Catalytic Plate Reactors
for Exothermic-Endothermic Reaction Coupling

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A thesis submitted for the degree of Doctor of Philosophy
of the University of London
To my beloved parents
“It is the fight alone that pleases us, not the victory”

Blaise Pascal
Abstract

Current technologies in chemical engineering focus on process intensification in order to remain cost efficient in an environmentally responsible manner. Catalytic Plate Reactors (CPRs) emerge as a novel design for intensification of conventional chemical reactors. Such a design consists of catalytically coated metal plates so that exothermic and endothermic reactions can take place in alternate channels, which have the channel height of order of millimetres and the catalyst thickness of order of micrometers. CPRs combine reaction with heat transfer in an intensified manner, representing a feasible alternative to conventional reactors. The reduced dimensions of the reacting channels minimise heat and mass transfer resistances leading to significant volume and catalyst amount reduction in comparison to conventional reactors. Suitable applications for CPRs include autothermal coupling by means of indirect heat transfer of strong endothermic processes such as hydrocarbon steam reforming, dehydrogenation, or catalytic cracking with an exothermic process, usually catalytic combustion. Despite their attractiveness CPRs have not been yet implemented in practice, and only a few experimental and theoretical studies exist. Although CPRs show important advantages compared to conventional reactors, in order to become a viable alternative it is necessary to demonstrate their feasibility and reliability.

This work is an initiation in the study of CPRs. Its main objective is oriented towards formulation of accurate mathematical models utilised further to investigate such reactors for illustrative case studies. Different reaction systems are considered and explored using parametric studies. The study of the system ethane-dehydrogenation – methane combustion revealed that the ratio of catalyst loading for the two reactions is a key variable and must be carefully adjusted in order to avoid severe hot or cold spots that can lead to either reactor run-away or extinction. A metallic wall with a thickness of 2 mm, due to its high thermal conductivity, makes possible an efficient heat transfer between the endothermic and exothermic channel for small temperature differences. Among all potential applications for CPR, small-scale hydrogen production is favoured due to an increasing demand of hydrogen for fuel cells. Thus, hydrogen production in a CPR from steam-reforming of methane coupled with methane catalytic combustion was investigated. It was shown that a reduction in the reformer volume by a factor of 150 and reduction for the necessary amount of catalyst by a factor of 85 could be achieved. The effectiveness factors for the chemical reactions of the reforming process are about one order of magnitude higher than in the conventional process, proving a significant reduction of intraphase resistances. The short distance between the heat source and heat sink increases the efficiency of heat transfer. The influence of channel height and catalyst thickness on reactor behaviour was also addressed. It was shown that the
intraphase resistances are important and cannot be neglected. In addition, the size of channel height has to be correlated with care with the flowrates and the amount of catalyst necessary to achieve desired CPR performance. A comparison between operation in co-current and counter-current showed that overall, the heat generation and consumption is balanced better for co-current operation than for counter-current one. Although, the counter-current flow arrangement may provide better thermal efficiency, due to opposite reactant concentration depletion along the reactor local heat balance proves difficult to achieve. Successful counter-current operation needs to use a non-uniform catalyst distribution as a degree of flexibility in adjusting the rate of heat generated and consumed.

Another objective of this thesis is to find criteria to identify suitable ranges for CPR design parameters and to evaluate if the reactor has a reliable and stable operation. Parametric sensitivity analysis was utilised to define such criteria and to identify the most important parameters that can affect CPR behaviour. Among the parameters studied the strongest influence comes from the activation energies followed by the inlet temperature. Sensitivity to inlet composition and velocities have moderate effect, while the lowest sensitivity was found with respect to geometrical parameters and wall thermal conductivity.

A generic procedure for CPRs design is summarised based on the understanding gained during the present work. The procedure includes preliminary, detailed and optimal design steps which are shortly described and discussed.

It was also aimed to use mathematical modelling in order to aid experimental work concerned with the study of catalytic combustion in small channels. Simulation of a 2 mm-diameter reacting channel having the catalyst coated on the walls, demonstrated that immersing the channel in a fluidised bed can keep the channel wall in almost isothermal conditions. It was also shown that the axial velocity profile does not affect the model accuracy. In addition, CFD simulations showed that an expansion-contraction geometry for the channel inlet eliminates recirculation patterns and minimises the experimental errors due to entrance effects.
Acknowledgements

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\[
\left( \tau_w \propto \frac{\delta_{\text{cat}} \cdot L}{u_z^0 \cdot R} \right),
\]

