than stoichiometric proportions, the zone appears blue-green, now as a result of radiation from excited $C_2$. In both flames,
OH radicals also contribute to the visible radiation, and to a lesser degree, chemiluminescence from the reaction $CO + O \rightarrow CO_2 + h\nu$. If the flame is made richer still, soot will form, with its consequent blackbody continuum radiation. Although the soot radiation has its maximum intensity in the infrared, the spectral sensitivity of the human eye causes us to see a bright yellow (nearly white) to dull orange emission, depending on the flame temperature.

3.3 \textit{CHEMKIN} Governing Equations for 1-D Premixed Laminar Flames$^\text{[1]}$

In this chapter will be developed the governing equations for steady, isobaric, quasi-one-dimensional flame propagation. These equations are those used to solve this two \textit{CHEMKIN} Reactor Models:

- Premixed Laminar Burner-stabilized Flame
- Premixed Laminar Flame-speed Calculation

The flame dynamics are described by a set of governing differential equations. In this Premixed Flame Models, those differential equations are solved using implicit finite difference methods and a combination of time-dependent and steady-state methods. In order to enhance the converge properties of the steady-state approach and to provide optimal mesh placement, the solver algorithm employed automates coarse-to-fine grid refinement.

When there is the need to analyze the species profile in flame experiments, where the mass flow rate through the burner is known, the Burner-stabilized Flame Model is one of the most used.

There are two options for the burner-stabilized flame, one where the temperature profile is known and one in which the temperature profile is determined by the energy conservation
equation. Often the temperatures are obtained from experiment. In this case, only the species transport equations are solved. In many flames there can be significant heat losses to the external environment, which are of unknown or questionable origin and thus are difficult to model. However, since the chemistry depends strongly on temperature, it is essential to know the temperatures accurately in order to draw conclusions about the chemical kinetics behavior. If a temperature profile can be measured accurately, it is often better to use this measurement than the temperature profile obtained by solving an energy conservation equation. For cases where the heat losses are known to be negligible, the application can solve a burner stabilized flame problem in which the temperatures are determined from the energy conservation equation. Comparing these two problem types for the burner-stabilized model may also provide some indication of the heat losses.

On the other hand the Flame-speed Calculation Model, which has been used for these simulations, involves a freely propagating flame. This configuration is used to determine the characteristic flame speed of the gas mixture at specified pressure and inlet temperature. In this case there are no heat losses (by definition) and thus the temperatures should be computed from the energy equation. Flame speed depends, in part, on the transport of heat, and predicting the temperature distribution is an integral part of the flame speed calculation.

3.3.1 1-D Flame Equations

Developing the following equation we made the simplification to have 1-dimensional flow with uniform inlet conditions. In this way the governing conservation equations will reduce to:
• Continuity:

\[ \dot{M} = \rho u A \]  

(3.2)

• Conservation of Energy:

\[ \dot{M} \frac{dT}{dx} - \frac{1}{c_p} \frac{d}{dx} \left( \frac{A}{c_p} \sum_{k=1}^{K} \rho Y_k V_k c_{pk} \frac{dT}{dx} \right) + \frac{A}{c_p} \sum_{k=1}^{K} \omega_k h_k W_k + \frac{A}{c_p} \dot{Q}_{rad} = 0 \]  

(3.3)

• Conservation of Species:

\[ \dot{M} \frac{dY_k}{dx} + \frac{d}{dx} (\rho A Y_k V_k) - A \dot{\omega}_k W_k = 0 \quad (k = 1, \ldots, K_g) \]  

(3.4)

• Equation of State:

\[ \rho = \frac{P \overline{W}}{RT} \]  

(3.5)

Before going ahead it is important to specify the nomenclature used in these equations. \( x \) denotes the spatial coordinate; \( \dot{M} \) the mass flow rate (which is independent of \( x \)); \( T \) the temperature; \( Y_k \) the mass fraction of the \( k_{th} \) species (there are \( K_g \) gas species); \( P \) the pressure; \( u \) the velocity of the fluid mixture \( \rho \) the mass density; \( W_k \) the molecular weight of the \( k_{th} \) species; \( \overline{W} \) the mean molecular weight of the mixture; \( R \) the universal gas constant; \( \lambda \) the thermal conductivity of the mixture; \( c_p \) the constant-pressure heat capacity of the mixture; \( c_{pk} \) the constant pressure heat capacity of the \( k_{th} \) species; \( \dot{\omega}_k \) the molar rate of production by chemical reaction of the \( k_{th} \) species per unit volume; \( h_k \) the specific enthalpy of the \( k_{th} \) species; \( \dot{Q}_{rad} \) the heat loss due
to gas and particle radiation; and \( A \) the cross-sectional area of the stream tube encompassing the flame (normally increasing due to thermal expansion) normalized by the burner area.

The net chemical production rate \( \omega_k \) of each species results from a competition between all the chemical reactions involving that species. We suppose that each reaction proceeds according to the law of mass action and the forward rate coefficients are in the modified Arrhenius form:

\[
k_f = AT^\beta \exp\left(\frac{-E_A}{RT}\right)
\]  

(3.6)

This expression will be very useful in the second part of this study, since it represents a fundamental point for studying chemical reactions occurring inside solid-oxide fuel cells.

In addition to chemical reaction rates, it is necessary to consider the transport properties of the species (thermal conductivities and diffusion coefficients). Stockmayer potentials are used throughout in evaluating transport properties. There is the possibility to choose if evaluate transport properties using mixture-averaged formulas or a multicomponent diffusion model. A very short description about the first option is provided here, since it is the one used in the numerical simulation performed in this work.

### 3.3.2 Mixture-Averaged Transport Properties

For the mixture-averaged formula, we assume the diffusion velocity \( V_k \) to be composed of three parts:

\[
V_k = \mathcal{V}_k + \mathcal{W}_k + V_c
\]

(3.7)
\( V_k \) is the ordinary diffusion velocity and is given in the Curtiss-Hirschfelder\cite{17} approximation by:

\[
V_k = -D_{km} \frac{dX_k}{dx} \frac{1}{X_k} \tag{3.8}
\]

where \( X_k \) is the mole fraction, and where the mixture-averaged diffusion coefficient \( D_{Km} \) is given explicitly in terms of the binary diffusion coefficients \( D_{kj} \)

\[
D_{km} = \frac{1 - Y_k}{\sum_{j \neq k} \frac{X_j}{D_{kj}}} \tag{3.9}
\]

A non-zero thermal diffusion velocity is included only for the low molecular weight species \( H, H_2 \) and \( He \). The trace, light-component limit is employed in determining \( W_k \), i.e.,

\[
W_k = \frac{D_{km} \theta_k}{X_k} \frac{1}{T} \frac{dT}{dx} \tag{3.10}
\]

where \( \theta_k \) is the thermal diffusion ratio\cite{18}. The sign of \( \theta_k \) makes the lower molecular weight species diffuse from low to high temperature regions.

The correction velocity \( V_c \) (independent of species but a function of the distance \( x \)) is included to insure that the mass fractions sum to unity or equivalently

\[
\sum_{k=1}^{K} Y_k V_k = 0 \tag{3.11}
\]
The formulation of the correction velocity is the one recommended by Coffee and Heimerl\cite{7} in their extensive investigation of approximate transport models in hydrogen and methane flames.

### 3.3.3 Multicomponent Transport Properties

For the multicomponent option, the transport property evaluation follows the method described by Dixon-Lewis\cite{19}. Multicomponent diffusion coefficients, thermal conductivities and thermal diffusion coefficients are computed through the solution of a system of equations involving the binary diffusion coefficients, the species mole fractions, and the thermodynamic and molecular properties of the species. These equations result in the determination of ordinary multicomponent diffusion coefficients, $D_{k,j}$, for species $k$ diffusing in species $j$, as well as species thermal diffusion coefficients and thermal conductivities.

For the multicomponent formulation, the correction velocity, $V_c$, is not required and the diffusion velocity is defined as:

$$V_k = \mathcal{V}_k + W_k$$

where now the ordinary diffusion velocity is:

$$\mathcal{V}_k = \frac{1}{X_k \overline{W}} \sum_{j \neq k} W_j D_{k,j} d_j$$

Here $\overline{W}$ is the mean molar mass, $W_j$ is the molar mass of species $j$, and $d_j$ is defined as:

$$d_j = \nabla X_k + (X_k - Y_k) \frac{1}{P} \nabla P$$
The thermal diffusion velocity is given as:

\[ W_k = \frac{D_k^T}{\rho Y_k T} \frac{1}{T} \nabla T \]  \hspace{1cm} (3.15)

where \( D_k^T \) is the thermal diffusion coefficient for species \( k \). It is strongly recommend to use the multicomponent option when thermal diffusion effects are important, as this is considerably more accurate than the mixture-averaged approach.

### 3.3.4 Boundary Conditions

Two different types of flames are considered: burner-stabilized flames and adiabatic, freely propagating flames. The conservation equations governing the two are the same, but the boundary conditions differ. In both cases the appropriate boundary conditions may be deduced from the early work of Curtiss and Hirschfelder\(^{[17]}\). For burner-stabilized flames \( \dot{M} \) is a known constant, the temperature and mass flux fractions \( \epsilon_k = Y_k = \rho Y_k V_k A / \dot{M} \) are specified at the cold boundary, and vanishing gradients are imposed at the hot boundary.

For freely propagating flames \( \dot{M} \) is an eigenvalue and must be determined as part of the solution. Therefore, an additional constraint is required, or alternatively one degree of freedom must be removed from the problem. We choose to fix the location of the flame by specifying and fixing the temperature at one point. This is sufficient to allow for the solution of the flame speed eigenvalue \( \dot{M} \). The user must select this point in such a way as to insure that the temperature and species gradients nearly vanish at the cold boundary. If this condition is not met then the resultant will be too low because some heat will be lost through the cold boundary.
The boundary conditions are relatively easily implemented. At the cold boundary we specify
the mass flux fractions and the temperature, i.e. we solve:

\[
\epsilon_{k,1} - Y_{k,1} - \left( \frac{p A Y_k V_k}{\dot{M}} \right)_{j=1/2} = 0
\]  

(3.16)

and

\[
T_1 - T_b = 0
\]  

(3.17)

where \(\epsilon_{k,1}\) is the inlet reactant fraction of the kth species and \(T_b\) is the specified burner tem-
perature. At the hot boundary we specify that all gradients vanish, i.e.,

\[
\frac{Y_{k,J} - Y_{k,J-1}}{x_J - x_{J-1}} = 0
\]  

(3.18)

and

\[
\frac{T_J - Y_{J-1}}{x_J - x_{J-1}} = 0
\]  

(3.19)

The boundary conditions for \(\dot{M}\) depend on whether the given problem is a burnerstabilized or
a freely propagating flame.

3.3.5 Finite Difference Approximations

The first task in solving the flame problem is to discretize the governing conservation equa-
tions. We use finite difference approximations on a non-uniform grid with points numbered
from 1 at the cold boundary to \(J\) at the hot boundary. On the convective terms the user has
the choice of using either first order windward differences or central differences. Both cases are
illustrated using the convective term in the energy equation. The windward difference is given as:

\[
\left( \frac{\dot{M} dT}{dx} \right)_j \approx \dot{M}_j \left( \frac{T_j - T_{j-1}}{x_j - x_{j-1}} \right) \tag{3.20}
\]

where the index \( j \) refers to the mesh point. The central difference formula is:

\[
\left( \frac{\dot{M} dT}{dx} \right)_j \approx \dot{M}_j \left( \frac{h_{j-1}}{h_j(h_j + h - j - 1)} T_{j+1} + \frac{h_j - h_{j-1}}{h_j h_{j-1}} T_j - \frac{h_j}{h_{j-1}(h_j + h_{j-1})} T_{j-1} \right) \tag{3.21}
\]

where \( h_j = x_{j+1} - x_j \). The windward difference formula introduce artificial diffusion on a coarse mesh; this has the effect of spreading out the solution and making the convergence of Newtons method less sensitive to the starting estimate. However, because the mesh is refined in regions of high gradient, the artificial diffusion becomes relatively unimportant after the solution has progressed to the fine meshes. Nevertheless, for a given mesh, the windward difference approximation is less accurate than the central difference formula. Therefore, the user may want to select the central difference formula on finer meshes or in cases where the solution is converging without difficulty.

The first derivative in the summation term in the energy Equation 3.13 always approximated by a central difference formula,

\[
\left( \frac{dT}{dx} \right)_j \approx \left( \frac{h_{j-1}}{h_j(h_j + h - j - 1)} T_{j+1} + \frac{h_j - h_{j-1}}{h_j h_{j-1}} T_j - \frac{h_j}{h_{j-1}(h_j + h_{j-1})} T_{j-1} \right) \tag{3.22}
\]

and the coefficients in the summation are evaluated at \( j \).
The second derivative term in the energy equation is approximated by the following second order central difference:

$$\frac{d}{dx} \left( (\lambda A) \frac{dT}{dx} \right)_j \approx \left( \frac{2}{x_{j+1} - x_{j-1}} \right) \left[ (\lambda A)_{j+1/2} \left( \frac{T_{j+1} - T_j}{x_{j+1} - x_j} \right) + (- (\lambda A)_{j+1/2}) \left( \frac{T_j - T_{j-1}}{x_j - x_{j-1}} \right) \right]$$

(3.23)

The coefficients in this formula (at $j \pm 1/2$) are evaluated using the averages of the dependent variables between mesh points.

The diffusive term in the species conservation equation is approximated in a similar way, but it appears to be different because we have written it using diffusion velocities. The ordinary (Equation 3.8) and thermal (Equation 3.10) diffusion velocities are approximated at the positions as illustrated by the following mixture-averaged evaluation:

$$\left( Y_k V_k \right)_{j+1/2} \approx - \left( \frac{W_k D_{km}}{W} \right)_{j+1/2} \left( \frac{X_{k,j+1} - X_{k,j}}{x_{j+1} - x_j} \right)$$

(3.24)

and

$$\left( Y_k W_k \right)_{j+1/2} \approx - \left( \frac{W_k D_{km} \theta_k}{WT} \right)_{j+1/2} \left( \frac{T_{j+1} - T_j}{x_{j+1} - x_j} \right)$$

(3.25)

Since the mole fraction of a species can be zero, we avoid difficulties by forming $Y_k, V_k$, which is the expression needed in Equation 4.8, rather than $V_k$ itself ($Y_k = X_k W_k / W$). After the diffusion velocities are computed at all the mesh midpoints, the correction velocity $V_c$ is computed at the midpoints from

$$V_c = \sum_{k=1}^{K} (V_k + W_k)$$

(3.26)
Upon forming the full diffusion velocities $V_k = \mathcal{V}_k + \mathcal{W}_k + V_c$ the diffusion term is evaluated with the following difference approximation.

$$
\frac{d}{dx}(\rho A Y_k V_k)_j \approx \frac{(\rho A Y_k V_k)_{j+1/2} - (\rho A Y_k V_k)_{j-1/2}}{x_{j+1/2} - x_{j-1/2}}
$$

(3.27)

All the non-differentiated terms, such as the chemical production rate terms, are evaluated at the mesh points $j$. Coefficients not appearing within derivatives are also evaluated at the mesh points.

3.3.6 Transient Forms of the Equations

Even though the Premixed Flame models are solved as steady-state problems, the steady-state solution algorithm sometimes requires pseudo time-stepping to condition the solution iterate. For this reason, we extend the discussion of the governing equations presented previously to include the transient terms used in time-stepping procedures. The transient equations are obtained by adding the time derivatives to Equation 4.7 and Equation 4.8, obtaining:

$$
\rho A \frac{\partial T}{\partial t} + \dot{M} \frac{\partial T}{\partial x} - \frac{1}{c_p} \frac{\partial}{\partial x} \left( \lambda A \frac{\partial T}{\partial x} \right) + \frac{A}{C_p} \sum_{k=1}^{K} \rho Y_k V_k c_{pk} \frac{\partial T}{\partial x} + \frac{A}{C_p} \sum_{k=1}^{K} \dot{\omega}_k h_k W_k = 0
$$

(3.28)

and

$$
\rho A \frac{\partial Y_k}{\partial t} + \dot{M} \frac{\partial Y_k}{\partial x} + \frac{\partial}{\partial x} (\rho A Y_k V_k) - A \dot{\omega}_k W_k = 0
$$

(3.29)

The full system now becomes a system of parabolic partial differential equations, rather than an ordinary differential equation boundary value system. Solution is obtained via the backward-
Euler method. In this method, the time derivatives are approximated by finite differences as illustrated by

$$\rho A \frac{\partial T}{\partial t} \approx \rho_j^{n+1} A_j \left( \frac{T_j^{n+1} - T_j^n}{h} \right)$$ (3.30)

where the superscript $n$ indicates the time level and $h$ represents the size of the time step. All other terms are approximated with finite differences as before, but at time level $n + 1$. Since all variables are known at time level $n$, the discretized problem is just a system of nonlinear algebraic equations for the dependent variable vector $\phi$ at time level $n + 1$.

### 3.4 Set-up a Flame-Speed Calculation with CHEMKIN

This kind of problem is more difficult to simulate than the previous one. First of all the user has to select in the model window the option to perform a Premixed Laminar Flame-Speed Calculation and associate to that the external source of inlet gas and the outlet flow of reactor. After that, again, the user has to choose whether to use a CHEMKIN sample or to create a new chemistry set if working with a new project. Here there is a difference compared to the previous simulations; three different files have to be entered: the first two are the Gas-Phase Kinetics File and the Thermodynamics Data File (like in the previous chapters) but now is needed the Gas Transport Data File (all of them are taken from the Davis Mechanism). After that, the user has to open the Cluster window and hence to define reactor physical properties. Under the window C1-Flame speed the user has to define the initial properties such as unburnt gas temperature, pressure, ambient temperature and the computational grid properties (in order to obtain the grid independence). The user has also to decide whether to use Mixture averaged Transport Model or Multicomponent Model. Once set the physical properties the
user has to define the inlet characteristics like the Steam Properties Data (the mass flow rate or the inlet velocity) and the Species-specific properties that are the Fuel components and the oxidizer mixture by expressing them on a mole-fraction or mass-fraction base and by specifying the equivalence ratio. After that in order to run a simulation must be set the Solver data (concerning tolerances, time-stepping, and finite difference methods) and the Output Control data (where Print Level Control is the only necessary parameter to be set). Finally there is the possibility to define a certain number of continuations in order to analyze the behavior under different conditions. When everything is done in the last window, the user can run a simulation and create an input file first. When the simulation is done, all quantities of interest can be examined by opening the output file and post-processor can be run.

3.5 **Experimental Validation and Grid Independence**

The simulated flame speeds in Figure 6 are included to show how flame speed data obtained in this work are in good agreement with those taken from the experiments\cite{20}\cite{21}. Figure 6 shows laminar flame speeds at different equivalence ratios and we can see that the Davis mechanism shows the best prediction. Once validated by a comparison with experimental results, a kinetic flame model can then be used to carry out detailed numerical simulations that provide a great deal of information on physical and chemical processes which occur in laminar premixed flames.

Figures 7(a) and 7(b) show the different results achieved by controlling the values of Adaptive Grid Control Based on the Solution Gradient (GRAD), Adaptive Grid Control Based on the Solution Curvature (CURV) parameters and using adaptive re-gridding of the *CHEMKIN* software in order to resolve the premixed reactions zone and obtain the grid independence.
Those parameters can be found on the window Grid Properties under C1-flame speed. In table V is explained the meaning of the different precision in order to understand the two figures. The parameter of heat flux is very significant because we have a peak value in a very narrow interval with a very high gradient. The grid independence is reached with precision 2 using 90 grid points, precision 1 reaches 156 grid points. At high pressure we need a higher number of grid points to ensure grid independence.

3.6 Simulation Results

The detailed flame structures for all syngas compositions are analyzed. Figure 8 shows the temperature, the axial-velocity, and the heat generation distributions, while figures 9 and 10 and selected species mole-fraction profiles at 1-atm, stoichiometric, syngas and air flames.
TABLE V: DIFFERENT PRECISION FOR GRID INDEPENDENCE

<table>
<thead>
<tr>
<th>Precision</th>
<th>Precision 1</th>
<th>Precision 2</th>
<th>Precision 3</th>
<th>Precision 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRAD</td>
<td>0.05</td>
<td>0.1</td>
<td>0.4</td>
<td>0.8</td>
</tr>
<tr>
<td>CURV</td>
<td>0.2</td>
<td>0.5</td>
<td>0.7</td>
<td>0.9</td>
</tr>
<tr>
<td>GRID POINTS</td>
<td>156</td>
<td>90</td>
<td>22</td>
<td>15</td>
</tr>
</tbody>
</table>

Figure 7: Grid independence Syngas 1
Unburned gas temperature is 300 K, while axial distance is set to 2 cm. Here we can see the consumption of the fuel, the appearance of the intermediate species and the formation of the final species.