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**Greek Symbols**

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</tr>
<tr>
<td>( \beta )</td>
<td>thermal diffusivity</td>
<td>m^2/s</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>dimensionless difference in activation energy, as defined by equation 5.2-10</td>
<td>-</td>
</tr>
<tr>
<td>( \Delta H )</td>
<td>heat of reaction</td>
<td>J/mol</td>
</tr>
<tr>
<td>( \delta )</td>
<td>thickness</td>
<td>m</td>
</tr>
<tr>
<td>( \delta_{\text{acc}} )</td>
<td>acceptable relative deviation for the input parameter, ( \Phi_j )</td>
<td></td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>dimensionless coefficient as defined in Table 5.3.2</td>
<td>-</td>
</tr>
<tr>
<td>( \epsilon )</td>
<td>emisivity</td>
<td>-</td>
</tr>
<tr>
<td>( \zeta )</td>
<td>dimensionless axial co-ordinate</td>
<td>-</td>
</tr>
<tr>
<td>( \eta )</td>
<td>effectiveness factor</td>
<td>-</td>
</tr>
<tr>
<td>( \eta_{\text{thermal}} )</td>
<td>thermal efficiency as defined by equation 4.3-10</td>
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<tr>
<td>( \theta )</td>
<td>dimensionless temperature</td>
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</tr>
<tr>
<td>( \lambda )</td>
<td>solid thermal conductivity</td>
<td>W / (m K)</td>
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<tr>
<td>( \delta_{\text{eff}} )</td>
<td>dimensionless coefficient as defined in Table 5.3.2</td>
<td>-</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
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<tr>
<td>--------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>$\lambda_{\text{eff}}$</td>
<td>catalyst effective thermal conductivity</td>
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<td>$\nu$</td>
<td>stoichiometric coefficient</td>
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<tr>
<td>$\xi$</td>
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</tr>
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<td>$\sigma$</td>
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<td>-</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Stefan-Boltzman constant</td>
<td>W(m$^2$ K$^4$)</td>
</tr>
<tr>
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<td>momentum flux</td>
<td>N/m$^2$</td>
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<td>diffusion time, see equation 4.3-13</td>
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</tr>
<tr>
<td>$\tau_w$</td>
<td>space time, see equation 4.3-16</td>
<td>s</td>
</tr>
<tr>
<td>$\tau_{\text{w}}$</td>
<td>catalyst residence time, see equation 4.3-11</td>
<td>s</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>input parameter</td>
<td>-</td>
</tr>
<tr>
<td>$\omega$</td>
<td>mass fraction</td>
<td>-</td>
</tr>
</tbody>
</table>

**Superscript**
- 0 channel inlet
- g gas phase
- cat catalyst layer

**Subscript**
- ex external
- i chemical specie in a reacting mixture
- in internal
- j reaction mixture for
  - 1-endothermic channel
  - 2-exothermic channel
- k chemical reaction
- s solid wall
1.1 Catalytic Plate Reactor (CPR) a Novel Reactor Design

The current trends in chemical engineering increase the pressures to remain cost competitive in an environmentally responsible manner, leading to an increased interest in Process Intensification (PI). PI is a design philosophy aiming for energy, capital, environmental and safety benefits through radical reductions in equipment and plant size, at the same time integrating multiple functions such as mass, heat and momentum transport, and chemical reaction in the same equipment (Green 1998). Within the frame of this tendency, Catalytic Plate Reactors (CPRs) emerge as a novel design for intensification of the conventional chemical reactors. Such a design consists of catalytically coated metal plates so that exothermic and endothermic reactions can take place in alternate channels, which have the channel height of order of millimetres and the catalyst thickness of order of micrometers. The advantages of CPR design over the conventional reactors comes from the fact that CPR shorts-circuits heat and mass transfer resistances between the reaction site and the bulk of the fluid, leading to a significant size reduction and high reactor efficiency (Reay 1993). Suitable applications for CPRs include autothermal coupling by means of indirect heat transfer of strong endothermic processes such as hydrocarbon steam reforming, dehydrogenation, or catalytic cracking with an exothermic process, usually catalytic combustion. The replacement of the homogeneous combustion used in conventional reactors by the catalytic one brings additional benefits. Because catalytic combustion proceeds at lower
temperature than conventional one, it poses fewer constraints for materials of construction, and produces lower emissions of nitrogen oxides (Hayes and Kolaczkowski 1997). Since it is a flameless process, long radiation paths needed in conventional furnaces are replaced by channel dimensions of one or two mm in the plate matrices, with an obvious impact on reactor size. Among all potential applications for CPR, small-scale hydrogen production is favoured due to an increasing demand of hydrogen for fuel cells. A small reactor enables the placement of the hydrogen generation unit near the point of use. Methane is a convenient feedstock because the existing natural gas pipeline infrastructure makes it readily available and accessible at any point along the distribution chain. Availability of highly compact hydrogen generators will make possible electrical power generation by fuel cells at central stations, substations, or residences. Hydrogen offers a potentially non-polluting inexhaustible, efficient and cost attractive fuel for energy demand. It is forecast to become a major source of energy in the future (Armor 1999).

The central idea for CPR is autothermal coupling of exothermic and endothermic processes by means of indirect heat transfer. Despite its attractiveness the autothermal coupling of chemical reactions with opposite heat effect within a heat exchanger equipment type have not been yet implemented in practice. However, the concept can be found in a few patents (Hunter and McGuire 1980; Kaminsky et al. 1997; Mulvaney and Dandekar 2000). From the experimental point of view only steam reforming of methane coupled with methane catalytic combustion has been investigated recently (Polman et al. 1999; Frauhammer et al. 1999, Ismagilov et al. 2001). As for theoretical point of view the availability of studies related to the autothermal coupling of exothermic and endothermic reactions in small channels is even more scarce. Although, a CPR has similarities with the concept of catalytic wall reactor, which attracted
attention since early '50s especially due to higher controllability of the temperature for
highly exothermic reactions (Baron et al. 1952; Katz 1959, Smith and Carberry 1974;
Huang and Varma 1980; Goyal et al. 1988), most of the mathematical models available
in the literature related to catalytic wall reactor refer to exothermic reactions operating
adiabatically or with external cooling. Only Frauhammer et al. (1999) and later Kolios
et al. (2001) addressed theoretically coupling of exothermic-endothermic reactions by
means of indirect heat transfer, using simplified models.

Although CPRs show important advantages compared to the conventional reactors, in
order to become a viable alternative it is necessary to demonstrate their feasibility and
reliability. Thus, a detailed theoretical study for fully understanding of how a CPR
operates, what are the key issues that influence its performance and thermal behaviour is
necessary to open the investigation routes of this new concept. It becomes clear that a
size reduction of two orders of magnitude (Charlesworth et al. 1995), elimination of
additional heat transfer equipment by local heat generation are high desirable objectives.
But at the same time to achieve them may prove a serious challenge one need to
overcome the conventional design mentality and to gain sufficient trust for their
practical implementation. The importance of the present work lies on the novelty of the
CPR concept and oriented towards an initial elucidation of such concept aiming to
provide theoretical approaches and tools that can be used to generate a general guidance
for CPR design.
1.2 Thesis Objectives

This work attempts to be an initiation in the study of Catalytic Plate Reactors (CPRs). Its main objective is oriented towards formulation of mathematical models utilised further to investigate such reactors for illustrative case studies. Different reaction systems such as ethane dehydrogenation-methane catalytic combustion, and steam reforming of methane- methane catalytic combustion are considered and explored using parametric studies. Moreover it is aimed to find criteria to identify suitable ranges for CPR design parameters and to evaluate if the reactor has a reliable and stable operation. The understanding gained during the present work is summarised in a generic procedure for CPRs design.

In order to achieve these objectives, comprehensive two-dimensional models with different degree of complexity are proposed and solved using general PROcess Modelling System (gPROMS) simulation package (Oh and Pandelides 1995). For the cases considered parametric studies related to catalyst loading and thickness, flowrates, wall thickness and thermal conductivity, channel gap are developed in order to explore the reactor performance and thermal behaviour. Parametric Sensitivity Analysis is applied to investigate CPRs leading to criteria that evaluate their stability and identify suitable design parameter ranges.

The design of a CPR is a more complex task than the design of conventional reactors because it needs to be based on the accurate understanding not only of the two exothermic and endothermic process considered, but also of the conditions that allow their autothermal coupling with beneficial results. General design guidance is necessary in order to establish a procedure that helps in surmounting this challenge. Eventually, the present thesis attempts to suggest, based on the knowledge gained during this work,
Introduction

a design procedure with general validity recommended as a starting point for CPR design.

1.3 Thesis Structure

In Chapter 1, the novel concept of Catalytic Plate Reactor is introduced, together with its advantages compared to the conventional reactors and potential applications. The need for theoretical investigation of CPR is also outlined and justified. The objectives of the present work are thereafter given. Chapter 2 is a broad literature survey related to autothermal coupling of endothermic and exothermic reactions; catalytic combustion of methane; steam reforming of methane; light alkane dehydrogenation; modelling of wall reactors; and parametric sensitivity analysis. In Chapter 3, a two dimensional model without intraphase resistances is developed, and used to study ethane dehydrogenation coupled with methane combustion. After solving the mathematical model, the reactor thermal behaviour and performance are examined. Model simulations are used to determine the impact of variation of the catalyst loading in both channels on the CPR thermal behaviour. Further the influence of inlet flowrate, and wall thickness and thermal conductivity is examined. In Chapter 4, the previous model is refined by including the catalyst layer for both endothermic and exothermic processes. This is used to study methane steam reforming coupled with methane catalytic combustion. Two different kinetic sets for steam reforming are employed to generate case studies. A comparison with an industrial steam reformer in terms of reactor size and performance is discussed. Further, the influence of several design parameters such as catalyst thickness and channel gap is explored. Chapter 5 uses Parametric Sensitivity Analysis (PSA) to evaluate the CPR sensitivity behaviour. The reactor sensitivity with respect to kinetic parameters (pre-exponential factors and activation energy); geometrical parameters (channel gap and wall thickness); inlet conditions (temperature and
composition) for both endothermic and exothermic process is determined considering a one-dimensional and a two-dimensional approach. Parametric sensitivity criteria are defined in order to evaluate the reactor stability and reliability. Chapter 6 addresses the influence of flow arrangement for steam reforming of methane coupled with methane catalytic combustion in a CPR. A comparison between co-current and counter current flow arrangement is developed in order to determine the advantages and disadvantages of these flow arrangements. In addition, the option for a non-uniform catalyst distribution in combustion channel is explored to improve the thermal behaviour for counter-current flow. It must be noted that the present work is part of a joint project in collaboration with the Department of Chemical Engineering from the University of Newcastle, where catalytic combustion was studied experimentally. Chapter 7 provides a two dimensional model to study the catalytic combustion of methane in small channels with two different options for the external heat transfer needed to maintain an isothermal temperature profile along the channel. This modelling approach is used to make quick checks and evaluations of catalytic combustion in small channels in order to aid the experimental study. Finally, chapter 8 outlines the conclusions and suggestions for future work. The understanding gained during this work are summarised in a general guidance for CPR design.
CHAPTER 2

LITERATURE SURVEY

2.1 Introduction

The concept of *Catalytic Plate Reactor (CPR)* emerges recently as a consequence of process intensification tendency in chemical engineering. It can be categorised as an innovative multifunctional reactor that uses an exothermic chemical process to intensify an endothermic one by their autothermal coupling within an equipment designed similarly to a plate heat exchanger. Since the present work aims to open a theoretical investigation of such a reactor, this chapter intends to address an inclusive literature review that defines the general frame along with the main related topics that characterise it.