The $CO_2$ concentration has its maximum value at approximately the same location where the carbon monoxide concentration goes to zero and then continues to rise. This could have been clearer if a local-molar-production/destruction-rate was carried out. Note that the bulk of chemical activity is restricted in a small interval from 8 to 12 mm. Figures 10(a) and 10(b) shows that all the intermediate species are produced and destroyed in a narrow interval too their peak concentrations appear slightly earlier in the flame. Looking at figure 10(d) is possible to note that water vapor reaches the major portion of its equilibrium a little bit sooner than the carbon dioxide. Analyzing figure 8 permits us to make the following considerations. While the fuel is completely gone in approximately 2 mm and the major portion of the total temperature rise occurs in the same interval, the approach to equilibrium conditions is relatively slow beyond this point because we are in the wider region of slow chemistry. In fact, we can see that equilibrium has yet to be reached even at the 15-mm location. At atmospheric pressure, this zone may extend several mm. This slow approach to equilibrium is primarily a consequence of the dominance of three-body recombination reactions in this region (such as $CO + OH \rightarrow CO2 + H$). Plotting mole fractions as a function of distance, rather than time, emphasizes the slow approach to equilibrium somewhat as a consequence of the stretching of the distance-time relation ($dx = v_x dt$) through continuity ($\rho v_x = const$). For instance, given the same time interval, a fluid particle in the hot, high velocity region of the flame
travels along a distance which is greater than a fluid particle in the cold, low-velocity region. The reaction of \( OH \) with \( CO \) has been thoroughly studied experimentally and theoretically, because this reaction path is responsible for the major fraction of energy release in the oxidation of hydrocarbons to \( CO_2 \) and \( H_2O \), and this reaction rate is the most sensitive for the prediction of \( COH_2 \) flame speed data. Although this reaction exhibits strong non-Arrhenius behavior at moderate and low temperatures, its reaction rate approaches the low-pressure limit at the temperatures above 1000 K.

For what concerns fuel comparisons, we can easily state that all the four syngas compositions have the same behavior since the curve trend seems to be the same for all fuels, although all quantities can present quite large discrepancies. From simulations it seems that the laminar flame speed increases significantly with the \( H_2 \) content (especially for syngas 4). This can be explained by the fact that several factors combine to give \( H_2 \) its high flame speed: firstly the thermal diffusivity of pure \( H_2 \) is several times greater than hydrocarbon fuels; secondly, the mass diffusivity of hydrogen likewise is much greater than for the hydrocarbons; and thirdly, the reaction kinetics for \( H_2 \) are very rapid since the relatively slow \( CO \rightarrow CO_2 \) step that is a major factor in hydrocarbon combustion is absent. This third factor should be attributed to the rapid production of the hydrogen-related radicals (figures 10(a) and 10(a)). In the first three compositions the effect of \( H_2 \) in increasing the laminar flame speed is less evident and this can be explained by the fact that the \( H_2 \) content is relatively lower in the syngas-air mixture. So, although the burning velocity of \( H_2 \) is an order of magnitude faster than those of \( CO \) (for the reasons explained above) its effect is somewhat suppressed because of the relatively low content.
Figure 8: Axial-velocity, heat generation, temperature for syngas laminar premixed flames  
(\(\phi = 1, T_{in} = 300K, p = 1atm\))
Figure 9: Selected species mole-fraction profiles for syngas laminar premixed flames
\( (\phi = 1, T_m = 300K, p = 1atm) \)
Figure 10: Selected species mole-fraction profiles for syngas laminar premixed flames
$(\phi = 1, T_{in} = 300K, p = 1atm)$
In particular, Figure 8 presents how temperature is almost the same for all cases, while the axial-velocity profiles are very far from each other. It is also very easy to see how the heat flux produced when burning the fourth composition which contains 95% of $H_2$ is considerably higher than the other three cases. Figure 9(c) focuses on nitric oxide production and a rapid rise in the NO mole fraction can be noticed. NO formation is dominated by the Zeldovich kinetics. The comparison of NO$_x$ characteristics of the four syngas flames is shown in the same figure. In the combustion of fuels that contain no nitrogen, nitric oxide is formed by four chemical mechanisms: the thermal or Zeldovich mechanism, which is the most important route forming NO, the Fenimore or prompt mechanism, the $N_2O$ intermediate mechanism and the NNH mechanism. The thermal NO mechanism dominate in high temperature combustion while the prompt mechanism is important in rich hydrocarbon combustion.

Figure 11 represents a bar diagram showing different values of flame speed for each syngas composition, with the same initial conditions used above. The maximum value in the axial velocity column on the output solution is used to calculate the flame speed. Once again the laminar flame speed is increased as the percentage of $H_2$ in the fuel mixture is increased. However, the NO emission should be more pronounced as the amount of $H_2$ is increased. Feeding a combustor with syngas would probably bring to a loss in performance but it is clear how losing performance may be necessary when we want to bring down the emissions.

3.6.1 Influence of Equivalence Ratio, Pressure and Temperature

Except for very rich mixtures, the primary effect of equivalence ratio on flame speed for similar fuels is a result of how this parameter affects flame temperatures; thus it is evident that
flames speed have a maximum at a slightly rich mixture and fall of on either side as shown in figure 12. The flame speed increases with equivalence ratio and decreases in the compositions with a small dilution of CO$_2$. That happens because CO$_2$ reduces the rate of CO and H$_2$ oxidation reaction. Laminar flame speeds at elevated pressure are important for refining the chemical kinetics that are relevant at engine conditions. That the maximum flame speed is at slightly rich equivalence ratio is related to the temperature and it is a consequence of both the heat of combustion and the heat capacity of the products declining beyond $\phi = 1$. For equivalence ratios between $\phi = 1$ and $\phi(T_{\text{max}})$ the heat capacity decreases more rapidly with $\phi$ than $\Delta H_c$, while beyond $\phi(T_{\text{max}})$, $\Delta H_c$ falls more rapidly than does heat capacity. The decrease in heat capacity is dominated by the decrease in amount of products formed per unit of fuel burned, with the decrease in the mean specific heat being less important.
Laminar flame speeds at elevated pressure are important for refining the chemical kinetics that are relevant at engine conditions. In order to study the effect of pressure we simulate the dependence of the laminar flame speed on this parameter as is possible to see in figure 14. For pressures up to 10 atm the unstreached laminar flame speed decrease very fast with the pressure but after this point the dependence become less important up to reach an asymptote. This trend is the same for all the four syngas compositions. The laminar flame speed as a function of the pressure can be expressed with the following formula \( S_L \propto P^{(n-2)/2} \) and \( n \) is the overall reaction order defined as \( n = 2 + 2 \left( \frac{\partial \ln(S_L)}{\partial \ln(P)} \right) \). Giles et al. revealed\(^{[20]}\) that the overall reaction order initially decrease with the increase in pressure which is related to the relative dominance of chain termination reactions instead of branching reactions.

![Figure 12: Influence of equivalence ratio on flame speed \((T_{in} = 300 K, p = 1 \text{ atm})\)](image-url)
Figure 13: Influence of equivalence ratio and pressure on flame speed for Syngas 1

\( T_{in} = 300 K \)

Figure 15 shows that the laminar flame speed has a strong dependence on the temperature of the unburned gas. As the unburned gas temperature increase the flame speed increases and this is due to the increased chemical rates and thermal and mass diffusivity. Furthermore the viscosity increases too so the flame can remain laminar.
Figure 14: Influence of pressure on flame speed ($T_{in} = 300K, \phi = 1$)

Figure 15: Influence of temperature on flame speed ($p = 1atm, \phi = 1$)
CHAPTER 4

SYNGAS LAMINAR DIFFUSION FLAMES

4.1 Introduction

In this chapter we focus on laminar diffusion flames where both the mixing of fuel and air and the combustion process occur at the interface. The fuel and oxygen meet to form a combustible mixture, and once ignition has taken place, burning starts immediately upon creation of such mixture. In this case, the flame appears at the border between the fuel and oxygen zones. Combustion products created by the flame spread to both side, and fuel and oxygen have to diffuse against those streams in order to mix and react. The more commonly flow configurations of diffusion flames are:

- co-flowing jets of the unmixed reactants
- opposed jets leading to stagnation points

4.2 Opposed Diffusion Flames

Often called counterflow flames, they are the more suitable for many aspects of the investigation of diffusion flame reaction zone structure and properties because they are approximated as one-dimensional which makes both experiments and numerical simulations much more practicable. For instance while performing experiments, temperature and species conservation measurements have to be made only along a single path; while, in numerical analysis, it is possible to use extremely complex chemical kinetics and at the same time only few run times are needed
for computation. Flame extinction resulting from excessive strain or dilution is of particular
importance and has received considerable attention.

Before analyzing the mathematical model it is important to understand the physics of
the counterflow flames. In Figure 16 is illustrated a typical configuration. Between the fuel
and oxidizer jets there is a stagnation plane \( (v_x = 0) \) whose location depends on the relative
magnitudes of the oxidizer and fuel jet initial momentum fluxes. In the situation of equal
momentum fluxes \( (\dot{m}_F v_F = \dot{m}_O v_O) \), the stagnation plane will be located at the midpoint
between the nozzle exit planes; however, if the momentum flux of one stream is increased over
the other, the stagnation plane moves closer to the low-momentum-flux stream outlet. The
combustion takes place in a single thin flame zone near the stagnation plane, and around the

Figure 16: Counter-flow flame configuration\(^2\)
location of the stoichiometric mixture. Normally, either the fuel or the oxidizer reaches the flame by diffusion from the stagnation plane in a direction counter to the convective flow, and the products of the combustion are converted back towards the stagnation plane. Sometimes the fuel stream is partially premixed with air in order to provide non-sooting operations\cite{22}.

4.3 **CHEMKIN Governing Equations for Opposed-flow Flames**\cite{1}

In this paragraph will be developed the conservation equations that describe the counter-flow flames. They are based on transformation equations that convert the three dimensional behavior of the flow to an axial one dimensional dependence. This analysis will be useful for the CHEMKIN reactor model for Diffusion or Premixed Opposed-flow Flame.

4.3.1 **Axisymmetric and Planar Diffusion**

For the Opposed-flow Flame model CHEMKIN uses a steady-state solution. First of all we assume that the radial velocity varies linearly in the $y$ direction which makes it possible to define the fluid properties only as function of the axial distance. In this way the problem is reduced mathematically from two or three-dimension to 1-D. This one-dimensional model then predicts the species, temperature, and velocity profiles in the core flow between the nozzles (neglecting edge effects). Both premixed and non-premixed flames can be simulated.

There are two possible geometries, the axisymmetric and the planar geometry, as shown in Figure 17(a) and Figure 17(b). The first one consists of two concentric, circular nozzles directed towards each other that produces an axisymmetric flow field with a stagnation plane between the nozzles, while the second one consists of two concentric linear nozzles directed towards each other that produces a 2-D planar flow field with a stagnation line between the
two nozzles. In both the figures the dashed line represents the stagnation plane, while the red region suggests the flame. The location of the stagnation plane, as said before, depends on the momentum balance of the two streams. When the streams are premixed, two premixed flames exist, one on either side of the stagnation plane. When one stream contains fuel and the other one oxidizer, a diffusion flame is established. Since most fuels require more air than fuel by mass, the diffusion flame usually sits on the oxidizer side of the stagnation plane; fuel diffuses through the stagnation plane to establish the flame in a stoichiometric mixture. In this specific case an axisymmetric geometry has been employed in order to point out the dominance of the phenomena occurring along the axial coordinate.

Figure 17: Geometry of the axisymmetric and planar opposed-flow diffusion flame respectively
The CHEMKIN Opposed-flow Flame Simulator is derived from a model initially developed by Kee\textsuperscript{[23]}, for premixed opposed-flow flames. The reduction of the three-dimensional stagnation flow is based on the similarity solutions developed for incompressible flows by von Karman\textsuperscript{[24]}. It is important to point out that the CHEMKIN impinging and stagnation-flow models are based on a finite domain, where the user has to specify the distance between the nozzles. For this approach, an eigenvalue must be included in the solution of the equations and the strain rate varies, such that a characteristic strain rate must be determined from the velocity profile. Following the analysis of Evans and Grief\textsuperscript{[25]}, Kee\textsuperscript{[23]} showed that this formulation allowed more accurate predictions of the extinction limits for premixed flames than other approaches.

At steady-state, conservation of mass in cylindrical or planar coordinates is:

\[
\frac{\partial (\rho u)}{\partial x} + \frac{1}{r} \frac{\partial (\rho v_r r)}{\partial r} = 0 \quad (4.1)
\]

where \(u\) and \(v_r\) are the axial and radial velocity components and \(\rho\) is the density. According to von Karman\textsuperscript{[24]} \(v_r/r\) and other variables should be functions of \(x\) only and for this reason we assume:

\[
G(x) = -\frac{\rho v_r}{r} \quad (4.2)
\]

\[
F(x) = \frac{\rho u}{2} \quad (4.3)
\]

Substituting into the Equation 4.1 we obtain:

\[
G(x) = \frac{dF(x)}{dx} \quad (4.4)
\]
for the axial velocity \( u \). Since \( F \) and \( G \) are functions of \( x \) only, so are \( \rho, u, T \) and \( Y_k \). The perpendicular momentum equation is satisfied by the eigenvalue:

\[
H = \frac{1}{r} \frac{\partial p}{\partial r} = \text{constant} \tag{4.5}
\]

The perpendicular momentum equation is:

\[
H - 2 \frac{d}{dx} \left( \frac{FG}{\rho} \right) + 3G^2 \frac{d}{dx} \left[ \mu \frac{d}{dx} \left( \frac{G}{\rho} \right) \right] = 0 \tag{4.6}
\]

Energy and species conservation are:

\[
\rho u \frac{dT}{dx} - \frac{1}{c_p} \frac{d}{dx} \left( \lambda \frac{dT}{dx} \right) + \frac{\rho}{c_p} \sum_k c_{pk} Y_k V_k \frac{dT}{dx} + \frac{1}{c_p} \sum_k h_k \dot{\omega}_k + \frac{1}{c_p} Q_{rad} = 0 \tag{4.7}
\]

where \( \dot{Q}_{rad} \) is the heat loss due to gas and particle radiation.

\[
\rho u \frac{dY_k}{dx} + \frac{d}{dx} (\rho Y_k V_k) - \dot{\omega}_k W_k = 0 \quad k = 1, \ldots, K \tag{4.8}
\]

where the diffusion velocities are given by either the multicomponent formulation:

\[
V_k = \frac{1}{X_k W} \sum_{j \neq k}^K W_{kj} \frac{dX_j}{dx} - \frac{D_{k,T}^T}{\rho Y_k T} \frac{dT}{dx} \tag{4.9}
\]
or the mixture-averaged formulation:

\[ V_k = -\frac{1}{X_k} D_{km} \frac{dY_k}{dx} - \frac{D_k^T}{\rho Y_k} \frac{1}{T} \frac{dT}{dx} \]  \hspace{1cm} (4.10)

where:

\[ D_{km} = \frac{1 - Y_k}{\sum_{j \neq k} \frac{X_j}{D_{jk}}} \]  \hspace{1cm} (4.11)

and \( D_{km} \), \( D_{km} \), \( D_{kj} \) and \( D_k^T \) are respectively the multicomponent, mixture-averaged, binary, and thermal diffusion coefficients.

The boundary conditions for the fuel (\( F \)) and oxidizer (\( O \)) streams at the nozzles are:

\[ x = 0 \quad F = \frac{\rho u_F}{2}; \quad G = 0; \quad T = T_F; \quad \rho u Y_k + \rho u Y_k V_k = (\rho u Y_k)_F \]  \hspace{1cm} (4.12)

\[ x = L \quad F = \frac{\rho o u_O}{2}; \quad G = 0; \quad T = T_O; \quad \rho u Y_k + \rho u Y_k V_k = (\rho u Y_k)_O \]  \hspace{1cm} (4.13)

It is important to point out that the inflow boundary conditions Equation 4.12 and Equation 4.13 define the total mass flux, including diffusion and convection, rather than the fixing species mass fraction \( Y_k = Y_{k,F} \). If gradients exist at the boundary, these conditions permit diffusion into the nozzle.

The differential Equation 4.4 through Equation 4.8 and boundary conditions Equation 4.12 and Equation 4.13 form a boundary value problem for the dependent variables (\( F, G, H, T, Y_k \)). The GAS-PHASE KINETICS Subroutine Library provides the reaction rates and
thermodynamic properties, while the TRANSPORT package evaluates the transport properties for these equations.

4.3.2 Finite-difference Approximations

In order to discretize the differential equations derived before standard conventional finite differencing techniques for non-uniform mesh spacing have been used. It is well known that diffusive terms use central differences, with truncation error that is second-order in the mesh spacing, while for better convergence, convective terms use upwind differencing, which uses the sign of the velocity to choose which direction the spatial difference will go. If $u_j = 0$, for example, then the convective term in the energy equation is differenced as:

$$
\rho u \frac{dT}{dx} \approx \rho_i u_j \left( \frac{T_j - T_{j-1}}{x_j - x_{j-1}} \right)
$$

The truncation error of this approximation is first-order in the mesh spacing, leading to what is often called artificial diffusion, but this form avoids unwanted oscillations during the solution on a coarse mesh.

4.3.3 Regrid Operation

A Regrid operation is useful for changing the number of grid points when restarting from one flame to another. Another use for Regrid is to revise the solution guess when a previous simulation made some progress towards a solution (by time integration, for example), but failed to converge to a steady solution.
The steady-state solver, TWOPNT’s grid refinement adds points in regions where they are needed to resolve the first and second derivatives of the solution, using criteria controlled by the GRAD and CURV keywords. TWOPNT never moves or removes points. If it reaches a maximum number of points (internally defined by the dimensions), it simply prints a message and quits. Sometimes it may be necessary to reduce the number of points when starting a new solution from a previous result. The Regrid operation redefines the solution guess on a specified number of mesh points, followed by the number of points.

The Regrid operation is different from the grid-point insertion operation performed by TWOPNT. Both operations aim to solve the gradient and curvature in the solution, except that TWOPNT considers all solution components, whereas Regrid only considers the temperature profile. TWOPNT only adds points, leaving the old points as they were, while Regrid change the location and solution of all the points interior to the boundaries. Regrid computes new locations for the given number of points, and then interpolates the solution from the previous grid to obtain a new solution. Regrid does not conserve any properties of the solution; in fact, it tends to smooth the solution by the error inherent in the interpolation.

Regrid redistributes a weighting function of the first and second derivatives of the temperature. The profiles of the other dependent variables are ignored on the assumption that the temperature profile defines the flame location well enough for the purposes of realigning the mesh for an initial condition. The redistribution uses a transformation from the physical coordinate $x$ to a new coordinate $\eta$. 
4.4 Set Up an Opposed-flow Flame Calculation on CHEMKIN

This simulation is slightly more complicated than the previous and requires the settings of different parameters in order to carry out a complete analysis. It is possible to choose whether to use a CHEMKIN sample or to create a new project. In the case of a new project the user has to select on the model panel the icon for Diffusion or Premixed Opposed-flow flame and drag it on the diagram view. Contrary to what has been done in the previous chapter now the user must connect two external sources of inlet gas and one outlet flow. The two inlets represent respectively the fuel and the oxidizer flows. At this point the user has to carry out the same preliminary operation as done in the previous cases and if he is working on a new project the chemistry set must be created and three different files must be entered: the Gas-Phase Kinetics File, the Thermodynamics Data File, and the Gas Transport Data File, which are all taken from the Davis modified mechanism. After creating the chemistry set the user can start to insert the physical properties. First of all the problem type has to be defined (i.e., Solve Gas Energy Equation), then in order plateau profile for initial guess, maximum temperature for initial profile, and pressure. The user can also decide whether to use Mixture averaged Transport Model or Multicomponent Model. The following window regards the grid properties and contains all the data about grid points and axial position (it is important to define the ending axial position, which represent the distance between the two nozzles). Then must be defined the properties of both fuel and oxidizer or rather the stream properties (mass flow rate or the inlet velocity and the inlet temperature) and the species-specific properties (reactant species by expressing them on mole-fraction or mass-fraction). In this latter case the user can
decide to perform a parameter study by varying the percentage of the components and evaluate
the effect of dilution. The last parameter to be defined are the ones regarding the numerical
parameters (tolerances, timestepping, and finite difference methods). Once again there is the
possibility to run a certain number of continuations. When everything is defined it is possible
to run the simulation and analyze the output data on Microsoft Excel or with the CHEMKIN
post-processor.

4.5 Simulation Results

The opposed-flow flame model described in the previous section has been used to analyze the
structure of syngas diffusion flames. In particular nonpremixed flame has been deeply studied
with a extensive analysis of extinction characteristic. The effect of partially premix the inlet
jet has been analyzed too. In the study of diffusion flames the strain rate is an important
parameter and it is defined as the fractional rate of change of area of an infinitesimal element
of the surface at that point. When performing the simulations the distance between the nozzles
is set to 1.5 cm, pressure is 1 atm and the temperature of the fuel inlet is 300 K. Since the
CHEMKIN opposed-flow model does not contain the option to define directly the strain rate it
has to be obtained by computing densities and velocities of both the fuel and oxidizer stream.
The velocities are chosen to conform to the global strain rate:

\[ a_s = \frac{2|V_O|}{L} \left( 1 + \frac{|V_F|\sqrt{\rho_F}}{|V_O|\sqrt{\rho_O}} \right) \] (4.15)
and to satisfy the momentum balance:

\[ \rho_O V_O^2 = \rho_F V_F^2 \] (4.16)

Using these two equations, the fuel and the air strain velocities can be computed for a given strain rate.