First, the concepts of *Process Intensification* and *Multifunctional Reactor* are highlighted and defined in order to identify the CPR contribution within such concepts.

Further, applications for coupling of chemical processes with opposite heat effects in order to meet the strong heat demand of an endothermic process are discussed and classified. Two categories of autothermal coupling are hereby defined as *direct* and *indirect* coupling, according to the spatial location of the exothermic and the endothermic process. *Direct Coupling* considers that both processes occur in the same reaction space, while during the *Indirect Coupling*, the reaction spaces are separated and the autothermal coupling occurs only by mean of indirect heat transfer.
The chapter proceeds further with a review of the catalytic combustion of methane, a typical suitable exothermic process that can be used within a CPR. In this section the advantages and the disadvantages of the catalytic versus homogeneous combustion are discussed, applications of catalytic combustion are shortly enumerated. Typical catalysts and kinetics for methane combustion published in the literature are then revised.

As potential candidates for suitable endothermic processes for CPR, steam reforming of methane and the dehydrogenation of light alkanes is also addressed by means of a short description of the conventional processes, and of the relevant catalysts and kinetics utilised.

Since CPR can be regarded as falling into the category of Catalytic Wall Reactors (CWR), the next section of the chapter focus on modelling of such reactors. A comparison with the conventional fixed bed reactors followed by a description of CWR applications introduces the concept. The general form of the governing equations are reviewed in order to emphasis the main reaction and transport phenomena characteristic to CWR. Several models with different level of complexity are discussed and compared.

Finally, the concept of Parametric Sensitivity Analysis is introduced with its applications especially for chemical reactors. Sensitivity concepts and their computation are also presented in their general form.
2.2 Process Intensification and Multifunctional Reactors

Since the topic of this thesis falls within the generic areas of *Process Intensification* and *Multifunctional Reactors*, a brief introduction of these concepts is given below. Process Intensification (PI), known also as the strategy of miniaturising process plants, is a novel design approach which can reduce equipment size by several orders of magnitude leading to substantial savings in capital cost, improvement of intrinsic safety and reducing environment impact. PI analysis of a process tries to establish where efficiency can be increased and then to find ways to achieve it (Green, 1998). Akay et al. (1997) suggests that intensification can be achieved by minimising parasitic factors such as concentration, temperature and pressure differences, and energy dissipation through viscous heating. Accordingly, PI techniques include high pressure operation to increase mass transfer and reaction rates; utilisation of fluid dynamic environments within the reactor so that its performance is dictated by intrinsic chemical kinetics rather than by heat or mass transfer (this can be achieved for example by exploiting the short diffusion and conduction path lengths associated with small channels); operation in the presence of intensified force fields (ultrasonic, electrostatic, magnetic, centrifugal etc.) which can provide opportunities for larger transfer coefficients.

Green (1998) describes several examples of equipment where PI is involved, such as compact heat exchangers, rotating packed beds, spinning disk reactors etc. Compact heat exchangers have higher surface area per unit volume in comparison with conventional heat exchangers. Rotating packed beds for gas-liquid or liquid-liquid systems ("higee" contactor) find applications ranging from calcium carbonate precipitation to deaeration of water for injection into oil wells. Spinning disk reactors take advantage of large mass and heat transfer coefficients obtained by the formation of thin and unstable liquid films and are employed in polymerisation reactions. Another
way to intensify a process is use of high intensity in-line mixing devices (static mixers, ejectors, rotor-stator mixers and tee mixers), which can give mixing rates up to 1000 times higher than traditional stirred tanks.

The concept of multifunctional reactors, understood as a reaction equipment in which one or more additional process functions such as mass, heat and momentum transport operation, or independent reactions are integrated (Westerterp 1992, Agar 1999), represents an option for process intensification. Coupling of the strong endothermic reactions with intensive heat exchange is well known for large scale processes such as hydrocarbon cracking, steam reforming, dehydrogenation. However, the heat and mass transfer limits such conventional processes (Farrauto and Bartholomew 1997). A new reactor design known as Catalytic Plate Reactor (CPR) emerges as a novel alternative to conventional processes. It consists of closely spaced catalytically coated plates so that endothermic and exothermic reactions take place in alternate channels (Reay 1993, Charlesworth 1995, Frauhammer et al. 1999, Zanfir and Gavriilidis 2001). The reduced size of the channel gap and catalyst layer leads to enhanced performances of this type of reactor compared to the conventional ones.

2.3 Autothermal Coupling of Endothermic and Exothermic Reactions

Agar (1999) shows that the heat demand of a strongly endothermic reaction at high temperatures can be met by three alternatives namely: recuperative heat exchange, regenerative heat exchange and use of an exothermic coupled reaction to supply the necessary heat. The recuperative heat exchange one consists of spatial segregation between the reaction system and the heating medium. It has the advantage that permits accurate temperature regulation and entails no product contamination by the heating medium. But, it has the disadvantage of temperature limitation due to material
properties, pressure differences and corrosive action. Most of the chemical processes use the recuperative heat exchange to supply or to remove heat (pre-heating the feed using the products is common for the autothermal operation for exothermic reactions such as sulphur dioxide oxidation, or ammonia synthesis, Farrauto and Bartholomew 1997). In the regenerative heat exchange the reaction system and the heating medium are chronologically segregated from one to another by means of heat storage in a fixed bed. This type of arrangement has applications for catalytic combustion of volatile organic compounds (Westerterp 1992). In their review about the autothermal fixed-bed reactor, Kolios et al. (2000) classified the modalities of coupling of endothermic and exothermic reactions for an autothermal operation as: simultaneous, asymmetric and symmetric operation. In the simultaneous operation the reactants for both endothermic and exothermic reactions are mixed and all reactions run more or less in parallel, subject to a direct heat transfer within the reacting mixture. While, under asymmetric and symmetric operation the reactions are separated in time or in space and they differ by the manner the flow arrangement is design. Under asymmetric conditions the heat generation and heat consumption takes place alternatively. The feed for the endothermic reaction always comes from one side (in the regenerative model during one portion of the whole period) and the feed for the exothermic reaction comes from the opposite side (during the rest of the period). Under the symmetric conditions the feed for the endothermic reaction comes from both sides while the necessary heat of reaction from the exothermic reaction is supplied directly or indirectly in the middle of the reactor.

Hereby a classification as direct and indirect autothermal coupling is proposed according to if the endothermic and exothermic process share the same reaction space or not. Within the first one both processes occur in the same reaction space and the overall autothermicity is ensured by either direct or regenerative heat exchange, while for the
second the processes are spatially separated. In the latter case the system autothermicity is a result of an indirect heat transfer across the wall that separates the exothermic from the endothermic reaction space. Table 2.1 summarises this classification.

2.3.1. Direct Autothermal Coupling

Direct autothermal coupling of endothermic and exothermic reaction has been applied a long time ago in industrial processes, such as secondary steam reforming within ammonia synthesis process (Ridler and Twigg 1989) or hydrogen cyanide synthesis (Agar 1999), where hydrogen combustion is used to produce in-situ heat for the endothermic reactions.

Blanks et al. (1990) present a reactor for production of synthesis gas from catalytic partial oxidation of natural gas. The reactions that take place in the reacting stream are methane combustion, combined steam and CO\textsubscript{2} reforming, and water gas shift reaction. The reactor consists of three different packed beds, stacked vertically on top of each other. The middle bed is the reaction zone containing a commercial nickel reforming catalyst, while the zones above and below are heat exchange zones and contain inert packing. The reactor operates in unsteady state mode and the flow directions of the feed (natural gas and air) and product (synthesis gas) is reversed periodically, so that the waste heat is efficiently recovered. It was possible to reach a pseudo-state where the overall average bed temperature remained constant and the upper and the lower bed temperature profiles mirror each other as the gas flow direction reverses. In order to avoid hot spots in the catalyst bed, better control can be achieved by pre-burning part of the feed in air to form CO\textsubscript{2} and H\textsubscript{2}O to moderate the heat generated in the reactor.
Kulkarni and Dudukovic (1997, 1998) have discussed coupling of solid catalysed endothermic reaction with an exothermic reaction in a bi-directional fixed bed reactor operated in periodic steady state. The exothermic reaction, usually methane combustion, takes place in the bed during an exothermic semicycle when a mixture of fuel and air is fed into the hot bed. The heat generated is then utilised to drive the endothermic reaction, which occurs during the next endothermic semicycle, the reactants being fed into the bed from the other end of the reactor. For a successful operation of the reactor, two conditions need to be satisfied. The heat liberated during the exothermic semicycle should be equal to or greater than the energy consumed during the endothermic semicycle, and the product of the front velocity and the semicycle period for the endothermic semicycle must be equal to or greater than that for the exothermic semicycle. The energy efficiency and conversion increase with increasing bed length and decreasing semicycle periods.

Recent studies are dedicated to in-situ hydrogen combustion during dehydrogenation reactions. Kolios and Eigenberger (1999) present two alternative operation modes for styrene production. Thus, in asymmetric operation mode, the feed changes with each semicycle between an ethylbenzene/steam and hydrogen/air mixture. While in the symmetric operation model the feed is the same in both semicycles and the necessary heat is supplied from a catalytic burner installed in the centre of the reactor. The discontinuous heat supply in the asymmetric operation mode causes strong periodic fluctuations in conversion and a poor efficiency of heat recovery. The symmetric operation mode allows for a high conversion, high styrene selectivity and high efficiency of heat recovery.
Choudhary et al. (2000) studied experimentally the coupling of the exothermic catalytic oxidative combustion and endothermic thermal cracking reactions of propane to propylene and ethylene in the temperature range of 750 – 850 °C. They show that the process can be guided in an efficient manner requiring no external energy and without coke formation. The exothermicity can be controlled by manipulating the temperature and concentration of O$_2$ related to propane in the feed which also strongly influence the propylene/ethylene product ratio.