### 4.5.1 Nonpremixed Case

It can be easily notice that there is a local maximum of CO on the fuel side at very low temperature. It seems that CO is been produced, but this is not the case. Due to high diffusivity and reactivity of hydrogen, the mole fraction of H\(_2\) decreases faster than that of CO; therefore, causing an increase of CO concentration locally and just ahead of flame zone. Similar results can be found at rich premixed reaction zone for the study of counterflow syngas flames. Furthermore, combustion of syngas mixture containing more hydrogen (Syngas 4) presents higher flame temperature and flame zone is wider and much closer to the air side. There is more production of H\(_2\)O and less of CO\(_2\) because of the high hydrogen content. Near the high temperature regions the peak mole fractions of H and OH radicals are larger for Syngas 4 flame. Apparently from H\(_2\)-enriched (Syngas 4) to CO-enriched syngas flames (Syngas 2), there are fundamental difference in the flame structures and corresponding chemical reactions as it is possible to see by a sensivity study. For syngas with higher amount of H\(_2\), H\(_2\)O is produced through the reactions of \(OH + H_2 \rightarrow H + H_2O\) and \(OH + HO_2 \rightarrow O_2 + H_2O\) together with the chain branching reactions involving the radicals \(OH\) and \(H\). CO\(_2\) is formed through
Figure 18: Axial-velocity, heat generation, temperature for syngas counterflow nonpremixed flames ($T_{in} = 300K, p = 1atm, a_s = 100s^{-1}$)
Figure 19: Selected species mole-fraction profiles for syngas counterflow nonpremixed flames \( (T_{in} = 300K, p = 1\, atm, a_s = 100\, s^{-1}) \)
Figure 20: Selected species mole-fraction profiles for syngas for syngas counterflow nonpremixed flames \((T_{in} = 300K, p = 1atm, a_t = 100s^{-1})\)

\[\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2\]. On the contrary for Syngas 2, with an higher amount of \(\text{CO}, \text{CO}_2\) the last reaction mentioned before become the most important. However a small amount of \(\text{CO}_2\) is converted back to \(\text{CO}\) through the same reaction and this means that the carbon monoxide at high temperature is not chemically inert. This consideration is useful in the following study of syngas extinction characteristic.

For what concerns greenhouse emissions, of course carbon-monoxide and carbon-dioxide emissions are higher for those syngas compositions that present more \(\text{CO}\) in the initial mixture like Syngas 2. Moreover the results show that \(\text{NO}\) is produced in the high temperature zone for all the types of syngas flames, but the \(\text{NO}\) production rate for Syngas 4 flame is higher due to higher flame temperature, a characteristics of thermal \(\text{NO}\) (Zeldovich mechanism). The \(\text{NO}\)
Figure 21: Axial-velocity, heat generation, temperature for syngas counterflow nonpremixed flames ($T_{in} = 300K, p = 1atm, a_s = 200s^{-1}$)
Figure 22: Selected species mole-fraction profiles for syngas counterflow nonpremixed flames
($T_{in} = 300K, p = 1atm, a_s = 200s^{-1}$)
formation for $H_2$-rich syngas flame is dominated by the following reactions $N_2 + O \rightarrow NO + N$, $N + O_2 \rightarrow NO + O$ and $N + OH \rightarrow NO + H$, while for $CO$-rich syngas flame, the reaction $N + CO_2 \rightarrow NO + CO$ becomes more active besides the three mentioned before, because more $CO_2$ is involved in the reactions.

Looking at the influence of the strain rate, it is easy to state that, as the strain rate increases, the flame becomes narrower, peak temperature decreases, while axial velocity slightly increases. Moreover, emissions of pollutants slightly decrease and the mole-fraction peaks are generally shifted towards the air nozzle.
4.5.2 Syngas Extinction Characteristics

In this section is reported a detailed study of extinction characteristics of opposed-jet syngas diffusion flames and it is shown how flame extinction is significantly affected by the compositions of syngas mixture. The effects of three dilution gases, \( CO_2 \), \( H_2O \) and \( N_2 \), have been studied since they may be present in the syngas fuel depending on the fuel sources and gasification and post-gasification processes. The extinction limit can be defined as the minimum mole fraction of diluent required to extinguish the flame. A sensitivity study has been performed too by modifying the mechanism file in order to analyze the effect of each different reaction on the extinction. Sensitivity coefficient \( (S_i) \) is defined as:

\[
S_i = \frac{\partial \ln m_b}{\partial \ln k_i} \tag{4.17}
\]

where \( k_i \) is the reaction rate of the elementary reaction and \( m_b \) is the mass burning rate.

The dilution components can be different effects on the syngas flames, such as inert gas effect, chemical effect, thermal effect and radiation effect. The inert effect is due to the fact that the addition of a component (in this case the diluent) in the syngas mixture reduces the relatively contentration of the other species and so of the reactants and in this way the overall reaction order will decrease. The diluents are not completely chemically inert and will be involved in the chemical reaction. For this reason a sensitivity study was performed by changing the rate coefficients of the reactions in the mechanism and analyzing the effect on the extinction limit. The thermal effect is related to the fact that the syngas will change its thermal and transport
properties because of the addition of the diluents. Last, radiation is one of important heat transfer modes involved in the diffusion flames, especially at low strain rates and $CO_2$ and $H_2O$ are strong radiation-participating gases\cite{26}.

Figure 24: Variations of maximum flame temperature with mole fraction of dilution for Syngas 1 ($T_{in} = 300K, p = 1\text{atm}$)

In the Figures 24, 25, 26 are reported the numerical results with different strain rates for the syngas compositions studied in this work. The mole fraction of dilution means the mole fraction of the dilution gas in the whole syngas-diluent mixture. In general it is easy to note that for all the strain rates and syngas compositions the maximum flame temperature decreases when the mole fraction of dilution increases up to reach the extinction. Starting analyzing the effect
Figure 25: Variations of maximum flame temperature with mole fraction of dilution for Syngas 2 \((T_{in} = 300K, p = 1\text{ atm})\)

Figure 26: Variations of maximum flame temperature with mole fraction of dilution for Syngas 4 \((T_{in} = 300K, p = 1\text{ atm})\)
of adding \( CO_2 \) with a strain rate of \( 100s^{-1} \) is possible to see that the temperature decreases the most compared with the other two types of dilution gases but increasing the strain rate to \( 200s^{-1} \) the drop is less pronounced (again compared with the other diluents). With a sensitivity study was possible to make the conclusion that \( CO_2 \) has not only an inert effect since the reaction \( H + CO_2 \rightarrow OH + CO \) contributes to the creation of the CO species. Moreover it is necessary less \( CO_2 \) than \( N_2 \) or \( H_2O \) to reach the flame extinction limit. In conclusion the extinction behavior with the addition of carbon monoxide is quite linear. For what concern the dilution with \( N_2 \) it is easy to see that it is less effective than \( CO_2 \) in the extinguish the flame but it is very sensitive to the strain rate since there is a huge drop in the extinction limit compared to that of carbon dioxide. In order to better understand the effect of dilution with nitrogen, several simulation were performed using the Davis mechanism without the \( NO_x \) chemistry and after that it was possible to state that there is only an inert effect of \( N_2 \) since there is no difference in the extinction limit compared with the results obtained using the modified Davis mechanism. The \( H_2O \)-diluted syngas flames present a very interesting behavior. Passing from Syngas 4 (\( H_2 \)-enriched) to Syngas 1 (\( CO \)-enriched) through Syngas 1 is evident that the difference in the extinction limit is very limited compared to the cases of dilution with \( CO_2 \) and \( N_2 \). Furthermore this case of extinction limit is not very affected by the strain rate. In addition to that in those simulations with a strain rate of \( 200s^{-1} \) the mixture doesn’t ignite in a range from 39,5% to 52,4% by volume of \( H_2O \). In order to better understand the reasons of this behaviour different analysis has been performed. First of all was studied the chemical effect of \( H_2O \) by performing a sensitivity study. The reaction \( OH + CO \rightarrow H + CO_2 \) has an
important role for Syngas 2 since lowering its rate coefficient will lead to an important reduction of the extinction limit because with the production of the H radicals it will promote the other reactions. For the same reason the reaction $H + HO_2 \rightarrow OH + OH$ become important too for the production of the OH radicals for the reaction $OH + HO_2 \rightarrow O2 + H_2O$. In conclusion the dilution with $H_2O$ has an important chemical effect, especially for Syngas 4, that increases the flame temperature and therefore the extinction limit will be higher. Figures 27, 28, 29 show the net heat production and indicate the heat generations are larger for high-stretch flames, and the chemical heat release decreases with increasing mole percentage of dilution due to the inert gas effect. Again for Syngas 2 ($CO$-enriched) there is an interesting behavior and we can see that at the same percentage of dilution, the heat generation is the largest with $H_2O$ as the diluents, because of the chemical effect from $H_2O$, but this behaviour will lower the maximum flame temperature.

**TABLE VI: SYNGAS EXTINCTION LIMITS ($A_S = 100S^{-1}$)**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Syngas 1</th>
<th>Syngas 2</th>
<th>Syngas 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CO_2$</td>
<td>71.83</td>
<td>1331.10</td>
<td>54.55</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>77.78</td>
<td>1206.63</td>
<td>71.43</td>
</tr>
<tr>
<td>$N_2$</td>
<td>82.14</td>
<td>1043.77</td>
<td>62.29</td>
</tr>
</tbody>
</table>
TABLE VII: SYNGAS EXTINCTION LIMITS \((A_S = 200 S^{-1})\)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Syngas 1</th>
<th></th>
<th>Syngas 2</th>
<th></th>
<th>Syngas 4</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(CO_2)</td>
<td>53,38</td>
<td>1635,41</td>
<td>25,37</td>
<td>1715,58</td>
<td>68,75</td>
<td>1509,80</td>
</tr>
<tr>
<td>(H_2O)</td>
<td>75,00</td>
<td>1307,19</td>
<td>67,21</td>
<td>1342,15</td>
<td>77,27</td>
<td>1429,01</td>
</tr>
<tr>
<td>(N_2)</td>
<td>56,52</td>
<td>1727,25</td>
<td>39,02</td>
<td>1678,74</td>
<td>76,74</td>
<td>1489,12</td>
</tr>
</tbody>
</table>
Figure 27: Variations of maximum flame temperature with mole fraction of dilution for Syngas 1 ($T_{in} = 300 K, p = 1 atm$)

Figure 28: Variations of maximum flame temperature with mole fraction of dilution for Syngas 2 ($T_{in} = 300 K, p = 1 atm$)
4.5.3 Syngas Partially Premixed Flames

In many applications of counterflow flames, the fuel stream is usually partially premixed with air, which is essential to provide non-sooting operation. Partially premixed flames have been the subject of several studies and recently they have been used to developed models capable to explain how soot is formed in diffusion burning. Of particular concern are the emissions of nitrogen dioxide and carbon monoxide. In this paragraph will be performed a comparison between a nonpremixed flame and two partially premixed flames with different values of equivalence ratio in order to understand the effects of partially premix the fuel stream with air. Since the *CHEMKIN* Opposed-flow Flame Simulator does not allow the user to directly
define the equivalence ratio of the fuel inlet, the simplest way to proceed is to fix the equivalence ratio by computing the air premixing and, consequently, the mole fractions of every chemical species at the fuel nozzle of the reaction \( CO + H_2 + O_2 + 3.76N_2 \rightarrow CO_2 + H_2O + 3.76N_2 \).

In this particular study only the syngas composition 1 has been analyzed and the simulations have been performed with a strain rate of \( 100s^{-1} \), while equivalence ratio has been set to values of 6.0 and 10.0 respectively. The initial conditions are the same of the previous paragraph or rather temperature of 300 K and pressure of 1 atm for both fuel and oxidizer. In Table VIII are reported the three cases analyzed.

<table>
<thead>
<tr>
<th>Case</th>
<th>Strain Rate</th>
<th>Equivalence Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100s(^{-1})</td>
<td>6.0</td>
</tr>
<tr>
<td>2</td>
<td>100s(^{-1})</td>
<td>10.0</td>
</tr>
<tr>
<td>3</td>
<td>100s(^{-1})</td>
<td>( \infty )</td>
</tr>
</tbody>
</table>

32 shows the equivalence ratio influence the structure of the syngas flame analyzed. In the partially premixed cases the flame structure presents two reaction zones since it presents two peaks, since it is possible to see in Figure 30(b). The first one is called rich premixed zone and it is located close to the fuel nozzle while the second one is the nonpremixed zone located
Figure 30: Effect of equivalence-ratio on axial-velocity, heat generation, temperature for Syngas 1 counter-flow flames ($T_{in} = 300 K, p = 1 atm, a_s = 100 s^{-1}$)
Figure 31: Effect of equivalence-ratio on selected species mole-fraction profiles for Syngas 1 counter-flow flames ($T_{in} = 300K, p = 1atm, a_s = 100s^{-1}$)
on the side of the oxidizer nozzle. For an higher value of equivalence ratio ($\phi = 10$) the two peaks are less pronounced and the temperature peaks are nearly merged. The axial velocity (Figure 30(a)) presents an higher value for the lowest value of equivalence ratio. For what concern the emissions, there is a single NO peak and for the leaner mixture ($\phi = 6$) this peak is shifted toward the oxidizer nozzle and present a lower value. The peak value of NO$_2$ is negligible compared to NO and does not seem to be affected by the equivalence ratio. However premixing the fuel nozzle results in an increase of the carbon dioxide emissions.

Figure 32: Effect of equivalence-ratio on selected species mole-fraction profiles for Syngas 1 counter-flow flames ($T_{in} = 300K, p = 1atm, a_s = 100s^{-1}$)
CHAPTER 5

INTRODUCTION TO SOFCS

5.1 Technology Overview

Fuel cells are electrochemical devices that convert chemical energy of fuels into electrical energy directly, promising power generation with high efficiency and low environmental impact, since no combustion is required. Because the intermediate steps of producing heat and mechanical work typical of most conventional power generation methods are avoided, fuel cells are not limited by thermodynamic limitations of heat engines such as the Carnot efficiency. In addition, because combustion is avoided, fuel cells produce power with minimal pollutant. However, unlike batteries the reductant and oxidant in fuel cells must be continuously replenished to allow continuous operation.\(^{27}\)\(^{28}\).

Research on fuel cells and systems is gathering pace in many countries. Various types of fuel cell have been proposed, with very different properties and possible applications. Mainstream work is currently focusing primarily on applications in the automotive industry, and referred to as miniature power supply and special applications. All of them are hardly suitable for use in power generation.

Currently, there are many variations of fuel cell types, characterized by the effects of construction materials, working agents or operation parameters. The most popular fuel cells are differentiated by the electrolyte used.
Electrolyte type has a crucial influence on fuel cell working operation, from available fuel through operational temperature. Electrolyte material determines the side of the fuel cell on which the main reactions occur and where reaction products are exhausted (anode or cathode). For each type of fuel cell, higher conductivity of the electrolyte means better cell performances. The conductivity depends strongly on temperature.

Broadly, the choice of electrolyte dictates the operating temperature range of the fuel cell. The operating temperature and useful life of a fuel cell dictate the physicochemical and thermomechanical properties of materials used in the cell components (i.e., electrodes, electrolyte, interconnect, current collector, etc.). Aqueous electrolytes are limited to temperatures of about 200 °C or lower because of their high vapor pressure and rapid degradation at higher temperatures. The operating temperature also plays an important role in dictating the degree of fuel processing required. In low-temperature fuel cells, all the fuel must be converted to hydrogen prior to entering the fuel cell. In addition, the anode catalyst in low temperature fuel cells (mainly platinum) is strongly poisoned by CO. In high-temperature fuel cells, CO and even
$CH_4$ can be internally converted to hydrogen or even directly oxidized electrochemically. Table IX provides an overview of the key characteristics of the main fuel cell types.

![Figure 33: Electrical efficiency of different types of fuel cells and combustion engines](image)

5.2 **SOFC Background**

Solid oxide fuel cells (SOFCs) have recently emerged as a serious high temperature fuel cell technology. They promise to be extremely useful in large, high-power applications such as full-scale industrial stations and large-scale electricity-generating stations. Some fuel cell developers see SOFCs being used in motor vehicles. Although the more common proton exchange membrane fuel cells (PEFMCs) require hydrogen fueling, SOFCs can oxidize essentially
<table>
<thead>
<tr>
<th>Fuel Cell Type</th>
<th>Common Electrolyte</th>
<th>Operating Temperature</th>
<th>Typical Stack Size</th>
<th>Efficiency</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Electrolyte Membrane (PEM)</td>
<td>Perfluoro sulfonic acid</td>
<td>50-100°C</td>
<td>1-100 KW</td>
<td>60%</td>
<td>Backup power, portable power, distributed generation, transportation, specialty vehicles</td>
</tr>
<tr>
<td>Alkaline (AFC)</td>
<td>Acqueous solution of potassium hydroxide soaked in a matrix</td>
<td>90-100°C</td>
<td>10KW-100 KW</td>
<td>60%</td>
<td>Military, space</td>
</tr>
<tr>
<td>Phosphoric Acid (PAFC)</td>
<td>Phosphoric acid soaked in a matrix</td>
<td>150-200°C</td>
<td>400 KW 100KW module</td>
<td>40%</td>
<td>Distribution generation</td>
</tr>
<tr>
<td>Molten Carbonate (MCFC)</td>
<td>Solution of lithium, sodium, and/or potassium carbonates, soaked in a matrix</td>
<td>600-700°C</td>
<td>300 KW 3MW</td>
<td>40%</td>
<td>Electricity utility, distributed generation</td>
</tr>
<tr>
<td>Solid Oxide (SOFC)</td>
<td>Yttria stabilized zirconia</td>
<td>700-1000°C</td>
<td>1-2 MW</td>
<td>60%</td>
<td>Auxiliary power, electric utility, distributed generation</td>
</tr>
</tbody>
</table>
any fuel, from hydrogen to hydrocarbons to even carbon, because the electrolyte transports an oxygen ion\cite{29}.

Solid oxide fuel cells (SOFCs) have an electrolyte that is a solid ceramic, non-porous metal oxide, usually $Y_2O_3$-stabilized $ZrO_2$. The cell operates at 600-1000°C where ionic conduction by oxygen ions takes place. Typically, the anode is a $Ni – ZrO_2$ cermet and the cathode is Sr-doped LaMnO3. There is no liquid electrolyte with its attendant material corrosion or electrolyte management problems. The high temperature of the SOFC, however, places stringent requirements on its materials. The development of suitable low cost materials and the low-cost fabrication of ceramic structures are presently the key technical challenges facing SOFCs.

The cell is constructed with two porous electrodes that sandwich an electrolyte (Figure 34). Air flows along the cathode. When an oxygen molecule contacts the cathode/electrolyte interface, it acquires electrons from the cathode. The oxygen ions diffuse into the electrolyte material and migrate to the other side of the cell where they contact the anode. The oxygen ions encounter the fuel at the anode/electrolyte interface and react catalytically, giving off water, carbon dioxide, heat, and electrons. The electrons transport through the external circuit, providing electrical energy. The SOFC reactions include on the anode side for fuel containing hydrogen:

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad (5.1)$$

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \quad (5.2)$$
$CH_4 + 4O^{2-} \rightarrow 2H_2O + CO_2 + 2e^-$  \hspace{1cm} (5.3)

Cathode side:

$O_2 + 4e^- \rightarrow 2O^{2-}$  \hspace{1cm} (5.4)

Solid oxide fuel cells (SOFC) allow conversion of a wide range of fuels, including various hydrocarbon fuels. The relatively high operating temperature allows for highly efficient conversion to power, internal reforming, and high quality by-product heat for cogeneration or for use in a bottoming cycle and when pressurized, can be integrated with a gas turbine to further increase the overall efficiency of the power system. Indeed, both simple-cycle and hybrid SOFC systems have demonstrated among the highest efficiencies of any power generation system, combined with minimal air pollutant emissions and low greenhouse gas emissions. These capabilities have
made SOFC an attractive emerging technology for stationary power generation in the 2 kW to 100 MW capacity range.

Figure 35: Schematic of SOFC microstructure[33]

More recently, (planar) SOFC systems with high power densities operating at lower temperatures (700 to 850°C instead of 900 to 1000°C as was previously the norm) have been developed. Combined with the ability of SOFC to use conventional fossil fuels, this could help reduce the cost of the fuel cell because less-expensive materials of construction could be used at
lower temperatures. This would improve the economy of applications ranging from small-scale stationary power (down to 2 kW) to auxiliary power units for vehicles and mobile generators for civilian as well as military applications. There is even the possibility that SOFC could eventually be used for part of the prime power in vehicles. The present challenge for developers is to produce robust, high-performance stack technologies based on suitable low-cost materials and fabrication methods. Derivatives from SOFC technology, such as oxygen sensors used in automobiles, are already in widespread commercial use.