A major interest existing currently is the production of hydrogen or synthesis gas from steam reforming of methane coupled with an exothermic reaction, usually methane combustion, due to increasing demand for hydrogen ranging from hydrogen plants for refineries to small units providing hydrogen for fuel cells (Rostrup-Nielsen 2000). De Groote and Froment (1996) modelled and simulated the catalytic partial oxidation of methane to synthesis gas on Ni base catalyst in an adiabatic fixed-bed reactor. Depending on the degree of reduction of Ni catalyst, reforming can be either consecutive to the total combustion or it can run in parallel. A temperature peak is observed for consecutive operation, which can be moderated if steam or carbon dioxide is added to the feed, leading also to carbon deposition reduction. High selectivities for CO (90 %) and H$_2$ (95 %) can be obtained if the same system is operated in reverse flow mode (De Groote et al. 1996), while coke formation is moderate.

Wolf et al. (1997) theoretically investigated, for atmospheric and elevated pressures, the partial oxidation of methane to synthesis gas over a highly active platinum catalyst. High hot-spot temperature at the catalyst surface together with large temperature gradients between the gas and catalyst surface were calculated, while the heat
conductivity of the catalytic material proved to be an important factor for the temperature control.

Ma and Trim (1996) studied experimentally the autothermal conversion of methane to hydrogen as a function of an oxidation and a steam reforming catalyst configuration. Preheating the catalyst bed at ca. 590 K initiates the methane oxidation over a platinum catalyst, the heat and steam produced facilitate further steam reforming over a nickel catalyst. A two-bed system was found to be inferior in performance to one bed containing two mixed catalysts located on the same support. The theoretical investigation of Avci et al. (2001) also confirmed these results. In addition, intraparticle diffusion limitations are found to be significant.

Gosiewski (2001) investigated the carbon deposition for several reactor types for partial oxidation of methane, finding that for the reversal-flow reactors the accumulation of the heat wave results in higher hot spots, and consequently higher carbon deposition, compared to reactors without flow reversal.

Vesser and Frauhammer (2000) investigated the oxidation of methane to synthesis gas over platinum in a monolith reactor. They found that a limited supply of oxygen is favourable to high hydrogen selectivity and that the importance of very high reaction temperature requires good heat integration for the reactor. Three solutions are suggested for an improved process: internal heat exchange between the hot reaction products and the cold reactor feed gases through a counter-current heat exchange reactor, a distributed oxygen feed along the reactor axis using a membrane shell around the catalyst bed, or a reverse-flow reactor where the gases are fed periodically from opposite ends to the catalytic bed. Simulation and experimental studies (Vesser et al.
2000), proving that high reaction temperature and selectivities can be reached have demonstrated the effectiveness of the first alternative. As for a membrane reactor configuration with distributed oxygen feed, this can avoid the high oxygen concentration in the reactor entrance, but no effective increase in reaction selectivity was reported.

2.3.2. Indirect Autothermal Coupling

Coupling of exothermic and endothermic reactions by means of indirect heat transfer is an alternative for the intensification of the conventional chemical reactors. Reay (1993) explained the benefits of such approach in the context of the Catalytic Plate Reactor (CPR) which is comprised of closely spaced catalytically coated metal plates. The CPR effectively short-circuits heat and mass transfer resistances between the reaction site and heating medium. When the process reaction is endothermic, the heat needed to drive the reaction could in principle be provided not only using a heating fluid but also by catalytic combustion on the other plate surface. The intimate linking of the catalytic combustion heat source with the endothermic reaction process reduces significantly the overall heat transfer resistance. The use of catalytic combustion to provide the heat required has additional advantages (Hayes and Kolaczkowski, 1997). It proceeds at lower temperature than homogeneous combustion, which reduces NOx formation. The operating window in terms of inlet fuel concentration is expanded. Lower operating temperature poses fewer constraints for materials of construction. Since it is a flameless process, long radiation paths needed in conventional furnaces are replaced by channel dimensions of one or two mm in the plate matrices, with an obvious impact on reactor size.
Hunter and McGuire (1980) were among the first to suggest the coupling of endothermic with exothermic reaction by means of indirect heat transfer. They considered catalytic heat exchangers where catalytic combustion or other highly exothermic reaction is used as a heat source for an endothermic reaction.

Branch and Tomlinson (1995) studied theoretically the feasibility of coupling methane reforming with catalytic combustion in a CPR. They showed that catalyst deactivation can have severe consequences on the operation and stability of the reactor. Charlesworth (1995) demonstrated that such a reactor would be two orders of magnitude smaller than a conventional steam reformer.

Kaminsky et al (1997) presented a “dual-flow chemical reactor” which employed oxidative coupling of methane on catalytically coated surfaces to provide heat for thermal hydrocarbon cracking. This particular combination of reactions allows the production of useful compounds from both sides of the reactor.