5.3 **Fuels for SOFCs**

The high operating temperature (700-1000 °C) of solid oxide fuel cells (SOFCs) has a number of consequences, the most important of which is the possibility of running the cells directly on practical hydrocarbon fuels without the need for a complex and expensive external fuel reformer that is necessary for low-temperature fuel cells. Low-temperature proton exchange membrane (PEM) fuel cells are poisoned by even a small quantity of carbon monoxide and require very pure hydrogen as the fuel, therefore placing significant demands, and hence cost, on a complex external fuel processor. By contrast, in an SOFC, the hydrocarbon fuel is catalytically converted (internally reformed), generally to hydrogen and carbon monoxide (synthesis gas) together with some carbon dioxide, within the cell stack, and the carbon monoxide and hydrogen are then electrochemically oxidised to carbon dioxide and water at the anode, with production of electrical power and high-grade heat$^{[30]}$.

SOFCs require only a single partial oxidation reformer to pre-process their fuel, which can be gasoline, diesel, natural gas, etc. The nature of the emissions from the fuel cell will vary
correspondingly with the fuel mix. Using hydrocarbons, for which a supply infrastructure is currently available, offers a variety of advantages over using hydrogen. First of all, hydrocarbons are much easier to transport and to store because they are in a stable state which requires no processing before use. They are also more efficient at producing energy. Methane for example yields eight electrons per molecule whereas hydrogen only yields two electrons energy. This advantage could be magnified with the use of more complex hydrocarbons, such as pentane\cite{31}.

The elevated operating temperature of an SOFC also leads to production of high-temperature heat as a by-product in addition to the electrical power. This high-quality heat is not wasted, but can be used in various ways, for example in combined heat and power (CHP) systems, or to drive a gas turbine to generate more electricity, in addition to providing the heat for the endothermic internal fuel reforming process. This significantly increases the overall efficiency of an SOFC compared to lower temperature fuel cells.

5.4 Components of a SOFC

A SOFC is mainly composed of two electrodes (the anode and the cathode), and a solid electrolyte. The fuel is also important as the principal parameter but independent of the other as it is most of the time converted into hydrogen. The SOFC, which relies on $O^{2-}$ oxygen ion transport, also works with high purity hydrogen, but it does not rely upon this fuel, which is expensive to produce and difficult to handle.

The materials for the cell components are selected by focusing on suitable electrical conducting properties required for these components to perform their intended cell functions, i.e. adequate chemical and structural stability at high temperatures encountered during cell op-
eration as well as during cell fabrication, minimal reactivity and diffusion among different components, and matching thermal expansion among different components.[7]

5.4.1 Electrolyte

As indicated by their name, SOFCs use solid oxide ceramics, typically perovskites, as the electrolyte. There are no chemical and electrochemical reactions inside, but it has a fundamental role in the charge transfer. In fact the electrolyte allows (at high temperatures) the passage of the oxygen ions to the anode and avoids the electronic conduction. It also must forbid the gases to flow between the electrodes. As anticipated in the ohmic resistance paragraph the electrolyte has a higher resistance with respect to the electrodes one[32].

Current technology employs several ceramic materials for the active SOFC components. Although a variety of oxide combinations has been used for solid non-porous electrolytes, the most common to date has been the stabilized zirconia with conductivity based on oxygen ions ($O^{2-}$), especially yttria-stabilized zirconia ($Y_2O_3$stabilized $ZrO_2$ or YSZ, ($ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ for example) in which a tiny amounts of the element yttrium, a silvery-grey metal, is added to the zirconia during manufacture. This choice is mainly due to availability and cost.

YSZ provides high conductivity at temperatures above 700 °C as shown in Figure 36, while exhibiting negligible electronic conductivity at these temperatures (above 1500 °C it becomes an electronic conductor). In a fuel cell operating with a current density of 250 mA cm$^{-2}$ at 1000 °C and an electrolyte of 200 µm thickness, the resistance loss in the electrolyte would be 50 mV. However, for mechanical reasons it is desirable to operate the SOFC at lower temperatures.
To operate at 800 °C, the electrolyte thickness would have to be reduced by about an order of magnitude to maintain a similar ohmic loss in the electrolyte.

![Graph showing typical ionic conductivity of some electrolyte materials as a function of operating temperature.](image)

**Figure 36:** Typical ionic conductivity of some electrolyte materials as a function of operating temperature[^27]

YSZ exhibits purely oxygen ionic conduction (with no electronic conduction). The crystalline array of ZrO2 has two oxide ions to every zirconium ion. But in Y₂O₃ there are only 1.5 oxide ions to every yttrium ion. The result is vacancies in the crystal structure where oxide ions are missing. So, oxide ions from the cathode leap from hole to hole until they reach the
anode. The most commonly used stabilising dopants are $CaO$, $MgO$, $Y_2O_3$, $Sc_2O_3$ and certain rare earth oxides such as $Nd_2O_3$, $Sm_2O_3$, $Yb_2O_3$. Analytically:

$$Y_2O_3(ZrO_2) \rightarrow 2Y_{2r} + 3O_0^+ + V_0 \quad (5.5)$$

It can be noticed that every Yttria molecule (or two atoms of Yttrium) a vacancy is given.

### 5.4.2 Anode

The duties of the anode are multiple; first of all it allows the fuel to diffuse in its structure and to reach the TPB area where the reaction takes place (figure 37); it also permits the oxide ions brought by the electrolyte to enter in contact with the fuel molecules and the reaction products to be removed. The anode also lets the electrons released from the reaction flow and reach the external circuit[30].

Figure 37: Illustration of the three-phase boundary regions of different SOFC anode materials

(a) Electronically conducting cermet

(b) Mixed electronic/ionic conductor
The materials selection for an SOFC anode is determined by a number of factors. First, the function required of it as the site for the electrochemical oxidation of the fuel associated with charge transfer to a conducting contact. Second, the environment in which it operates, at high temperature in contact not only with the fuel, including possible impurities and increasing concentrations of oxidation products, but also with the other materials, the electrolyte and contact components of the cell, and all this with stability over an adequate commercial lifetime at high efficiency. Third, the processability of the anode, which must be such that an open but well connected framework can be achieved and retained during the fabrication of the fuel cell. With regards to stability, whilst in normal operation the ambient oxygen partial pressure is low, it can vary over several orders of magnitude, and to accommodate fault conditions or even just to provide flexibility of operating parameters, the ability to recover even after brief exposure to air at high temperature would be advantageous. A further aspect of this stability is the maintenance of structural integrity over the whole temperature range to which the component is exposed, from the sintering temperature during fabrication through normal operating conditions and then, repeatedly, cycling down to ambient temperature. Compatibility with other cell component materials implies an absence of solid state contact reactions, with interdiffusion of constituent elements of those materials or formation of reaction product layers which would interfere with anode functionality. It also requires a match of properties, such as shrinkage during sintering and thermal expansivity to minimise stresses during temperature variations due to operating procedures, start-up and shut-down. By definition of its role, it is a requirement that the anode material should be an adequate electronic conductor, and also be
electrocatalytically sufficiently active to sustain a high current density with low overpotential loss. However the catalytic behaviour of anode materials should not extend to the promotion of unwanted side reactions, hydrocarbon pyrolysis followed by deposition of vitreous carbon being an example. An intimate contact between the two solid phases, the electrolyte delivering the oxide ions and the anode on which they are electrically neutralized, is clearly essential, as is access of the fuel and removal of reaction products, these being in the gas phase. On this model the reaction is therefore sited on a "three-phase boundary" zone. Low loss operation implies that the three-phase boundary is not dimensionally limited to a planar interface of solid materials, but that it be delocalized to provide a "volumetric" reaction region in three dimensions, porous for gas diffusion and permitting both electron and ion transport. One option is to provide a single-phase electrode with mixed conductivity permitting both oxygen ion and electron mobility within the anode material. The alternative is to employ a porous composite, as in the nickel cermets that have typically been used in SOFCs to date\textsuperscript{[33]}.

Nickel-YSZ composites are the most commonly used anode materials for SOFCs, since nickel is an excellent catalyst for fuel oxidation. However, nickel possesses a high thermal expansion coefficient, and exhibits coarsening of microstructure due to metal aggregation through grain growth at cell operation temperatures. YSZ in the anode constrains nickel aggregation and prevents sintering of nickel particles, decreases the effective thermal expansion coefficient bringing it closer to that of the electrolyte, and provides better adhesion of the anode with the electrolyte. In these anodes, nickel has dual roles of the catalyst for hydrogen oxidation and the electrical current conductor. In addition, it is also highly active for steam reforming of methane.
(this catalytic property is largely exploited in the so-called internal reforming SOFCs that can operate on fuels composed of mixtures of methane). Although nickel is an excellent hydrogen oxidation and methane-steam reforming catalyst, it also catalyzes the formation of carbon from hydrocarbons under reducing conditions and, unless sufficient amounts of steam are present along with the hydrocarbon to remove carbon from the nickel surface, the anode may be destroyed. As a result, even when using methane as the fuel, relatively high steam-to-carbon ratios are needed to suppress this deleterious reaction. Unfortunately, this approach does not work for higher hydrocarbons, and it is generally not possible to operate nickel-based anodes on higher hydrocarbon-containing fuels without pre-reforming. In spite of this drawback, nickel-YSZ composite remains the most commonly used anode material for SOFCs and is satisfactory for cells operating on clean and reformed fuel\cite{7}.

5.4.3 Cathode

The air electrode operates in an oxidizing environment of air or oxygen at 1000 °C and participates in the oxygen reduction. Cathodes for solid oxide fuel cells (SOFCs) have to possess many properties including high electrical conductivity, high catalytic activity for oxygen reduction, and compatibility with other cell components. The function of the cathode is to let the fed oxygen molecules are reduced to $O_2^-$ ions that then will cross the electrolyte and will oxidize the fuel molecules. Oxygen molecules (actually also $N_2$ molecules since air is commonly used as reagent) diffuse through the porous cathode and reach the reaction zone where the oxygen reduction takes place. The main required characteristic that it must possess is: a porous structure, high both ionic and electronic conductivity, a chemical and mechanical stability at high
temperatures and high catalytic activity for oxygen reduction. Moreover being the cathode in
contact with the electrolyte and the interconnections it must not react with them and thermally
mismatch them. These stringent electrochemical and mechanical requirements greatly restrict
the number of suitable candidate materials. To satisfy these requirements, lanthanium man-
ganite suitably doped with alkaline and rare earth elements is used. Lanthanium manganite
is a p-type perovskite oxide and shows reversible oxidation-reduction behaviour. The material
can have oxygen excess or deficiency depending upon the ambient oxygen partial pressure and
temperature. Although, it is stable in air and oxidizing atmospheres, it dissociates at 1000 °C
at oxygen pressures \( \leq 10^{-14} \) atm. The electronic conductivity of lanthanium manganite is due
to hopping of an electron hole between the +3 and +4 valence state of Mn. This conductivity
is enhanced by doping with a divalent ion such as calcium or strontium.

For even better electrode performance, some companies offer a line of composite electrode
powders, with electrolyte materials (YSZ, SDC or GDC) admixed with the perovskite electrode
materials (LSM, LSF, or PSMF). The incorporation of electrolyte material into the cathode
material has been shown to improve electrode performance at lower temperatures by increasing
the volume of active sites available for electrochemical reactions\(^{[31]}\).

5.4.4 Interconnect

Interconnects (or bipolar plates) are fundamental in SOFC systems operation since a single
cell only produces voltage less than 1 V and power around 1 W/cm\(^2\), many cells are electric-
ically connected together in a cell stack to obtain higher voltage and power. Two roles of the
interconnect in high-temperature solid oxide fuel cells (SOFCs) are the electrical connection
between cells and the gas separation within the cell stack. The fact that the interconnect must be compatible with all of the cell components as well as be stable with respect to both oxidizing and reducing gases places very stringent materials requirements on it. These requirements plus the additional constraints of cost and ease of fabrication tend to limit the possible choices to only a few materials. These materials come from either perovskite-type oxide ceramics based on rare earth chromites for operating temperatures in the 900-1000 °C range or metallic alloys for lower temperature cell operation. Typical requirements are\textsuperscript{[34]}:

- High electronic conductivity with low ionic conductivity
- Chemical stability in both fuel and air
- Thermal expansion match to other cell components
- High mechanical strength
- High thermal conductivity
- Chemical stability with regard to other cell components

The choice of the material depends on the operating temperatures; for high temperature solid oxide fuel cell (above 850 -900 °C ceramic based material seems to be interesting because of the lack of thermal expansion mismatches and catalytic poisoning of the cathode due, for example, to Chromium evaporation and deposition on the cathode surfaces typical of metal alloys based interconnects\textsuperscript{[30] [27] [35]}. 
5.5 **Cell and Stack Design**

The two most common designs of SOFCs are the tubular and planar. The interest in tubular cells is unique to SOFC: all other types of fuel cells focus exclusively on planar designs. Each of these two designs has a number of interesting variants: for example, the planar SOFC may be in the form of a circular disc fed with fuel from the central axis, or it may be in the form of a square plate fed from the edges while the tubular SOFC may be of a large diameter (more than 15 mm), or of much smaller diameter (less than 5 mm), representing the so-called microtubular cells. Also, the tubes may be flat and joined together to give higher power density and easily printable surfaces for depositing the electrode layers.

5.5.1 **Tubular SOFC**

Siemens Westinghouse has been developing tubular solid oxide fuel cells since late 1970s. Figure 38 schematically illustrates the design of a tubular configuration of solid oxide fuel cell. The lanthanum manganite-based air electrode tube is fabricated by extrusion followed by sintering to obtain about 30-35% porosity. Electrolyte is deposited in the form of about 40 µm thick layer by an electrochemical vapour deposition process (EVD)\(^{[36]}\)\(^{[37]}\). Oxygen mixed with steam is passed inside the cathode tube. In the first stage of the reaction, molecular diffusion of oxygen, steam, metal chlorides, and hydrogen occurs through the porous cathode and this react to fill the pores in the cathode with yttria-stabilized zirconia. During the second stage of the reaction after the pores in the air electrode are closed, electrochemical transport of oxide ions maintaining electroneutrality occurs through the already deposited yttria-stabilised zirconia in the pores from the high oxygen partial pressure side (oxygen/steam) to the low
Figure 38: Schematic illustration of a tubular SOFC$^{[36]}$

oxygen partial pressure side (chlorides). The oxide ions, upon reaching the low oxygen partial pressure side, react with the metal chlorides and the electrolyte film grows in thickness.

One of the problems of the tubular design is the low power density due to the long path of the electrical power through each cell (modern cells have 10 mm of diameter and 1500 mm of length$^{[30]}$) and the large voids within the stack structure. The interconnections between the cells are usually made of Nickel; the stacking is obtained arranging tubular cells both in series and parallel dispositions, making sort of cell-bundles. The high costs are due to the method of electrolyte and electrode deposition, electrochemical vapor deposition (EVD). One great advantage of the tubular design of SOFC is that high-temperature gas-tight seals are eliminated. Each tube is fabricated like a large test tube, sealed at one end. Fuel flows along the outside of the tube, towards the open end. Air is fed through a thin alumina air supply tube located centrally inside each tubular fuel cell. Heat generated within the cell brings the air up to the
operating temperature. The air then flows through the fuel cell back-up to the open end. At this point air and unused fuel from the anode exhaust mix are instantly combusted and so the cell exit is above 1000°C. This combustion provides additional heat to preheat the air supply tube. Thus the tubular SOFC has a built-in air preheat and anode exhaust gas combustor and does not require high-temperature seals. Finally, by allowing imperfect sealing around the tubes, some recirculation of the anode product gas occurs, allowing internal reforming of fuel gas on the SOFC anode, as the anode product contains steam\cite{35}. 

Figure 39: Tubular stack\cite{30}
5.5.2 Planar SOFC

Alternatives to the tubular SOFC the planar SOFC have been developed for many years and for that reason there are several types of this configuration. In a planar SOFC, cell components are configured as flat plates which are connected in electrical series. Since this configuration is very compact is possible to achieve higher power densities and this can be a very important benefit in small scale applications; electrical connections are short and the consequence is lower ohmic losses with respect to the tubular configuration. Furthermore this configuration can be advantageous economically because of the possibility to develop more economical fabrication methods such as screen printing and tape casting. Planar arrangements also have problems with sealing and mechanical degradation because of the thermal stresses at the interfaces between different cells and stack materials. There are many different shapes of the cell (Figure 40) and the selection of a particular one has significant effects on the temperature and current distribution within the stack.

- Rectangular, with gases flowing in co-flow, counter-flow, or cross-flow
- Circular, typically with gases flowing out from the center in co-flow, and mixing and burning at the edge of the cells. Spiral flow arrangements and counter-flow arrangements have also been proposed.

Various flow patterns can be implemented in the different flow configurations. Flowfields are used in planar SOFCs to increase uniformity of gas distribution and to promote heat and mass transport in each cell.
Figure 40: Overview of types of planar SOFC[27]
CHAPTER 6

SOFC MODELING

6.1 Introduction

The aim of the second part of this work, concerning the SOFCs, is to develop a numerical model and validate it through different experimental tests in order to employ this powerful tool for the optimum design of the SOFC for applications with syngas. This model takes as input a set of geometrical, physical and chemical parameters and produces as output the exhaust gas composition. The tools used for this purpose are MATLAB r2012a and Cantera 2.0.1 for a ring-type planar, anode supported SOFC type 4(AS4), provided by the German manufacturer H.C. Stark.

MATLAB is a high-level language and problem solving environment for numerical computation, implement algorithms, analyze data and create numerical models, that enable the users to obtain a solution faster than with traditional programming languages such as C/C++ or Java. MATLAB is widely used in academic and research institutions as well as industrial enterprises. Otherwise Cantera is a suite of object-oriented software tools for problems involving chemical kinetics, thermodynamics, and/or transport processes and electrochemistry. It provides types (or classes) of objects representing phases of matter, interfaces between these phases, reaction managers, time-dependent reactor networks, and steady one-dimensional reacting flows. Cantera is currently used for applications including combustion, detonations, electrochemical
energy conversion and storage, fuel cells, batteries, aqueous electrolyte solutions, plasmas, and thin film deposition. Cantera can be used from Python and MATLAB by adding toolboxes that implement kinetics, thermo, and transport functionality.

6.2 Electrode Polarizations

This chapter is very important in order to deeply understand the physics of SOFCs since the charge-transfer processes are one of the least well-understood aspects of fuel-cell chemistry. Nowadays, the common objective in fuel-cell research is to describe all the charge transfer kinetics in terms of reaction steps, in a manner that parallels the treatment of thermal heterogeneous chemistry.

However, it is still important to retain a Butler-Volmer formalism for the charge-transfer steps, since this kind of approach provides important information about functional dependencies such as the reaction orders in the exchange current density. The classical approach of fuel cell modeling is based on approximation of the current-voltage curve \( E = f(i) \), which is obtained from experimental studies. The current-voltage curve for modeling purposes is divided into three parts: activation loss, ohmic loss, and concentration loss as shown in figure 41. Those losses are subtracted from the maximum voltage defined by the Nernst equation. The potential difference \( E_{cell} \) across the cell is given by:

\[
E_{cell} = \phi_c - \phi_a = E_c + (\phi_{e,c} - \phi_e, a) - E_a = E_c - E_a - \eta_{ohm}(i)
\]  

(6.1)

where the subscripts \( c \) and \( a \) represent respectively the cathode and the anode and the terms \( \phi_i \) and \( \phi_{e,i} \) are the electrode potential and the potential within the electrolyte.
The term $\eta_{ohm}$ is the ohmic overpotential where the current-voltage curve becomes almost linear in its middle range. It is due primarily to resistance of ion transport in the electrolyte and is represented by the following relationship:

$$\eta_{ohm} = (\rho_{el}l_{el} + \rho_{c}l_{c} + \rho_{a}l_{a} + R_{contact}) = i \cdot R_{tot} \quad (6.2)$$

where $R_{tot}$ is the total area-specific cell resistance, including the solid electrolyte $R_{el}$, the area-specific resistance in the electrodes $R_{a}$ and $R_{c}$ and $R_{contact}$ is any possible contact resistance. Usually in certain electrodes the electrode resistance $R_{ed}$ is negligible. In most SOFCs, the main contribution to $\eta_{ohm}$ is from the electrolyte, since its ionic resistivity is much greater...
than electronic resistivities of the anode and the cathode. The electrolyte resistance can be
determined from the ionic conductivity of the electrolyte \( \sigma_{el} \):

\[
R_{el} = \frac{L_{el}}{\sigma_{el}}
\]  

(6.3)

where \( L_{el} \) is the electrolyte thickness and \( \sigma_{el} \) is given by the following:

\[
\sigma_{el} = \sigma_0 T^{-1} \exp \left( -\frac{E_{el}}{RT} \right)
\]  

(6.4)

where \( E_{el} \) is the activation energy for ion transport. Further explanations can be found on
Supporting Online Material for Lowering the Temperature of SOFC\(^{[29]} \).

Continuing from Equation 6.1 to compute \( E_{cell}(i) \) as a function of current density we need
more equations to evaluate \( E_c \) and \( E_a \) or rather the potential differences across both the elec-

\[
E_{rev} = E_{c,rev} - E_{a,rev}
\]  

(6.5)

Now it is necessary to introduce the activation overpotential which is the voltage drop in the
initial part of the current-voltage curve:

\[
\eta_{act} = E - E_{rev}
\]  

(6.6)
Then, subtracting Equation 6.5 from Equation 6.1 the potential difference across the cell can be written as:

\[ E_{cell} = E_{rev} - \eta_{act,a}(i) - \eta_{ahm}(i) - |\eta_{act,c}(i)| \tag{6.7} \]

The reversible potential can be computed by applying the Nernst equation if it is well-defined, in other words if the gas composition at the triple-phase regions of each electrode are locally in chemical equilibrium. For this reason the current generated in the fuel cell is linked to the number of ions passing through the electrolyte, which carries out the work. Using Faradays law equation, the reversible fuel cell voltage is the following:

\[ E_{rev} = \frac{RT}{4F} \ln \frac{P_{O_2,c}}{P_{O_2,a}} \tag{6.8} \]

where \( F \) is the Faraday constant and \( P_O \) is the oxygen pressure. This equilibrium assumption is usually very good on the cathode side where there is the oxidant, but may not hold on the anode side if there are still hydrocarbons in the gas in the triple-phase regions. If the gas composition on the anode side is not locally in equilibrium, then the oxidation reaction for each fuel species would give a different cell potential. In this situation we need to know something precise about electrochemically active species in order to compute \( E_{cell} \) and often this is defined in relation to the reaction of hydrogen with oxygen:

\[ E_{rev} = -\frac{E_0}{2F} + \frac{RT}{2F} \ln A + \frac{RT}{2F} \ln \frac{p_{H_2,a} \cdot p_{O_2,c}^{1/2}}{p_{H_2O,a} \cdot p_{ref}^{1/2}} \tag{6.9} \]
where $E_0$ is standard-state chemical potential and $A$ the chemical equilibrium constant coefficient for the reaction $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$. As indicated by the subscripts $a$ and $c$, the partial pressure of the gas-phase species (measured in atmospheres) are evaluated at the anode and cathode interfaces with the electrolyte.

In the final part of the current - voltage curve, the dominant role is played by the losses associated with the transport of gases in a perpendicular direction to the surface of the electrodes. In the fuel cells, the reacting species are gaseous; at the anode $H_2$ (or $H_2 + CO$), and at the cathode $O_2$. Since the current density $i(x)$ is known as input data, the molar flux of the gas species from the electrochemical reactions can be evaluated as:

$$J_{H_2,a} = -\frac{i}{2F}$$  \hspace{1cm} (6.10)

$$J_{H_2O,a} = \frac{i}{2F}$$  \hspace{1cm} (6.11)

for the $H_2$ electrochemical oxidation at the anode, and:

$$J_{O_2,c} = \frac{i}{4F}$$  \hspace{1cm} (6.12)

for the $O_2$ electrochemical reduction at the cathode. $j_{H_2,a}$ is the molar flux of hydrogen through the porous anode to the anode/electrolyte interface while $J_{H_2O,a}$ is the molar flux of water vapor through the porous anode away from the anode/electrolyte interface and $J_{O_2,c}$ is the molar flux of oxygen through the porous cathode to the cathode/electrolyte. The full reactive
transport problem within the fuel channel and on the anode surface is already solved in this
model by implementing the Nerst equation, so there is no need for the explicit evaluation of
the concentration overpotential once we have the exact concentration in every point of the cell.

As said before the voltage drop in the initial part of the current-voltage curve is due to
the activation losses, which can be identified by the Butler-Volmer equation at the electrode-
electrolyte interface. In order to develop this equation is very useful to consider five elementary
reactions in Ni-YSZ region where hydrogen is electrochemically oxidized.

1. Adsorption/desorption on the nickel surface:

\[ H_2(g) + 2(Ni) \leftrightarrow 2H(Ni) \]  \hspace{1cm} (6.13)

2. Charge-transfer reactions at the TPB region

\[ H(Ni) + O^{2-}(YSZ) \leftrightarrow (Ni) + OH^{-}(YSZ) + e^{-}(Ni) \]  \hspace{1cm} (6.14)

\[ H(Ni) + OH^{-}(YSZ) \leftrightarrow (Ni) + H_2O(YSZ) + e^{-}(Ni) \]  \hspace{1cm} (6.15)

3. Adsorption/desorption on the YSZ surface:

\[ H_2O(YSZ) \leftrightarrow H_2O(g) + (YSZ) \]  \hspace{1cm} (6.16)
4. Transfer of oxygen ions between the surface and the bulk YSZ

\[ O_\text{O}(YSZ) + (YSZ) \leftrightarrow O^2-(YSZ) + V_O(YSZ) \]  \hspace{1cm} (6.17)

where \( H(Ni) \) is an adsorbed atomic hydrogen, \( Ni \) is an empty surface site, and \( e^-(Ni) \) is an electron within the \( Ni \) anode. Within the \( YSZ \) electrolyte, \( O_\text{O}(YSZ) \) is a lattice oxygen and \( V_O(YSZ) \) is an oxygen vacancy. On the \( YSZ \) surface there can be three species, \( O_2^-(YSZ) \), \( OH^-(YSZ) \) and \( H_2O(YSZ) \), and empty sites \( YSZ \). The hydrogen adsorption-desorption reaction also appears in the thermal heterogeneous chemistry (reactions 1 and 2 in Table X).

Of the two charge-transfer reactions (reactions 34 and 33), reaction 34 can be assumed as rate-limiting. Consequently, the other four reactions are assumed to be equilibrated. Furthermore, it is useful to make the assumption that the electrolyte surface is nearly fully covered by \( O_2^-(YSZ) \).

Using these assumptions is possible to write the current density in a Butler-Volmer form as:

\[ i = i_0 \left[ \exp \left( \frac{\alpha n F}{R T} \eta_a \right) - \exp \left( - \frac{\alpha n F}{R T} \eta_a \right) \right] \]  \hspace{1cm} (6.18)

where:

\[ i_0 = i_{H_2}^* \left( \frac{p_{H_2}/p_{H_2}^*}{1 + (p_{H_2}/p_{H_2}^*)^{1/2}} \right) \]  \hspace{1cm} (6.19)

The quantity \( p_{H_2}^* \) is calculated from the balance between adsorption and desorption of hydrogen on the \( Ni \) and \( i_{H_2}^* \) can be taken as constant.
Like for the oxidation at the anode, is possible to follow the same path also for the oxygen reduction at the cathode. Here we have two steps:

1. Adsorption/desorption

\[ O_2(g) + 2(c) \leftrightarrow 2O_{ad}(c) \] \hspace{1cm} (6.20)

2. Charge-transfer reactions and incorporation at the TPB region

\[ O_{ad}(c) + V_O(el) + 2e^-(c) \leftrightarrow O_O^{el}(el) + (c) \] \hspace{1cm} (6.21)

where \( O_{ad}(c) \) is adsorbed atomic oxygen on the cathode surface, \((c)\) is an unoccupied cathode surface site, \( V_O(el) \) is an oxygen vacancy, \( e^-(c) \) is an electron within the cathode and \( O_O^{el}(el) \) is a lattice oxygen ion in the bulk of the electrolyte. Then the current density can be written as:

\[ i = i_0 \left[ \exp \left( \frac{\alpha n F}{RT} \eta_c \right) - \exp \left( -\frac{\alpha n F}{RT} \eta_c \right) \right] \] \hspace{1cm} (6.22)

and the exchange current density is:

\[ i_0 = i_0^* \left( \frac{p_{O_2}}{p_{O_2}^*} \right)^{1/4} \frac{1}{1 + \left( \frac{p_{O_2}}{p_{O_2}^*} \right)^{1/2}} \] \hspace{1cm} (6.23)

The complexity of this functions makes it impossible to formulate a direct equation for \( \eta_{act} \) and the calculations must take an iterative approach. The relationship of activation loss is a function of current density \( \eta_{act} = f(i) \). In order to simplify the calculation of the Butler-
Volmer equation, the main relationship could be linearized to the form of the Tafel equation. At sufficiently small $\eta_{act}$, the Butler-Volmer equation can be developed into series and then obtain a linear representation of it\textsuperscript{[40]}:

$$\eta_{act} = \frac{RT}{\alpha n F} \ln i_0 - \frac{RT}{\alpha n F} \ln i$$  \hspace{1cm} (6.24)

6.3 Reaction Mechanism

In the present work the same heterogeneous reaction mechanism of the Hecht et al.\textsuperscript{[38]} and Zhu et al.\textsuperscript{[39]} has been used. The difference is only in the molar fractions since methane in this case is present in a very small amount and the reforming is very low. In the anode application, as said before, Ni serves as both a reforming catalyst and an electrical current conductor. Because nickel is widely used as a reforming catalyst there is a great deal of information available about its catalytic behavior. Since the reforming is limited there could be the possibility to use Ni-free anodes that will be more convenient in order to avoid the C-deposition. This can be a future research topic but now the experiments have been carried out with Ni(YSZ) anodes.

In the table X below there is the reaction mechanism that has been developed to describe the heterogeneous kinetics within a Ni(YSZ) anode. This mechanism was first developed and validated for a steam-assisted catalytic partial oxidation of methane in small-channel monolith reactors. The 42 irreversible reactions involve 6 gas-phase and 12 surface-adsorbed species.
Most reaction rates are represented in the Arrenius form. However the net, activation energy of reactions 12, 20, 21 and 23 depend on the $CO(s)$ coverage $\theta_{CO(s)}$:

$$k = AT^n \exp \left( -\frac{E}{RT} \right) \exp \left( -\frac{\epsilon_{CO(s)} \theta_{CO(s)}}{RT} \right) \quad (6.25)$$

Further details on this mechanism can be found on\cite{38,39}. The reaction mechanism described above is incorporated in the mechanism used for the present thesis taken from reference\cite{41} which contains software tools specifically designed for the modeling and simulation of reacting flows, in particular to heterogeneous systems such as catalysis, materials synthesis, fuel cells. The core of DETCHEM is a collection of routines for the calculation of chemical reaction rates, species transport, and thermodynamic properties called the library modules. The mechanism was manually translated from CHEMKIN to Cantera format by Francesco Quesito\cite{7} and adjusted by the author for the purpose of this work.

### 6.4 Cantera Equations for the SOFC model

In this section are explained the governing equations and the theoretical model used by Cantera to solve general axisymmetric 1-D problems (flame, fuel cell stack, CVD stagnation flow), because as said before, this software can solve heterogeneous chemistry. The approach described here was studied specifically for a ring-type planar SOFC adapting the one-dimensional flames modeling of Cantera, since this software was initially born to study combustion process and flames\cite{42}. This behavior is 1-D in the sense that, when certain conditions are fulfilled, the governing equations reduce to a system of ODEs in the axial coordinate. This occurs either
TABLE X: HETEROGENEOUS REACTION MECHANISM FOR CH4 REFORMING ON
NI-BASED CATALYSTS

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A^a$</th>
<th>n</th>
<th>$E^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2 + (Ni) + (Ni) \rightarrow H(Ni) + H(Ni)$</td>
<td>$1.00 \times 10^{0.026}$</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>$H(Ni) + H(Ni) \rightarrow (Ni) + (Ni) + H_2$</td>
<td>$5.593 \times 10^{+19}$</td>
<td>0.0</td>
<td>88.12</td>
</tr>
<tr>
<td>$O_2 + (Ni) + (Ni) \rightarrow O(Ni) + O(Ni)$</td>
<td>$1.00 \times 10^{-02b}$</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>$O(Ni) + O(Ni) \rightarrow (Ni) + (Ni) + O_2$</td>
<td>$2.508 \times 10^{+23}$</td>
<td>0.0</td>
<td>470.39</td>
</tr>
<tr>
<td>$CH_4 + (Ni) \rightarrow CH_4(Ni)$</td>
<td>$8.000 \times 10^{-03b}$</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>$CH_4(Ni) \rightarrow CH_4 + (Ni)$</td>
<td>$5.302 \times 10^{+15}$</td>
<td>0.0</td>
<td>33.15</td>
</tr>
<tr>
<td>$H_2O + (Ni) \rightarrow H_2O(Ni)$</td>
<td>$1.000 \times 10^{-01b}$</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>$H_2O(Ni) \rightarrow H_2O + (Ni)$</td>
<td>$4.579 \times 10^{+12}$</td>
<td>0.0</td>
<td>62.68</td>
</tr>
<tr>
<td>$CO_2 + (Ni) \rightarrow CO_2(Ni)$</td>
<td>$1.000 \times 10^{-05b}$</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>$CO_2(Ni) \rightarrow CO_2 + (Ni)$</td>
<td>$9.334 \times 10^{+07}$</td>
<td>0.0</td>
<td>28.80</td>
</tr>
<tr>
<td>$CO + (Ni) \rightarrow CO(Ni)$</td>
<td>$5.000 \times 10^{-01b}$</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>$CO(Ni) \rightarrow CO + (Ni)$</td>
<td>$4.041 \times 10^{+11}$</td>
<td>0.0</td>
<td>112.85</td>
</tr>
<tr>
<td>$O(Ni) + H(Ni) \rightarrow OH(Ni) + (Ni)$</td>
<td>$5.000 \times 10^{+22}$</td>
<td>0.0</td>
<td>97.90</td>
</tr>
<tr>
<td>$OH(Ni) + (Ni) \rightarrow O(Ni) + H(Ni)$</td>
<td>$2.005 \times 10^{+21}$</td>
<td>0.0</td>
<td>37.19</td>
</tr>
<tr>
<td>$OH(Ni) + H(Ni) \rightarrow H_2O(Ni) + (Ni)$</td>
<td>$3.000 \times 10^{+20}$</td>
<td>0.0</td>
<td>42.70</td>
</tr>
<tr>
<td>$H_2O(Ni) + (Ni) \rightarrow OH(Ni) + H(Ni)$</td>
<td>$2.175 \times 10^{+21}$</td>
<td>0.0</td>
<td>91.36</td>
</tr>
<tr>
<td>$OH(Ni) + OH(Ni) \rightarrow O(Ni) + H_2O(Ni)$</td>
<td>$3.000 \times 10^{+21}$</td>
<td>0.0</td>
<td>100.00</td>
</tr>
<tr>
<td>$O(Ni) + H_2O(Ni) \rightarrow OH(Ni) + OH(Ni)$</td>
<td>$5.423 \times 10^{+23}$</td>
<td>0.0</td>
<td>209.37</td>
</tr>
<tr>
<td>$O(Ni) + C(Ni) \rightarrow CO(Ni) + (Ni)$</td>
<td>$5.200 \times 10^{+23}$</td>
<td>0.0</td>
<td>148.10</td>
</tr>
<tr>
<td>$CO(Ni) + (Ni) \rightarrow O(Ni) + C(Ni)$</td>
<td>$1.418 \times 10^{+22}$</td>
<td>-3.0</td>
<td>115.97</td>
</tr>
<tr>
<td>$CO(Ni) + CO(Ni) \rightarrow CO_2(Ni) + (Ni)$</td>
<td>$2.000 \times 10^{+19}$</td>
<td>0.0</td>
<td>123.60</td>
</tr>
<tr>
<td>$CO_2(Ni) + (Ni) \rightarrow O(Ni) + CO(Ni)$</td>
<td>$3.214 \times 10^{+23}$</td>
<td>-1.0</td>
<td>86.50</td>
</tr>
<tr>
<td>$HCH(Ni) + (Ni) \rightarrow CO(Ni) + H(Ni)$</td>
<td>$3.700 \times 10^{+21}$</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>$CO(Ni) + H(Ni) \rightarrow HCO(Ni) + (Ni)$</td>
<td>$2.338 \times 10^{+20}$</td>
<td>-1.0</td>
<td>127.98</td>
</tr>
<tr>
<td>$HCO(Ni) + (Ni) \rightarrow O(Ni) + CH(Ni)$</td>
<td>$3.700 \times 10^{+24}$</td>
<td>-3.0</td>
<td>95.80</td>
</tr>
<tr>
<td>$O(Ni) + CH(Ni) \rightarrow HCO(Ni) + (Ni)$</td>
<td>$7.914 \times 10^{+20}$</td>
<td>0.0</td>
<td>114.22</td>
</tr>
<tr>
<td>$CH_3(Ni) + (Ni) \rightarrow CH_3(Ni) + H(Ni)$</td>
<td>$3.700 \times 10^{+21}$</td>
<td>0.0</td>
<td>57.70</td>
</tr>
<tr>
<td>$CH_3(Ni) + H(Ni) \rightarrow CH_3(Ni) + H(Ni)$</td>
<td>$4.438 \times 10^{+21}$</td>
<td>0.0</td>
<td>58.83</td>
</tr>
<tr>
<td>$CH_3(Ni) + (Ni) \rightarrow CH_3(Ni) + H(Ni)$</td>
<td>$3.700 \times 10^{+24}$</td>
<td>0.0</td>
<td>100.00</td>
</tr>
<tr>
<td>$CH_2(Ni) + H(Ni) \rightarrow CH_2(Ni) + H(Ni)$</td>
<td>$9.513 \times 10^{+22}$</td>
<td>0.0</td>
<td>52.58</td>
</tr>
<tr>
<td>$CH_2(Ni) + (Ni) \rightarrow CH(Ni) + H(Ni)$</td>
<td>$3.700 \times 10^{+24}$</td>
<td>0.0</td>
<td>97.10</td>
</tr>
<tr>
<td>$CH(Ni) + H(Ni) \rightarrow CH_2(Ni) + (Ni)$</td>
<td>$3.008 \times 10^{+24}$</td>
<td>0.0</td>
<td>76.43</td>
</tr>
<tr>
<td>$CH(Ni) + (Ni) \rightarrow C(Ni) + H(Ni)$</td>
<td>$3.700 \times 10^{+21}$</td>
<td>0.0</td>
<td>18.50</td>
</tr>
<tr>
<td>$C(Ni) + H(Ni) \rightarrow CH(Ni) + (Ni)$</td>
<td>$4.400 \times 10^{+21}$</td>
<td>0.0</td>
<td>160.49</td>
</tr>
<tr>
<td>$O(Ni) + CH_3(Ni) \rightarrow CH_3(Ni) + OH(Ni)$</td>
<td>$1.700 \times 10^{+24}$</td>
<td>0.0</td>
<td>88.30</td>
</tr>
<tr>
<td>$CH_3(Ni) + O(Ni) \rightarrow O(Ni) + CH_3(Ni)$</td>
<td>$8.178 \times 10^{+22}$</td>
<td>0.0</td>
<td>28.72</td>
</tr>
<tr>
<td>$O(Ni) + CH_3(Ni) \rightarrow CH_3(Ni) + OH(Ni)$</td>
<td>$3.700 \times 10^{+24}$</td>
<td>0.0</td>
<td>130.10</td>
</tr>
<tr>
<td>$CH_2(Ni) + O(Ni) \rightarrow O(Ni) + CH_3(Ni)$</td>
<td>$3.815 \times 10^{+21}$</td>
<td>0.0</td>
<td>21.97</td>
</tr>
<tr>
<td>$O(Ni) + CH_2(Ni) \rightarrow CH(Ni) + OH(Ni)$</td>
<td>$3.700 \times 10^{+24}$</td>
<td>0.0</td>
<td>126.80</td>
</tr>
<tr>
<td>$CH(Ni) + O(Ni) \rightarrow O(Ni) + CH_3(Ni)$</td>
<td>$1.206 \times 10^{+23}$</td>
<td>0.0</td>
<td>45.42</td>
</tr>
<tr>
<td>$O(Ni) + CH(Ni) \rightarrow C(Ni) + OH(Ni)$</td>
<td>$3.700 \times 10^{+21}$</td>
<td>0.0</td>
<td>48.10</td>
</tr>
<tr>
<td>$C(Ni) + OH(Ni) \rightarrow O(Ni) + CH_2(Ni)$</td>
<td>$1.764 \times 10^{+21}$</td>
<td>0.0</td>
<td>129.08</td>
</tr>
</tbody>
</table>

\(^a\) Arrhenius parameters for the rate constants written in the form: $k = \frac{A^a}{RT^m} \exp(-E/RT)$. The units of $A$ are given in terms of moles, centimeters, and seconds. $E$ is in kJ/mol.

\(^b\) Sticking coefficient

\(^c\) Coverage-dependent activation energy. Total available surface density $\Gamma$ is expressed in mol/cm$^2$ and represents the tuning parameter.
because the flow is physically 1-D or the flow is physically 2-D, but a similarity transformation reduces the problem dimensionality to 1-D. Although the modeling approach described here focuses on planar solid oxide fuel cells it could be used with any SOFC configurations by modifying few parameters.