Ioannides and Verykios (1997, 1998) and Piga and Verykios (2000) have studied another concept of integrating different reactions for synthesis gas production. The reactor consists of a non-porous ceramic tube with high thermal conductivity, whose surfaces are coated with metal catalyst films. A CH$_4$ / O$_2$ feed enters the tube and part of it combusts on its inner catalytic surface. Subsequently the reaction mixture comes in contact with the outside catalytic surface where reforming takes place. A large fraction of the heat generated on the inside wall by methane combustion is transported to the outside wall where the endothermic reforming reactions occur.
The feasibility of using CPR to carry out steam reforming with catalytic combustion as heat source in a co-current arrangement has been experimentally demonstrated recently by Polman et al. (1999). The conversion of combustion and reforming reactions were more than 99.98 % and 97 % respectively, while NOx levels were within the ppb range.

Coupling of steam reforming and catalytic combustion in adjacent channels has also been studied by Frauhammer et al. (1999) both experimentally and theoretically, but in counter-current configuration utilising a ceramic honeycomb monolith with specially designed reactor heads. It was found that the inlets and exits of both streams have low temperature while a high temperature zone in the middle of the reactor results to high conversion. Furthermore, it was shown that reactor performance is affected by the presence of homogeneous reactions, ratio of heat capacities of the two streams and axial catalyst distribution. The analysis of the thermal behaviour for the counter-current arrangement (Kolios et al. 2001) revealed that the raise of temperature of the exothermic reaction in the reaction zone quickly above the temperature of the endothermic reaction is necessary in order to avoid back-transfer of heat within the main reaction zone. Improvements in the reactor behaviour can be achieved utilising a suitable catalyst distribution along the reacting zone or combining the co-current arrangement for the overlapping reaction zones with counter-current arrangement for the purely heat-exchange zones.

Mulvaney and Dandekar (2000) patented recently a new process and equipment design consisting of alternate small channels with catalyst for endothermic and exothermic reactions. Different flowsheet configuration, including pre-heating arrangements with catalyst-free section for endothermic streams, are proposed to ensure a highly heat integrated process.
Ismagilov et al. (2001) developed and tested a heat exchanging tubular reactor for combining methane catalytic oxidation and methane steam reforming. The methane combustion and steam reforming catalysts were prepared on the heat-conducting metal foam support materials by application of preliminary plasma spraying of alumina. Thus, increased adhesive properties of the active layer, protection of the metal support substrates from aggressive medium, and improved durability for high temperature are achieved at the same time. Steam reforming reacting mixture fed into the reactor within temperature range of 100-300 °C reaches an exit conversion of 65 % and temperature of 1007K.
Table 2.1 Examples of coupling of exothermic-endothermic reaction systems E- experimental; T-Theoretical; P-Patent