A 1-D problem is partitioned into domains and each domain represents a distinct phase, flowfield, or interface (figure 42. The extended spatial domains define governing equations and the boundary domains provide boundary / interfacial conditions. For 1-D axisymmetric flow geometric (figure 43) the variable are the following: $u$ that represent the axial velocity of the flow in the cylinder, $r$ is the radial coordinate along the radius of the cylinder, $v$ is the radial velocity of the flow, $T$ the temperature and $Y_k$ the mass fractions of the $k_{th}$ species while $z$ is
the axial coordinate. The boundary conditions at \( z = 0 \) and \( z = L \) are \( u, T \) and \( Y_k \) independent of \( r \) while \( v \) is linear in \( r \) (usually zero). In order to apply the similarity solution the following conditions must be satisfied:

- \( \frac{L}{D} \ll 1 \)
- \( Ma \ll 1 \)

where low Mach number means \( P \) nearly constant (the pressure profile is complicated to simulate and moreover it has a modest importance). If these limits are satisfied, and if the boundary conditions are satisfied, then the exact flow equations admit a solution with the properties:

\[
 u = u(z) \tag{6.26}
\]
\( v = rV(z) \) \hspace{1cm} (6.27)

\( T = T(z) \) \hspace{1cm} (6.28)

\( Y_k = Y_k(z) \) \hspace{1cm} (6.29)

\( P = P_0 + \Lambda \frac{r^2}{2} \) \hspace{1cm} (6.30)

where \( P \) is the pressure, \( P_0 \) the reference pressure and \( \Lambda \) is a constant that must be determined as part of the solution. For conditions where similarity solution holds, flow equations reduce to ODEs in axial coordinate \( z \). This is a good approximation because in the experimental case the height of the channel is very small compared to the diameter so the Reynolds number is less than 2300 and we are in the case of laminar flow.

- Continuity:
  \[
  \frac{d}{dz}(\rho u) + 2\rho V = 0
  \]  \hspace{1cm} (6.31)

- Radial Momentum:
  \[
  \rho \frac{dV}{dt} = \frac{d}{dz} \left( \mu \frac{dV}{dz} \right) - \Lambda - \rho u \frac{dV}{dz} - \rho V^2
  \]  \hspace{1cm} (6.32)

- Species Conservation:
  \[
  \rho \frac{dY_k}{dt} = -\rho u \frac{dY_k}{dz} - \frac{dJ_k}{dz} + W_k \dot{\omega}_k
  \]  \hspace{1cm} (6.33)
• Energy Conservation:

\[
\rho c_p \frac{dT}{dt} = -\rho c_p u \frac{dT}{dz} + \frac{d}{dz} \left( \lambda \frac{dT}{dz} \right) - \sum_k W_k \dot{\omega}_k h_k - \sum_k J_k c_{p,k} \frac{dT}{dz}
\]  

(6.34)

The net production rate \( \dot{\omega}_k \) is computed from:

\[
\dot{\omega}_k = \sum_i V_{k,i} q_i
\]

(6.35)

The rate coefficient \( q \) is specified with an embedded entry corresponding to the rate coefficient type. At present, the only implemented type is the modified Arrhenius function:

\[
k_i = A_i T^n \exp \left( -\frac{E_i}{RT} \right)
\]

(6.36)

At this point an upwind differencing method is used to calculate the convective terms of the equations above: \( \frac{dV}{dz}, \frac{dY_k}{dz} \) and \( \frac{dT}{dz} \):

• if \( u_j > 0 \):

\[
\left( \frac{df}{dz} \right)_i = \frac{f_j - f_{j-1}}{z_j - z_{j-1}}
\]

(6.37)

• otherwise if \( u_j < 0 \):

\[
\left( \frac{df}{dz} \right)_i = \frac{f_{j+1} - f_j}{z_{j+1} - z_j}
\]

(6.38)
On the other hand central differencing (Equation 6.39) is used for diffusive terms which are
\[ \frac{d}{dz} (\mu \frac{dV}{dz}) \, , \, \frac{dJ_k}{dz} \, \text{and} \, \frac{d}{dz} (\lambda \frac{dT}{dz}) \]

\[ \left( \frac{df}{dz} \right)_i = \frac{f_{j+1} - f_{j-1}}{2(z_{j+1} - z_{j-1})} \]  \hspace{1cm} (6.39)

For what concerns the axial velocity information flow we can state that the continuity equation propagates information right to left and $\rho u$ is defined by the right boundary object:

\[ \frac{(\rho u)_{j+1} - (\rho u)_j}{\Delta z_{j+1/2}} + (\rho V)_j + (\rho V)_{j+1} = 0 \] \hspace{1cm} (6.40)

Lambda equation propagates information left to right and $\Lambda$ is defined by the left boundary object:

\[ \Lambda_j = \Lambda_{j-1} \] \hspace{1cm} (6.41)

If mass flow rate from left is specified, then residual equation for $\Lambda$ at left is:

\[ (\rho u)_0 = \dot{m}_{left} \] \hspace{1cm} (6.42)

6.5 Cantera Model Analysis

In this chapter it is explained the code used to compute the mole fractions of all chemical species involved in the reaction inside the ring type planar SOFC. This model is based on the Cantera tutorial Catcomb. In this script it is solved a catalytic combustion problem. The first approximation done was to consider the anode like a wall, because the species react on the surface and in order to compute what happen inside the anode, at microscopic level it is
necessary another approach that go beyond the purpose of this work. Moreover for sake of
simplicity it has been assumed that the electrochemically active region on the anode is thinner
than the total anode thickness. In this way the active surface on the anode is the only interface
of the fuel channel with the anode. This approximation helps to improve chemical reactions
occurring inside the anode channel and may represent the initial step for further research in
order to precisely explain what happen inside the anode.

First of all the user must specify all the inputs like temperature, pressure (that are assumed
constant in a good approximation), the translated mechanism file for the catalytic reactions
on nickel, the current density applied at the cell and the composition of the fuel gas entering
the channel in [l/min] that should be converted in [kmol/s] and used to compute the initial
mole fractions of all the chemical species and the mass flow rate of the mixture.

Then there are the geometric parameters such as the radius of the cell, the height of the fuel
channel, the anode height and the number of axial and radial subdivision. All these parameters
will be used to create a mesh for the numerical discretization of the problem and to compute
the inlet area and the reactive - surface area. Gas composition is initially taken from the input
data and then updated at every iteration with the final result coming from the previous cell.
It is possible to change the velocity of the computation by changing the numerical parameters
for the steady state problem and for the time stepping, while the radial grid can be refined if
needed. We can also decide if enable or disable the printing of the figures.

Now will be described the core part of this problem, that analyze the axial behaviour of
a cell (here the word cell is referred to the cell obtained from the discretization of the control
volume) along the channel height and of course the coordinate for the 1-D channel is the axial one along the inlet channel of the SOFC. This is an approximation because in order to analyze this axial behaviour in the z-coordinate (as explained in the previous section) an axial wedge is considered to be a one-dimensional rectangular channel.

First of all it is created the gas object that will be used to evaluate all thermodynamic, kinetic and transport properties. The gas phase will be taken from the definition of the phase "gas" in the input file nickelmod.cti. Then we create the interface object whose purpose is to evaluate all surface chemical production rate and it will be created from the interface definition "Ni-surface" on the same input file of before. After that there is a function to integrate the coverage equations in time for 1s, holding the gas composition fixed in order to generate a good starting estimate for the coverages. The two objects created before are independent of the kind of problem but they are useful in 0-D simulations, 1-D simulations etc. The following objects are specifically for 1-D simulations and will be "stacked" together to create the complete simulation. The first one is the flow object which is responsible to evaluate the 1-D governing equations for the flow along the axial coordinate. It will be initialized with the gas object created before. Then it is created the inlet that provides the inlet boundary conditions and the surface that provides the surface boundary conditions, both for the flow equations.

Once the components parts have been created, they can be assembled in the stack object to create the 1-D simulation and solve for every cell the axial problem. After setting the boundary conditions for the main quantities the stack object created before can be solved. First it is solved
the energy equation with the surface coverage equations, gas and surface chemistry turned off. Then all surface chemistry relations are turned on.

In order to calculate the final gas composition of a cell and consequently the initial gas composition for the following cell to be computed, the net production rates of all the chemical species are calculated from the input mechanism file while the Faraday’s lay is used to estimate the production and destruction rates due to the current applied. At this point it is possible to calculate in a easy way all the mole and mass fractions that can be employed in the next cell to carry out the same cycle described above.

Now it is evident that the main purpose is to create a radial flow along the channel by dividing it into a series of axial flows. In other words the fuel channel is divided into a certain number of radial cells, while every cell is analyzed along the radial coordinate with the script described before. In order to perform this a for cycle is employed to compute the algorithm described above with the number of iterations equal to the number of radial cells. In this way we consider more interesting the radial behaviour instead of the axial one.
CHAPTER 7

EXPERIMENTAL ANALYSIS

7.1 Introduction

This chapter shows a large collection of experimental data obtained during different tests on the ring-type planar Solid Oxide Fuel Cell as anticipated on the previous chapter. All the experiments were performed at the IN.TEN.SE (Innovation Technologies for Energy Sustainability) laboratory at the Energy Department of the Polytechnic University of Turin. The polarization curves are analyzed and then used to validate the numerical model described before. Both dry and steam reforming cases were studied.

7.2 Syngas Composition

It is important to point out that it was not possible to use the same precise syngas composition of the combustion study. All the tests were performed using three syngas mixtures provided by ENEA. ENEA is the Italian National Agency for New Technologies, Energy and Sustainable Economic Development and it is involved in collaborations with some Italian universities (such as the Polytechnic University of Turin). Among all the projects that ENEA is following they are performing several experiments on gasification processes from different feedstocks. Different syngas compositions have been obtained and after further treatments, such as processes of cleaning-up and conditioning, the final syngas mixtures are achieved and can be used as fuel in SOFCs. Table XI shows the three mixtures obtained: As said before the
TABLE XI: SYNGAS MIXTURES PROVIDED BY ENEA

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>High range South African coal - B1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Species</td>
<td>$H_2$  $CO$  $CO_2$  $CH_4$  $H_2S$  $O_2$  $N_2$</td>
</tr>
<tr>
<td>Composition (%vol.)</td>
<td>20,00  18,00  9,00  2,00  0,02  0,00  50,98</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Low range Alaskan Coal - B2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Species</td>
<td>$H_2$  $CO$  $CO_2$  $CH_4$  $H_2S$  $O_2$  $N_2$</td>
</tr>
<tr>
<td>Composition (%vol.)</td>
<td>16,00  27,00  5,00  2,00  0,02  0,00  49,98</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>High range coal and 10% vol. beech in pellets - B3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Species</td>
<td>$H_2$  $CO$  $CO_2$  $CH_4$  $H_2S$  $O_2$  $N_2$</td>
</tr>
<tr>
<td>Composition (%vol.)</td>
<td>22,00  18,00  10,00  2,00  0,02  0,00  47,98</td>
</tr>
</tbody>
</table>

Anode material mostly used for SOFCs is Nickel Oxide/Yttria Stabilized Zirconia ($NI/YSZ$). The use of this material causes problems of poisoning of sulfurs and chlorine and especially carbon deposition because nickel is an excellent catalyst of different types of reactions. For this reason, in order to avoid carbon deposition process, $H_2O$ or $CO_2$ are added at the syngas compositions, respectively 0.242 and 0.19 moles of each mole of dry syngas. Furthermore, the hydrogen sulfide has not been considered since the maximum tolerance for the SOFCs is 1 ppm (0.0001%), much less than the concentrations present in the mixture. The final syngas compositions used for the experiments are listed in Table XII.

7.3 Experimental Set-Up

The experimental tests were performed on an anode supported planar Solid Oxide Fuel Cell. The geometry consists of several parts.
TABLE XII: SYNGAS REFORMED WITH \( \text{H}_2\text{O} \) AND \( \text{CO}_2 \)

<table>
<thead>
<tr>
<th>Syngas</th>
<th>( \text{H}_2 )</th>
<th>( \text{CO} )</th>
<th>( \text{CO}_2 )</th>
<th>( \text{CH}_4 )</th>
<th>( \text{N}_2 )</th>
<th>( \text{H}_2\text{O} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{B1 + H}_2\text{O} )</td>
<td>16.11%</td>
<td>14.50%</td>
<td>7.25%</td>
<td>1.61%</td>
<td>41.05%</td>
<td>19.49%</td>
</tr>
<tr>
<td>( \text{B2 + H}_2\text{O} )</td>
<td>12.88%</td>
<td>21.74%</td>
<td>4.03%</td>
<td>1.61%</td>
<td>40.25%</td>
<td>19.49%</td>
</tr>
<tr>
<td>( \text{B3 + H}_2\text{O} )</td>
<td>17.72%</td>
<td>14.50%</td>
<td>8.05%</td>
<td>1.61%</td>
<td>38.64%</td>
<td>19.49%</td>
</tr>
<tr>
<td>( \text{B1 + CO}_2 )</td>
<td>16.81%</td>
<td>15.13%</td>
<td>25.53%</td>
<td>1.68%</td>
<td>42.85%</td>
<td>0%</td>
</tr>
<tr>
<td>( \text{B2 + CO}_2 )</td>
<td>13.45%</td>
<td>22.69%</td>
<td>20.17%</td>
<td>1.68%</td>
<td>42.01%</td>
<td>0%</td>
</tr>
<tr>
<td>( \text{B3 + CO}_2 )</td>
<td>19.49%</td>
<td>15.13%</td>
<td>24.37%</td>
<td>1.68%</td>
<td>40.33%</td>
<td>0%</td>
</tr>
</tbody>
</table>

- An anode thick 525-610 \( \mu \text{m} \) with two layers; both made of \( \text{NiO}/8\text{YSZ} \) cermet. The first one is the functional layer which is 5-10 \( \mu \text{m} \) thick while the second one is the support layer which is 520-600 \( \mu \text{m} \) thick.
- A 4-6 \( \mu \text{m} \) thick dense electrolyte \( \text{Y}_{0.16}\text{Zr}_{0.84}\text{O}_2 \) (8YSZ)
- A 2-4 \( \mu \text{m} \) barrier layer made of yttria doped ceria (YDC)
- A cathode thick 30-40 \( \mu \text{m} \) made of porous lanthanium strontium cobal ferrite oxide (\( \text{LSCF} \))

The cell is a circular type seal-less SOFC with a diameter of 80 mm and a screen printed cathode of 78 mm. The active surface area of the cell is 47 m\(^2\)\[^{[43]}\].

Fuel flow is distributed through an array of pin-type separators with edge of 1.5 mm and height of 0.8 mm. The SOFC stack needs to work temperatures higher than 650 °C hence the cell is located inside an oven equipped with several devices for operation control and measurements.
During the tests the cells are placed in an inert ceramic housing consisting of alumina, with alumina flanges for gas distribution, platinum meshes for cathode current collection, and nickel ones for anode anode current collection. Current collectors are of double grids mesh type and directly contact both the electrodes:

- fine grid, wire diameter of 0.11/022 mm, 3600 meshes/cm²
- coarse grid, wire diameter of 0.25 mm, 100 meshes/cm². Platinum wires are used as current leads and for the cell voltage measurement.

The anode and cathode chambers are not sealed, allowing the fuel to react with oxygen directly outside the fuel cell through combustion reaction. Information of the thermal distribution is obtained through thermocouples which are placed in the cell center (reference temperature) and outside of the circular housing. The central thermocouple is affected by the processes which happen at the cell surface, while the outer thermocouples describe the evolution of combustion reactions at the cell outlet due to the not sealed anodic and cathodic compartments. The oxidant flow consists of 21% oxygen and 79% nitrogen, without humidification. Before starting the experiments is necessary to carry out a preparation procedure whose purpose is to heat up the SOFC to the testing temperature, provide the proper mechanical load, starting the anode reduction.

### 7.4 Polarization Tests

Polarization tests have been performed starting from the OCV (Open Circuit Voltage) condition and increasing manually from the control panel the current load by 1 A each time.
As the considered value becomes stable it can be registered. Current load can be increased as long as it remains higher than a somehow critical threshold set to 200 mV. This procedure has been repeated for different conditions of fuel utilization and steam or dry reforming.

The fuel utilization efficiency is defined as the ratio of the fuel used by the fuel cell to total fuel input. It is defined as:

$$\eta_f = \frac{i}{nF}$$ \hspace{1cm} (7.1)

where $i$ is the current generated by the fuel cell, $v_f$ is the fuel flow rate in mol/sec and $F$ is the Faraday constant. Alternatively the fuel utilization can be written as:

$$\eta_f = \frac{G_{in} - G_{out}}{G_{in}}$$ \hspace{1cm} (7.2)

As fuel passes through the anode channel, it is used in the reaction. So the partial pressure of its elements will progressively decrease as it flows from one end to the other of the anode. For high fuel cell efficiency, it is required that all the fuel supplied to the cell is used in the reaction. But at the same time the pressure of the fuel mixture should not be reduced to very low levels. As a result, fuel utilization need to be carefully optimizing, especially for high temperature fuel cells. For instance overused-fuel condition ($\eta_f > 0.9$), will lead to fuel starvation near the outlet and cause permanent damage to cells while underused-fuel condition ($\eta_f < 0.7$), will cause unexpectedly high cell voltages. Table XIII and Table XIV present the mass flow rates sent to the experimental station in both cases of fuel utilization. Figures 44 and 45 present some examples of polarization curves and it is shown the dependence of the potential
TABLE XIII: SYNGAS COMPONENTS MASS FLOW RATE FOR $\eta_F = 80\%$

<table>
<thead>
<tr>
<th>G [ml/min]</th>
<th>$H_2$</th>
<th>CO</th>
<th>CO$_2$</th>
<th>CH$_4$</th>
<th>$N_2$</th>
<th>H$_2$O [gr/h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B1 + H_2O$</td>
<td>87.924</td>
<td>73.131</td>
<td>41.295</td>
<td>8.792</td>
<td>224.117</td>
<td>5.15</td>
</tr>
<tr>
<td>$B2 + H_2O$</td>
<td>70.339</td>
<td>118.697</td>
<td>21.981</td>
<td>8.792</td>
<td>219.721</td>
<td>5.13</td>
</tr>
<tr>
<td>$B3 + H_2O$</td>
<td>96.716</td>
<td>118.697</td>
<td>43.962</td>
<td>8.792</td>
<td>210.929</td>
<td>5.13</td>
</tr>
<tr>
<td>$B1 + CO_2$</td>
<td>91.766</td>
<td>82.590</td>
<td>128.473</td>
<td>9.177</td>
<td>233.912</td>
<td>0</td>
</tr>
<tr>
<td>$B2 + CO_2$</td>
<td>73.413</td>
<td>123.885</td>
<td>110.120</td>
<td>9.177</td>
<td>229.324</td>
<td>0</td>
</tr>
<tr>
<td>$B3 + CO_2$</td>
<td>100.943</td>
<td>82.590</td>
<td>133.061</td>
<td>9.177</td>
<td>220.147</td>
<td>0</td>
</tr>
</tbody>
</table>

TABLE XIV: SYNGAS COMPONENTS MASS FLOW RATE FOR $\eta_F = 30\%$

<table>
<thead>
<tr>
<th>G [ml/min]</th>
<th>$H_2$</th>
<th>CO</th>
<th>CO$_2$</th>
<th>CH$_4$</th>
<th>$N_2$</th>
<th>H$_2$O [gr/h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B1 + H_2O$</td>
<td>237.356</td>
<td>213.620</td>
<td>111.478</td>
<td>23.736</td>
<td>605.020</td>
<td>13.890</td>
</tr>
<tr>
<td>$B2 + H_2O$</td>
<td>171.268</td>
<td>289.015</td>
<td>53.521</td>
<td>21.409</td>
<td>535</td>
<td>12.479</td>
</tr>
<tr>
<td>$B3 + H_2O$</td>
<td>250.212</td>
<td>204.719</td>
<td>113.733</td>
<td>22.747</td>
<td>545.691</td>
<td>13.259</td>
</tr>
<tr>
<td>$B1 + CO_2$</td>
<td>237.356</td>
<td>213.620</td>
<td>332.298</td>
<td>23.736</td>
<td>605.020</td>
<td>0</td>
</tr>
<tr>
<td>$B2 + CO_2$</td>
<td>171.268</td>
<td>289.015</td>
<td>256.903</td>
<td>21.409</td>
<td>535</td>
<td>0</td>
</tr>
<tr>
<td>$B3 + CO_2$</td>
<td>250.212</td>
<td>204.719</td>
<td>329.825</td>
<td>22.747</td>
<td>545.691</td>
<td>0</td>
</tr>
</tbody>
</table>
different across the cell from the current density. These curves are quite useful in order to understand the model explained in the previous chapter. It is easy to note the effects of the syngas composition, type of reforming and fuel utilization on the cell voltage. The trend of the curves is always the same with the dominance of activation losses and ohmic losses for low and high values of current density respectively.

![Polarization curves for FU=30](image)

**Figure 44: Polarization curves for FU=30**
7.5 **Model Validation**

In this paragraph the model described in the previous chapter and reported in appendix has been validated through a series of experimental results. The number of radial cells has been set to 8 in order to get a small error and a quickly convergence. The surface site density has been set to $2.6 \cdot 10^{-9} \text{mol/cm}^2$ according to reference\textsuperscript{[38]} and this is the only parameter in this model that characterize the anode and it depends on the crystalline structure. This parameters, together with the numerical parameters can be modified in order to get a better agreement with the experimental results and to adapt this model to the variuos types of cell.

Since the model produces as output the exhaust gas composition at the exit of the fuel cell it was necessary to calculate for each case the cell voltage through the Equation 6.9, Equation 6.2
and Equation 6.24 for the reversible cell voltage, ohmic and activation losses respectively. As said before the concentration losses are implemented directly in the model. In order to obtain the different polarizations the data in Table XV have been used. The activation losses can be problematic to evaluate since the linear representation of the Butler-Volmer equation is valid only for $\eta_{act} < 0.01$. Furthermore the analysis performed on this study assumes that all charge transfer chemistry happens through $H_2$. Although this is an universal assumption in the SOFC modeling, it is also well known that this kind of cells can function on even pure $CO^{[39]}$.

### TABLE XV: EXCHANGE CURRENT DENSITY AND OHMIC RESISTANCE

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$R_{ohm}[\text{Ω/cm}^2]$</th>
<th>$V_{nernst}$</th>
<th>$i_0[\text{mA/cm}^2]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2FU30$</td>
<td>0.45</td>
<td>1.0209</td>
<td>746.39</td>
</tr>
<tr>
<td>$H_2FU80$</td>
<td>0.479</td>
<td>0.9469</td>
<td>645.33</td>
</tr>
<tr>
<td>$B1 + H_2OFU80$</td>
<td>0.589</td>
<td>0.8988</td>
<td>270.05</td>
</tr>
<tr>
<td>$B2 + H_2OFU80$</td>
<td>0.53</td>
<td>0.9235</td>
<td>333.33</td>
</tr>
<tr>
<td>$B3 + H_2OFU80$</td>
<td>0.523</td>
<td>0.9039</td>
<td>634.62</td>
</tr>
<tr>
<td>$B1 + H_2OFU30$</td>
<td>0.402</td>
<td>0.9169</td>
<td>587.14</td>
</tr>
<tr>
<td>$B2 + H_2OFU30$</td>
<td>0.411</td>
<td>0.9266</td>
<td>535.26</td>
</tr>
<tr>
<td>$B3 + H_2OFU30$</td>
<td>0.403</td>
<td>0.9226</td>
<td>691.05</td>
</tr>
<tr>
<td>$B1 + CO_2FU30$</td>
<td>0.45</td>
<td>0.9215</td>
<td>716.56</td>
</tr>
<tr>
<td>$B2 + CO_2FU30$</td>
<td>0.451</td>
<td>0.9525</td>
<td>415.56</td>
</tr>
<tr>
<td>$B3 + CO_2FU30$</td>
<td>0.432</td>
<td>0.9449</td>
<td>439.55</td>
</tr>
</tbody>
</table>
Figure 46 presents a comparison between the experimental data acquired by the polarization tests and the results obtained from the present model. This data have been taken in OCV configuration since no current load was applied to the cell and the inlet mass flow rates have been set according to the data on Table XIII and XIV. Results obtained from the model presents a quite good approximation but in all the cases the data are overestimated but with an error within the 4%. The reason could be that in the computation of the OCV voltage the electrolyte and electric resistance have not been considered.

Figure 47 through 52 show the validation of the polarization curves for different compositions and fuel utilizations. In each case the errors are under the 5% but is interesting to understand the meaning of the differences between the numerical model and the experimental data and specify why errors occur. In OCV configuration and at the end of the curve, for high values of current, the model seems to overestimate the voltage of the cell. The can be two possible reasons for this behaviour. The first one is the air infiltration. If air enters the fuel channel, the oxygen contained is free to react inside the channel and alternative combustion reactions and gas-shift process may take place. It is evident that if there is air infiltration during the experiments, the model validation become more difficult. The second reason could be the dominance of water gas-shift reaction in the reaction mechanism used for this analysis. This usually involve a much lower value of carbon-monoxide mole-fraction and highcarbon dioxide production (compared to the experiments if we could measure the exhaust compositions). In order to reduce the dominance of this kind of reaction by modifying the mechanism can be useful a sensitivity analysis of the Arrenhius parameters, but on the other hand this mechanism
Figure 46: Cell voltage validation for selected compositions - OCV configuration
has been extensively validated. Except for Figure 47, the numerical results for the first half of the current-voltage curve underestimate the experimental results. This can be due to the fact that the development into series of the Butler-Volmer equation for a linear representation of activation losses (Equation 6.24) can overestimate them.

Figure 47: Polarization curve validation for composition B1+CO$_2$FU = 30%
Figure 48: Polarization curve validation for composition B3+$CO_2FU = 30\%$.

Figure 49: Polarization curve validation for composition B1+$H_2OFU = 30\%$. 
Figure 50: Polarization curve validation for composition B1+$H_2OFU = 80\%$

Figure 51: Polarization curve validation for composition B3+$H_2OFU = 30\%$
Figure 52: Polarization curve validation for composition B3+$H_2OFU = 80\%$

7.5.1 Mole Fraction Profiles

Figure 53 through Figure 56 show the mole fraction profile of the main chemical species along the cell radius for different compositions, type of reforming and fuel utilization in OCV configuration. For the dry reformed syngas it is possible to see a consumption of carbon dioxide and an increase of carbon monoxide mole fraction. The amount of methane is approximatively the same along the fuel channel while a small amount of water is produce, probably due to the inverse gas-shift reaction (the amount of hydrogen diminish). On the other hand for what concern the steam reforming cases there is a consumption of water and carbon monoxide and a rise of carbon dioxide and hydrogen. The consumption of water lead directly to the production
of hydrogen, while the consumption of carbon monoxide is probably due to the water gas-shift reaction. Also in this case the methane content remains approximately the same.

Figure 53: Mole fraction profiles of main chemical species for composition B1+CO₂
(FU = 30% OCV configuration)

Figure 57 through Figure 59 show the mole fraction profile of the main chemical species along the cell radius for different compositions, type of reforming and fuel utilization for current loads of 10 A and 15 A respectively. For both dry reforming and steam reforming with a current load of 10 A there is large production of water and consumption of hydrogen because of the electrochemistry of the cell, but the amounts of carbon monoxide and carbon dioxide do not suffer big changes along the cell radius. For a current load of 15 A a large amount of water is still
Figure 54: Mole fraction profiles of main chemical species for composition B2+CO₂

(FU = 30% OCV configuration)

Figure 55: Mole fraction profiles of main chemical species for composition B1+H₂O

(FU = 30% OCV configuration)
produced but there is a production of carbon dioxide and a consumption of carbon monoxide too. Carbon monoxide is consumed in the last part of the cell, when reacting with water in order to produce carbon monoxide.
Figure 57: Mole fraction profiles of main chemical species for composition B1+CO₂
\((FU = 30\%, I = 10\text{A})\)

Figure 58: Mole fraction profiles of main chemical species for composition B3+H₂O
\((FU = 30\%, I = 10\text{A})\)
7.5.2 Effect of the Cell Radius on the Exhaust Composition and Cell Voltage

In this section are shown the results of a sensitivity study performed in order to understand the effect of modifying the cell radius on the mole fraction profile and on the cell voltage. In both Figure 60 and Figure 60 it is possible to see the same trend. In the new section added at the fuel channel, there is the consumption of carbon monoxide in order to form carbon dioxide when reacting with water. This behaviour, with a normal radius of 0.04 m, usually begins with a current load of 15 A. For what concerns the cell voltage, we can state that increasing the cell radius brings to a diminish in the voltage because of the concentration losses that become more important. For instance for the syngas composition B2+CO$_2$ with a 30% of fuel utilization we switch from a voltage of 0.817 V, for a radius of 0.04 m, to a voltage of 0.817 V, for a radius of...
0,06 m. For composition B3+H\textsubscript{2}O with a 30\% of fuel utilization the cell voltage change from 0,767 V to 0,733 V for a cell radius of 0,04 m and 0,06 m respectively.

![Diagram](image-url)

Figure 60: Mole fraction profiles of main chemical species for composition B1+H\textsubscript{2}O (\textit{FU} = 30\%, \textit{I} = 10A) for different cell radius
Figure 61: Mole fraction profiles of main chemical species for composition B2+CO₂
(FU = 30%, I = 10A) for different cell radius
8.1 Emission Comparison

The combustion of syngas produces different pollutants like $NO_x$ and carbon monoxide and carbon dioxide even though in low quantities compared to the conventional hydrocarbon fuels. Taking as reference the study on counterflow nonpremixed flames with Syngas 1 the exhaust stream is mainly composed by $N_2$ with a percentage of 61%, then $CO$ and $CO_2$ present percentages of 4% and 6% respectively. There is the presence of significant amounts of $NO$ which is very dangerous for the human health.

On the contrary in the SOFC exhaust gases there is not the presence of these chemical species since in this device there is the production of energy through an electrochemical path. There is no production of nitrogen since it is in the same amount of the inlet. Main pollutants are $CO$ and $CO_2$ due to their presence in the inlet fuel, but with the increasing in the current density the amount of carbon monoxide drops very quickly.

In conclusion the combustion of syngas is characterized by the production of $NO_X$ and in general by lower amounts of carbon dioxide and carbon monoxide, compared to the SOFCs which are, however, influenced by the significant present of these two pollutant in the fuel initial composition.
8.2 Exergy analysis

The purpose of the exergy analysis is to determine exergy losses (true thermodynamic losses) in processes and systems and minimize these losses by the optimisation of the driving forces. In thermodynamics, the exergy of a system is the maximum theoretical work that can be obtained from an amount of energy and specifically it is the work that can be obtained from an amount of energy (converted in a well-defined system), under ideal conditions (applying reversible processes), using the environment only as a reservoir of heat and matter. Exergy analysis is very useful in the field of industrial ecology to define which device is more efficient. With an energy analysis input and output will always balance according to the First Law of Thermodynamics or the energy conservation principle, on the other hand Exergy output will not balance the exergy input for real processes since a part of the exergy input is always destroyed according to the Second Law of Thermodynamics for real processes. An exergy efficiency can allow the designer to choose the most efficient process based on wasting and destroying as little available work as possible from a given input of available work.

If we consider a system, which intake or release exergy through mass flows $G_i$, heat transfer $\Psi$ and mechanical power $W_t$ the exergy equation is the following:

$$\sum_{j=0}^{M} \Psi_j - W_t = \frac{d}{dt} (A^t)_{CV} + \sum_{i=0}^{N} G_i b_i^t + \Psi_{irr}$$

(8.1)
where $\Psi_j$ is the thermal exergetic flux:

$$\Psi_j = \Phi_j \eta_j \quad (8.2)$$

$\eta_j = 1 - \frac{T_0}{T_j}$ is the Carnot factor, $-\frac{d}{dt}(A^T)_{CV}$ is the accumulation of nonflow exergy and $G_i b^t_i$ is the exergy via mass flow. This exergy via mass flow is composed by the contribution of chemical and physical exergy.

$$b^t = [h - h^* - T_0(s - s^*) + e_m] + \left[ \sum_{k=0}^{K} (\mu_k^* - \mu_{k,0})x_k \right] \quad (8.3)$$

The notation $^*$ is used to indicate properties related to the restricted dead state where only the temperature and pressure match the corresponding environmental values. At the dead state we will have the chemical composition of the biosphere. For what concern syngas combustion exergy, for the fuel there is only the contribution of the flow chemical exergy (since we are in a restricted dead state) while for the exhausts there is the contribution of the thermal, flow physical exergy and flow chemical exergy. For SOFC exergy analysis there are the same type of exergy but on the exhaust there is even the contribution of the electric power.

The functional exergetic efficiency is the only true thermodynamic efficiency. As it is possible to see in Table XVI SOFCs present better values of exergy efficiency compared to the counterflow nonpremixed flames, and this is due primarily to the higher chemical exergy still present in the exhaust gases. The electrochemical oxidation eliminates all the irreversibilities of the combustion process. But, in order to take advantage from the exergy of the SOFC exhaust
### TABLE XVI: EXERGY ANALYSIS

<table>
<thead>
<tr>
<th>Exergy Type</th>
<th>Flow Chemical</th>
<th>Flow Physical</th>
<th>Thermal</th>
<th>Electrical</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Exergy</td>
<td>2.34 [kW]</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.34 [kW]</td>
</tr>
<tr>
<td>Exhaust Exergy</td>
<td>0.26 [kW]</td>
<td>0.86 [kW]</td>
<td>0.019 [kW]</td>
<td>0</td>
<td>1.139 [kW]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Exergy Type</th>
<th>Flow Chemical</th>
<th>Flow Physical</th>
<th>Thermal</th>
<th>Electrical</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Exergy</td>
<td>2.34 [kW]</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.34 [kW]</td>
</tr>
<tr>
<td>Exhaust Exergy</td>
<td>0.27 [kW]</td>
<td>0.87 [kW]</td>
<td>0.023 [kW]</td>
<td>0</td>
<td>1.139 [kW]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Exergy Type</th>
<th>Flow Chemical</th>
<th>Flow Physical</th>
<th>Thermal</th>
<th>Electrical</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Exergy</td>
<td>33.34 [kW]</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>33.34 [kW]</td>
</tr>
<tr>
<td>Exhaust Exergy</td>
<td>16.49 [kW]</td>
<td>7.72 [kW]</td>
<td>0</td>
<td>0.011 [kW]</td>
<td>24.11 [kW]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Exergy Type</th>
<th>Flow Chemical</th>
<th>Flow Physical</th>
<th>Thermal</th>
<th>Electrical</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Exergy</td>
<td>33.34 [kW]</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>33.34 [kW]</td>
</tr>
<tr>
<td>Exhaust Exergy</td>
<td>18.89 [kW]</td>
<td>7.72 [kW]</td>
<td>0</td>
<td>0.008 [kW]</td>
<td>26.618 [kW]</td>
</tr>
</tbody>
</table>

- **Syngas 1 counterflow nonpremixed configuration** \( a_s = 100s^{-1} \)
- **Syngas 1 counterflow nonpremixed configuration** \( a_s = 200s^{-1} \)
- **SOFC B3+H\(_2\)O FU = 30% 15 A**
- **SOFC B3+H\(_2\)O FU = 30% 10 A**
gases it is necessary an utilization of them in combined cycles. In conclusion it is important
to point out that exergy efficiency is an indicator of the quality with which engineers convert
resources available to them, but it does not give indications concerning the use or not of renew-
able resources, account for the relative difficulty of conversion of a given primary energy, give
indications on the local environmental impacts (pollutants affecting health) and only indirectly
give global environment indications.
CHAPTER 9

CONCLUSIONS

In this first part of this work a detailed numerical study of combustion of syngas in many different conditions has been reported in order to make a comparison between four different reference compositions. Davis mechanism provides accurate prediction of syngas combustion for all the different syngas compositions at atmospheric condition at different equivalence ratio.

An equilibrium composition study shows that syngas composition considerably affect the carbon-dioxide emissions. However all the compositions guarantee an high adiabatic-flame-temperature. Dilution (carbon dioxide, water vapor, nitrogen) is the main cause for the adiabatic flame temperature to decrease. Equivalence ratio strongly affects the adiabatic flame temperature by acting on the heat of combustion and heat capacity. Furthermore for rich mixtures not all the heat is released. Pressure and temperature have an important role too. At any fixed temperature, increasing the pressure suppresses the dissociation of \( CO_2 \) into \( CO \) and \( O_2 \); second, increasing the temperature at a fixed pressure promotes the dissociation. Both of these trends are consistent with the principle of Le Chatelier.

For what concern laminar premixed flames it was possible to understand that the laminar flame speed increases significantly with the \( H_2 \) concentration as it is possible to see with the fourth syngas mixture. This is due to both thermal diffusivity and mass diffusivity and the rapid reaction kinetics of \( H_2 \). The net heat production rate is considerably higher with an higher percentage of hydrogen in the fuel mixture. The effect of equivalence ratios on flame
speed is a result of how this parameter affects flame temperature and it is evident that we have a maximum of flame speed at slightly rich mixture and fall on either sides. For what concerns the pressure there is a similar trend for all the four syngas compositions. For pressures up to 10 atm there is a relevant drop in the flame speed and after this limit the dependence of the flame speed from the pressure become weaker. There is a strong dependence of flame speed from the temperature. As the temperature increases, the flame speed increases too. This is due to the chemical rates and thermal and mass.

Counterflow flames then have been analyzed. Like in laminar premixed flames increasing the \( H_2 \) content in the initial composition bring to an increase in the axial velocity, net heat production and temperature while \( CO_2 \) reduces the maximum temperature. For what concerns greenhouse emissions, of course carbon-monoxide and carbon-dioxide emissions are higher for those syngas compositions that present more \( CO \) in the initial mixture like Syngas 2. Moreover the results show that \( NO \) is produced in the high temperature zone for all the types of syngas flames, but the \( NO \) production rate for Syngas 4 flame is higher due to higher flame temperature, a characteristics of thermal \( NO \) (Zeldovich mechanism). A detailed extinction study has been performed and it shows how flame extinction is significantly affected by the compositions of syngas mixture. The effects of three dilution gases, \( CO_2 \), \( H_2O \) and \( N_2 \), have been studied since they may be present in the syngas fuel depending on the fuel sources and gasification and post-gasification processes. The \( H_2O \)-diluted syngas flames present a very interesting behaviour. Passing from Syngas 4 (\( H_2 \)-enriched) to Syngas 1 (\( CO \)-enriched) through Syngas 1 is evidentent that the difference in the extinction limit is very limited compared to the cases of
dilution with $CO_2$ and $N_2$. Furthermore this case of extinction limit is not very affected by the strain rate. Different explanations have been guessed for this behavior but further investigations may be needed. The effects of partially premix the flame has been studied too, in order to understand how this can affect the flame structure and the emissions. For leaner mixtures ($\phi = 6$) the $NO$ peak is shifted toward the oxidizer nozzle and present a lower value.

In the second part of this study has been investigated how syngas can be used to directly feed solid oxide fuel cells for the production of energy by electrochemical processes. Solid-oxide fuel cell systems have the potential to convert hydrocarbon and bio-derived fuels to electricity with very high conversion efficiencies. In particular a numerical model has been developed for SOFC simulation and implemented through Cantera and MATLAB. This model can be applied for the purpose of best design and optimization of the SOFCs, seeking to enhance understanding and interpretation of the physical and chemical processes happening within the cell. The model take as input a set of physical (temperature and pressure), chemical (reaction mechanism) and geometrical (dimensions of the cell) and gives as output the exhaust gas compositions that have been compared to experiment performed in the laboratories of the Polytechnic University of Turin. Several examples were provided in order to demonstrate the model capabilities. Several problems can find an answer using this model like what anode design suite the best performance in order to avoid the carbon deposition? What is the effect of load conditions, temperature and mass flow rate? The match between the numerical and experimental results are quite good but there are several improvement that can be done in further research. For instance was an approximation to consider the anode like a wall, because the species react on the surface and
in order to compute what happen inside the anode may be useful to consider the electrodes as porous and analyze the molar fluxes within. The underlying approaches in this model for representing chemistry and transport may be useful for the incorporation into a CFD software that include three-dimensional heat transfer and fluid flow. Furthermore the analysis on this work is made on the assumption that all charge trasfer chemistry happen through the hydrogen. This is an usual assumption in world of SOFC modeling but it is well known that a cell can operate even with only carbon monoxide, thus a future goal could be the implementation of an elementary electrochemistry that will include multiple charge transfer ways in the reaction mechanism.

In the last chapter a comparison between the two paths of producing energy has been performed. In particular syngas combustion exhaust are characterized by the presence of $NO_x$, which are the main pollutants, but lower quantities of carbon dioxide and carbon monoxide. However from an exergetic analysis the electrochemical path seems to be more efficient because of the more chemical exergy of the exhaust. It is important to note that the functional exergetic efficiency is the only true thermodynamic efficiency but it does not give indications concerning the use or not of renewable resources, account for the relative difficulty of conversion of a given primary energy, give indications on the local environmental impacts (pollutants affecting health) and only indirectly give global environment indications.

In conclusion syngas may represent an efficient alternative to conventional fuels for both chemically and electrochemically producing energy and it is particularly attractive for stationary power generation. Furthermore one great advantage is the flexibility of power sources. On one
hand, when involved in combustion processes syngas can considerably break down the emissions
of pollutants but at the same time they can offer good performances in terms of temperature,
flame speed, and heat generation. For what concern solid oxide fuel cells syngas can offer
high efficiency and good performances in terms of voltage and electrical power and the model
developed in this work may represent a powerful tool for the optimum design of the cell and
avoid phenomenon of carbon deposition. It is important to remark that the carbon-dioxide
emission are strongly influenced by the amount of $CO_2$ present in the initial composition.
Hydrogen may represent potentially an important source of energy but it has many critical
issue in terms of safety and storage. Consequently, blending hydrogen with other hydrocarbon
fuels to form syngas is a very important way to create a viable energy source.
APPENDICES
Appendix A

ELEMENTS
O  H  C  N  AR  HE
END

SPECIES
!

First Two Species Must be H2 and H for Modified Burner Stabilized Flame Calc.

H2  H

AR  N2  HE

Radicals in order of increasing molecular weight:

O  OH  HCO  HO2

Stable molecules in order of increasing molecular weight:

H20  CO  O2  H2O2  CO2

N  NH

NH2  NH3  NNH  NO  NO2  N2O  HNO  CN

HCN  CH4  HCN  HCNO  NCO

CH3  CH2  C2H6  HCCO  CH2(S)

REACTIONS

Reactions of H2/O2

H+O2 = O+OH  2.644E+16 -0.6707 17041.00 !GRI3.0 * 1.00
OH+H2 = H+OH  4.589E+04  2.700  6260.00 !GRI3.0 * 1.00
OH+OH = O+H2O  1.780E+18  -1.000  0.00 !GRI3.0 * 1.78
H2+O  = H2O/0.0/ CO2/0.0/ AR/0.63/ HE/0.63/
H+H+H2 = H2+H2  9.000E+16  -0.600  0.00 !GRI3.0
H+H+H2O = H2+H2O  5.624E+0  -1.250  0.00 !GRI3.0
H+O+M = H2+M  1.200E+17  -1.000  0.00 !GRI3.0
H+O+H+M = H2+M  4.400E+0  -2.000  0.00 !GRI3.0
H2/2.0/ H2O/6.30/ CO/1.75/ CO2/3.6/ AR/0.38/ HE/0.38/
O+H+M = OH+M  9.428E+18  -1.000  0.00 !GRI3.0
H+O2(+M) = HO2(+M)  3.970E+12  0.000  671.00 !GRI3.0
H+O2(+M) = HO2(+M)  5.116E+12  0.000  671.00 !GRI3.0

TROE/  94.00  1.00  1.00
LOW/ 6.328E+19 -1.400  0.00/

Reactions of HO2

HO2+H = O+H2O  5.916E+05  2.433  53502.00 !GRI3.0 * 1.00
OH+HO2(+M) = H2O2(+M)  1.110E+14  -0.370  0.00 !GRI3.0
HO2/2.0/ H2O/6.00/ CO/1.75/ CO2/3.6/ AR/0.7/ HE/0.7/
H+O2/2.0/ H2O/6.00/ CO/1.75/ CO2/3.6/ AR/0.7/ HE/0.7/
H+O2/2.0/ H2O/6.00/ CO/1.75/ CO2/3.6/ AR/0.7/ HE/0.7/
H+O2/2.0/ H2O/6.00/ CO/1.75/ CO2/3.6/ AR/0.7/ HE/0.7/
H+O2/2.0/ H2O/6.00/ CO/1.75/ CO2/3.6/ AR/0.7/ HE/0.7/
H+O2/2.0/ H2O/6.00/ CO/1.75/ CO2/3.6/ AR/0.7/ HE/0.7/
H+O2/2.0/ H2O/6.00/ CO/1.75/ CO2/3.6/ AR/0.7/ HE/0.7/

Low/ 5.753E+20  -1.400  0.00/

H2+O2 = HO2+H  3.970E+12  0.000  671.00 !GRI3.0

164
### Reactions of \( \text{H}_2\text{O}_2 \)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Activation Energy</th>
<th>Temperature</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{O}_2 + \text{H} \rightarrow \text{HO}_2 + \text{H}_2 )</td>
<td>( 6.05 \times 10^6 )</td>
<td>5200</td>
<td>295</td>
<td>( \text{GRI} 3.0 \times 0.50 )</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{HO}_2 + \text{H}_2\text{O} )</td>
<td>( 9.63 \times 10^6 )</td>
<td>3970</td>
<td>295</td>
<td>( \text{GRI} 3.0 \times 0.50 )</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2 + \text{O} \rightarrow \text{O}_2 + \text{H}_2\text{O} )</td>
<td>( 2.00 \times 10^7 )</td>
<td>427</td>
<td>295</td>
<td>( \text{GRI} 3.0 \times 0.50 )</td>
</tr>
</tbody>
</table>

### Reactions of \( \text{CO} / \text{CO}_2 \)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Activation Energy</th>
<th>Temperature</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO} + \text{O} \rightarrow \text{CO}_2 )</td>
<td>( 1.36 \times 10^2 )</td>
<td>2384</td>
<td>295</td>
<td>( \text{GRI} 3.0 \times 0.76 )</td>
</tr>
</tbody>
</table>

### Reactions of \( \text{HCO} \)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Activation Energy</th>
<th>Temperature</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{HCO} + \text{H} \rightarrow \text{CO} + \text{H}_2 )</td>
<td>( 1.20 \times 10^{14} )</td>
<td>0</td>
<td>( \text{GRI} 3.0 \times 0.76 )</td>
<td></td>
</tr>
<tr>
<td>( \text{HCO} + \text{O} \rightarrow \text{CO} + \text{OH} )</td>
<td>( 3.00 \times 10^{13} )</td>
<td>0</td>
<td>( \text{GRI} 3.0 \times 0.76 )</td>
<td></td>
</tr>
</tbody>
</table>

### Reactions of \( \text{N} / \text{N}_2 \)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Activation Energy</th>
<th>Temperature</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O} )</td>
<td>( 7.48 \times 10^5 )</td>
<td>295</td>
<td>( \text{GRI} 3.0 \times 0.76 )</td>
<td></td>
</tr>
<tr>
<td>( \text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O} )</td>
<td>( 4.00 \times 10^7 )</td>
<td>0</td>
<td>( \text{GRI} 3.0 \times 0.76 )</td>
<td></td>
</tr>
</tbody>
</table>
### Appendix A (continued)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Preexponent</th>
<th>Temperature</th>
<th>Product(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH + H ⇌ N + H₂</td>
<td>3.200E+13</td>
<td>.000</td>
<td>330.00</td>
<td></td>
</tr>
<tr>
<td>NH + OH ⇌ H₂ + NO</td>
<td>2.000E+13</td>
<td>.000</td>
<td>.00</td>
<td></td>
</tr>
<tr>
<td>NH + O₂ ⇌ NO + O₂</td>
<td>1.280E+06</td>
<td>1.500</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>NH + N₂ + H</td>
<td>1.500E+13</td>
<td>.000</td>
<td>.00</td>
<td></td>
</tr>
<tr>
<td>NH + O₂ ⇌ HNO + H₂</td>
<td>2.000E+13</td>
<td>.000</td>
<td>13850.00</td>
<td></td>
</tr>
<tr>
<td>NH + NO ⇌ N₂ + OH</td>
<td>2.160E+13</td>
<td>-.230</td>
<td>.00</td>
<td></td>
</tr>
<tr>
<td>NH + N₂ + O₂</td>
<td>3.650E+14</td>
<td>-.450</td>
<td>.00</td>
<td></td>
</tr>
<tr>
<td>NH + O₂ + OH ⇌ NO + H₂O</td>
<td>2.000E+13</td>
<td>1.200</td>
<td>.00</td>
<td></td>
</tr>
<tr>
<td>NH + O₂ ⇌ NO + OH</td>
<td>1.280E+13</td>
<td>.000</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>NH + H₂O ⇌ HNO + H₂</td>
<td>2.000E+13</td>
<td>.000</td>
<td>13850.00</td>
<td></td>
</tr>
<tr>
<td>NH + NO ⇌ N₂ + OH</td>
<td>1.300E+14</td>
<td>-.230</td>
<td>.00</td>
<td></td>
</tr>
<tr>
<td>NH + NO ⇌ N₂O + H</td>
<td>4.000E+13</td>
<td>.000</td>
<td>3650.00</td>
<td></td>
</tr>
<tr>
<td>NH + O₂ + OH ⇌ NO₂ + H₂O</td>
<td>2.000E+13</td>
<td>1.200</td>
<td>.00</td>
<td></td>
</tr>
<tr>
<td>NH + N ⇌ N₂ + H</td>
<td>2.000E+13</td>
<td>.000</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>NH + O₂ ⇌ HNO + O</td>
<td>4.610E+05</td>
<td>2.000</td>
<td>6500.00</td>
<td></td>
</tr>
<tr>
<td>NH + O₂ ⇌ NO + O₂</td>
<td>2.000E+13</td>
<td>.000</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>NH + N₂ + O₂</td>
<td>2.000E+13</td>
<td>.000</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>NH + O₂ ⇌ HNO + O</td>
<td>4.610E+05</td>
<td>2.000</td>
<td>6500.00</td>
<td></td>
</tr>
<tr>
<td>NH + O₂ ⇌ NO + O₂</td>
<td>2.000E+13</td>
<td>.000</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>NH + N₂ + O₂</td>
<td>2.000E+13</td>
<td>.000</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>NH + O₂ ⇌ HNO + O</td>
<td>4.610E+05</td>
<td>2.000</td>
<td>6500.00</td>
<td></td>
</tr>
<tr>
<td>NH + O₂ ⇌ NO + O₂</td>
<td>2.000E+13</td>
<td>.000</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>NH + N₂ + O₂</td>
<td>2.000E+13</td>
<td>.000</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>NH + O₂ ⇌ HNO + O</td>
<td>4.610E+05</td>
<td>2.000</td>
<td>6500.00</td>
<td></td>
</tr>
<tr>
<td>NH + O₂ ⇌ NO + O₂</td>
<td>2.000E+13</td>
<td>.000</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>NH + N₂ + O₂</td>
<td>2.000E+13</td>
<td>.000</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

**Note:** All reactions are presented in the context of a chemical reaction network, typically involving the formation and decomposition of nitrogen-containing species in a plasma or combustion environment.
Appendix A (continued)

C+NO<=>CO+N  2.900E+13  .000  .00
CH+NO<=>HCN+O  4.100E+13  .000  .00
CH+NO<=>H+HNCO  1.620E+13  .000  .00
CH+NO<=>H+HCO  2.460E+13  .000  .00
CH2+NO<=>H+HNOCO  3.100E+17  -1.380  1270.00
CH2+NO<=>OH+HCN  2.900E+14  -.690  760.00
CH2+NO<=>H+NCO  3.800E+13  -.360  580.00
CH2+NO<=>N+HCO  2.460E+13  .000  .00
CH2(S)+NO<=>H+HNCO  3.100E+17  -1.380  1270.00
CH2(S)+NO<=>OH+HCN  2.900E+14  -.690  760.00
CH2(S)+NO<=>H+HCNO  3.800E+13  -.360  580.00
C3+NO<=>HCN+H2O  9.600E+13  .000  28800.00
C3+NO<=>H2CN+OH  2.900E+14  -.690  760.00
C3+NO<=>H+HCNO  3.800E+13  -.360  580.00
CH3+NO<=>HCN+H2O  9.600E+13  .000  28800.00
CH3+NO<=>H2CN+OH  2.900E+14  -.690  760.00
CH3+NO<=>H+HCNO  3.800E+13  -.360  580.00
HCNN+O<=>CO+H+N2  2.200E+13  .000  .00
HCNN+O<=>HCN+NO  2.000E+12  .000  .00
HCNN+O2<=>O+HCO+N2  1.200E+13  .000  .00
HCNN+O2<=>H+HCNO+N2  1.200E+13  .000  .00
HCNN+H<=>CH2+N2  1.000E+14  .000  .00
HCNO+O<=>NH+CO2  9.800E+07  1.410  8500.00
HCNO+O<=>HNO+CO  1.500E+08  1.570  44000.00
HCNO+O<=>NCO+OH  2.250E+12  2.110  11400.00
HCNO+H<=>NH2+CO  2.250E+07  1.700  3800.00
HCNO+H<=>H2+CO  1.050E+05  2.500  13300.00
HCNO+OH<=>NCO+H2O  3.300E+07  1.500  3600.00
HCNO+OH<=>NH2+CO2  3.300E+06  1.500  3600.00
HCNO+M<=>NH+CO+M  1.180E+16  .000  84720.00
H2/2.00/  H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
Appendix B

Here is reported the Matlab script of the numerical model developed to predict the mass-fraction profiles of main chemical species inside the anode channel of a ring-type planar SOFC.

```matlab
clear all;
close all;
clc;

% Parameters;

p = oneatm; % pressure
t = 1073.0; % temperature [K]
Faraday = 96485000;

transport = 'Mix';
gas = importPhase ('nickelmod.cti', 'gas');
Wi = molecularWeights(gas)'; % kg/kmol
conc0 = p/(gasconstant* t_amb); % concentration (kmol/mˆ3)

current_d density = 0; % [A/mˆ2]

CH4_flow = 0.02355; % [l/min]
CO_flow = 0.214;
CO2_flow = 0.339;
O2_flow = 0.0;
H2_flow = 0.238;
Ar_flow = 0;
N2_flow = 0.221;
H2O_flow = 0.02;

% Geometry

R_max = 0.04; % [m]
anode_height = 0.00052; % [m]
channel_height = 0.0005; % [m]
area_inlet = pi * 0.005ˆ2; % [mˆ2]
axial_subdivision = 6; % points
```
Appendix B (continued)

radial_subdivision = 10; % cells
molar_flow = zeros(1,max(size(names))); % kmol/s
molar_flow(12) = CH4 flow/60/1000*conc0; % kmol/s
molar_flow(13) = CO flow/60/1000*conc0;
molar_flow(14) = CO2 flow/60/1000*conc0;
molar_flow(1) = H2 flow/60/1000*conc0;
molar_flow(4) = O2 flow/60/1000*conc0;
molar_flow(17) = Ar flow/60/1000*conc0;
molar_flow(16) = N2 flow/60/1000*conc0;
molar_flow(6) = H2O flow/60/1000*conc0;

total_flow = sum(molar_flow); % kmol/s
X0 = molar_flow/total_flow; % mole fractions
W0 = sum(X0.*Wi);
total_mass_flow = total_flow*W0; % kg/s

comp = ";

results = zeros(max(size(names)),radial_subdivision+1);
results(:,1) = X0';

for m=1:max(size(names))
    comp = [comp cell2mat(names(m)) ': num2str(X0(m)) ', '];
end

comp = comp(1:end-2);

initial_grid = linspace(0,channel_height,axial_subdivision); % [m]
radial_grid = linspace(0,R_max,radial_subdivision+1); % [m]
A = pi*(radial_grid(2:end).^2-radial_grid(1:end-1).^2); %[reacting surface area]
A_inlet = 2*pi*radial_grid(1:end-1)*channel_height;
A_inlet(1) = area_inlet;

tol_ss = [1.0e-5 1.0e-9]; % [rtol atol] for steady-state problem
tol_ts = [1.0e-3 1.0e-9]; % [rtol atol] for time stepping
loglevel = 2; %[amount of diagnostic output]
printfigures = 1; % 1 to enable printing, 0 to disable
refine_grid = 1; % 1 to enable refinement, 0 to disable

molar_flow 0 = molar_flow;
Appendix B (continued)

```matlab
wdot_current = zeros(1,max(size(names)));

for j=1:radial_subdivision
    current_induced_mass_flow = sum(wdot_current.*Wi);
    total_mass_flow = total_mass_flow + current_induced_mass_flow;
    mdot = total_mass_flow/A_inlet(j);

    % This object will be used to evaluate all thermodynamic, kinetic, and transport properties
    set(gas,'T',t,'P',p,'X',comp);

    % This object will be used to evaluate all surface chemical production
    % rates. It will be created from the interface definition 'Ni_surf'
    % in input file 'nickelmod.cti,' which implements the reaction
    % mechanism of Deutschmann et al., 1995 for catalytic combustion on nickel.
    surf1 = importInterface('nickelmod.cti','Ni_surf', gas);
    setTemperature(surf1, t);

    advanceCoverages(surf1, 1.0);

    % The flow object is responsible for evaluating the 1D governing
    % equations for the flow. We will initialize it with the gas
    % object, and assign it the name 'flow'
    f = AxisymmetricFlow(gas,'flow');
    set(f, 'P', p, 'grid', initial_grid, 'tol', tol_ss, 'tol-time', tol_ts);

    % This object provides the inlet boundary conditions for
    % the flow equations.
    inlt = Inlet('inlet');
    set(inlt, 'T', t, 'MassFlux', mdot, 'X', comp);
```
create the surface

This object provides the surface boundary conditions for the flow equations. By supplying object surface_phase as an argument, the coverage equations for its surface species will be added to the equation set, and used to compute the surface production rates of the gas-phase species.

```
surf = Surface('surface', surf1);
setTemperature(surf, t);
```

create the stack

Once the component parts have been created, they can be assembled to create the 1D simulation.

```
sim1D = Stack([inlt, f, surf]);
```

set the initial profiles.

```
setProfile(sim1D, 2, {'u', 'T', 'V'}, [0.0 1.0 % z/zmax
  0.06 0.0 % u
  t t % T
  0.0 0.0]);
```

for k = 1:nSpecies(gas)

```
y = massFraction(inlt, k);
setProfile(sim1D, 2, namesk, [0 1; y y]);
```
end

start with the energy equation on

```
enableEnergy(f);
```

disable the surface coverage equations, and turn off all gas and surface chemistry

```
setCoverageEqs(surf, 'off');
setMultiplier(surf1, 0.0);
setMultiplier(gas, 0.0);
```

solve the problem, refining the grid if needed

```
solve(sim1D, loglevel, refine_grid);
```

set more stringent grid refinement criteria

```
setRefineCriteria(sim1D, 2, 100.0, 0.15, 0.2);
```

now turn on the surface coverage equations, and turn the chemistry on slowly
setCoverageEqs(surf, ’on’);

for iter=1:6
    mult = 1.0ˆ(iter - 6);
    setMultiplier(surf1, mult);
    setMultiplier(gas, mult);
    solve(sim1D, loglevel, refine_grid);
end

if printfigures == 1
    figure(j)
    clf;
    subplot(3,3,1);
    plotSolution(sim1D, ’flow’, ’T’);
    title(’Temperature [K]’);
    subplot(3,3,2);
    plotSolution(sim1D, ’flow’, ’u’);
    title(’Axial Velocity [m/s]’);
    subplot(3,3,3);
    plotSolution(sim1D, ’flow’, ’CH4’);
    title(’CH4 Mass Fraction’);
    subplot(3,3,4);
    plotSolution(sim1D, ’flow’, ’CO’);
    title(’CO Mass Fraction’);
    subplot(3,3,5);
    plotSolution(sim1D, ’flow’, ’CO2’);
    title(’CO2 Mass Fraction’);
    subplot(3,3,6);
    plotSolution(sim1D, ’flow’, ’H2O’);
    title(’H2O Mass Fraction’);
    subplot(3,3,7);
    plotSolution(sim1D, ’flow’, ’H2’);
    title(’H2 Mass Fraction’);
    subplot(3,3,8);
    plotSolution(sim1D, ’flow’, ’V’);
    title(’Radial Velocity [1/s]’);
end

% Rates computation

wdot_surf = netProdRates(surf1);  % [kmol/m^2-s]
wdot_surf = wdot_surf(1:max(size(names)));
Appendix B (continued)

\[
\begin{align*}
\text{wdot}_\text{surf} &= \text{wdot}_\text{surf}' \cdot A(j); \quad \% \text{ [kmol/s]} \\
\text{wdot}_\text{current}(1) &= -\text{current}_\text{density}/(2 \cdot \text{Faraday}) \cdot A(j); \quad \% \text{ [kmol/s]} \\
\text{wdot}_\text{current}(6) &= \text{current}_\text{density}/(2 \cdot \text{Faraday}) \cdot A(j); \quad \% \text{ [kmol/s]} \\
\text{molar}_\text{flow} &= \text{molar}_\text{flow} + \text{wdot}_\text{surf} + \text{wdot}_\text{current}; \quad \% \text{ [kmol/s]}
\end{align*}
\]

\[
\text{for } m=1:\text{max(size(names))}
\]
\[
\quad \text{if molar}_\text{flow}(m) \neq 0;
\quad \text{molar}_\text{flow}(m) = 0;
\quad \text{end}
\]
\[
\text{end}
\]

\[
\text{total}_\text{flow} = \text{sum(molar}_\text{flow});
\]

\[
\text{X} = \text{molar}_\text{flow}/\text{total}_\text{flow}; \quad \% \text{final composition of the cell}
\]

\[
\text{W} = \text{sum(X} \cdot \text{Wi});
\]

\[
\text{total}_\text{mass}_\text{flow} = \text{total}_\text{flow} \cdot \text{W};
\]

\[
\text{results(:,j+1)} = \text{X}; \quad \% \text{mole fraction profiles}
\]

\[
\text{comp} = ' '; \\
\text{for } m=1:\text{max(size(names))}
\]
\[
\quad \text{comp} = [\text{comp} \text{cell2mat(names(m))} ': ' \text{num2str(X(m))} ', '];
\quad \text{end}
\]

\[
\text{comp} = \text{comp(1:end-2)};
\]
\[
\text{end}
\]


5. IEA: Bioenergy and biomass supply. 2007.


CITED LITERATURE (continued)


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B.Sc., Mechanical Engineering, Politecnico di Torino, Italy, 2011  
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