<table>
<thead>
<tr>
<th>Authors</th>
<th>Reaction system</th>
<th>Reactor Type</th>
<th>E</th>
<th>T</th>
<th>P</th>
<th>Comments</th>
</tr>
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<td>Blanks et al.</td>
<td><strong>Exo:</strong></td>
<td>Fixed bed</td>
<td>✓</td>
<td></td>
<td></td>
<td>Operation in unsteady state mode and reverse flow</td>
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<td>(1990)</td>
<td>CH₄ + 0.5O₂ + 1.9N₂ →</td>
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<tr>
<td></td>
<td>0.75CH₄ + 0.25CO₂ + 0.5H₂O + 1.9N₂</td>
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<td></td>
<td><strong>Endo:</strong></td>
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<tr>
<td></td>
<td>0.75CH₄ + 0.5 H₂O + 0.25CO₂ + 1.9N₂ →</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO + 2H₂ + 1.9N₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>De Groote and</td>
<td><strong>Exo:</strong></td>
<td>Fixed bed</td>
<td>✓</td>
<td></td>
<td></td>
<td>Operation in steady-state using a Ni-based catalyst for both endothermic</td>
</tr>
<tr>
<td>Froment (1996)</td>
<td>CH₄ + 2O₂ → CO₂ + 2H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Endo:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>and exothermic reactions;</td>
</tr>
<tr>
<td></td>
<td>CH₄ + H₂O → CO + 3H₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₄ + 2H₂O → CO₂ + 4H₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO + H₂O → CO₂ + H₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₄ + CO₂ → 2CO + 2H₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ma and Trimm</td>
<td><strong>Exo:</strong></td>
<td>Fixed bed</td>
<td>✓</td>
<td></td>
<td></td>
<td>Operation in steady state for Pt and Ni catalyst in a two-bed configuration</td>
</tr>
<tr>
<td>(1996)</td>
<td>CH₄ + 2O₂ → CO₂ + 2H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₃OH + 1.5O₂ → CO₂ + 2H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Endo:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>and one bed with mixed catalysts.</td>
</tr>
<tr>
<td></td>
<td>CH₄ + H₂O → CO + 3H₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₃OH + H₂O → CO₂ + 3H₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO + H₂O → CO₂ + H₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Authors</td>
<td>Reaction system</td>
<td>Reactor Type</td>
<td>E</td>
<td>T</td>
<td>P</td>
<td>Comments</td>
</tr>
<tr>
<td>------------------</td>
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<td>--------------------------------------------------------------------------</td>
</tr>
</tbody>
</table>
| De Groote et al. (1997) | Exo: CH₄+2O₂ → CO₂+2H₂O  
Endo: CH₄ +H₂O →CO +3H₂  
CH₄ +2H₂O →CO₂ +4H₂  
CO+ H₂O→CO₂ +H₂  
CH₄ + CO₂ →2CO +2H₂ | Fixed bed | ✓            |   |   | Reverse flow operation                                                  |
Endo: B→D  
Generic, irreversible first order slightly based on methane combustion – steam reforming | Fixed bed | ✓            |   |   | The reactants for the exothermic and the endothermic reactions are fed alternatively at the opposite end of the reactor |
| Kulkarni and Dudukovic (1998) | Exo: CH₄+2O₂ → CO₂+2H₂O  
Endo: CH₄ +H₂O →CO +3H₂  
CO+ H₂O→CO₂ +H₂ | Fixed bed | ✓            |   |   | The reactants for the exothermic and the endothermic reactions are fed alternatively at the opposite end of the reactor |
| Kolios and Eigenberger (1999) | Exo: H₂+0.5O₂ → H₂O  
Endo: C₆H₅C₂H₅ → C₆H₅C₂H₃ +H₂  
C₆H₅C₂H₅ → C₆H₆+C₂H₄  
C₆H₅C₂H₅ → C₆H₅CH₃ +CH₄ | Fixed bed | ✓  ✓         |   |   | Asymmetric operation changes the feed each semicycle between an ethylbenzene/steam and hydrogen/air mixture; Symmetric operation mode has the same feed in both semicycles, and the necessary heat is provided from a catalytic burner in the reactor middle. |
<table>
<thead>
<tr>
<th>Authors</th>
<th>Reaction system</th>
<th>Reactor Type</th>
<th>E</th>
<th>T</th>
<th>P</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Choudhary et al. (2000)</td>
<td><strong>Exo:</strong> $\text{C}_3\text{H}_8 + \text{O}_2 \rightarrow \text{CO}, \text{CO}_2, \text{CH}_4$ and $\text{H}_2\text{O}$  &lt;br&gt;<strong>Endo:</strong> $\text{C}_3\text{H}_8 + 0.5\text{O}_2 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O}$  &lt;br&gt;$\text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_6 + \text{CH}_4$  &lt;br&gt;$\text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2$</td>
<td>Fixed bed</td>
<td>✓</td>
<td></td>
<td></td>
<td>The exothermic and endothermic reactions take place in parallel.</td>
</tr>
<tr>
<td>Vesser and Frauenhammer (2000)</td>
<td>$\text{CH}_4 + 0.5\text{O}_2 \rightarrow \text{CO} + \text{H}_2$  &lt;br&gt;(via an indirect reaction mechanism in which part of the methane is initially combusted to $\text{CO}_2$ and $\text{H}_2\text{O}$ and the remaining methane is then converted by steam/CO$_2$ reforming - see also 4)</td>
<td>Monolith</td>
<td>✓</td>
<td></td>
<td></td>
<td>Operation in unsteady-state in a monolith reactor containing Pt.</td>
</tr>
<tr>
<td>Vesser et al. (2000)</td>
<td>$\text{CH}_4 + 0.5\text{O}_2 \rightarrow \text{CO} + \text{H}_2$  &lt;br&gt;(via an indirect reaction mechanism in which part of the methane is initially combusted to $\text{CO}_2$ and $\text{H}_2\text{O}$ and the remaining methane is then converted by steam/CO$_2$ reforming - see also 4)</td>
<td>Fixed bed</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>Integrated recuperative heat exchange design</td>
</tr>
<tr>
<td>Avci et al. (2001)</td>
<td><strong>Exo:</strong> $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$  &lt;br&gt;<strong>Endo:</strong> $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$  &lt;br&gt;$\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$  &lt;br&gt;$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$</td>
<td>Fixed bed</td>
<td>✓</td>
<td></td>
<td></td>
<td>Operation in steady state for Pt and Ni catalyst in a two bed configuration and one bed with mixed catalysts.</td>
</tr>
<tr>
<td>Authors</td>
<td>Reaction system</td>
<td>Reactor Type</td>
<td>E</td>
<td>T</td>
<td>P</td>
<td>Comments</td>
</tr>
<tr>
<td>----------------------</td>
<td>----------------------------------------------------------------------------------</td>
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<td>---</td>
<td>---</td>
<td>--------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Gosiewski et al.</td>
<td>( \text{CH}_4 + 0.5\text{O}_2 \rightarrow \text{CO} + \text{H}_2 ) (via an indirect reaction mechanism in which part of the methane is initially combusted to ( \text{CO}_2 ) and ( \text{H}_2\text{O} ) and the remaining methane is then converted by steam/( \text{CO}_2 ) reforming)</td>
<td>Fixed bed Monolith</td>
<td>✓</td>
<td></td>
<td></td>
<td>Operation in reverse flow and feed composition cycling</td>
</tr>
<tr>
<td>Hunter and McGuire</td>
<td>Generic</td>
<td>Catalytic coated metallic surfaces</td>
<td></td>
<td></td>
<td>✓</td>
<td>Patent for catalytic heat exchanger for an endothermic and exothermic process using co-current, counter current and cross-flow arrangement</td>
</tr>
<tr>
<td>Branch and Tomlinson</td>
<td>Exo: ( \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} )</td>
<td>Catalytic coated metallic plates</td>
<td></td>
<td></td>
<td>✓</td>
<td>Catalytic plate reactor in co-current flow arrangement</td>
</tr>
<tr>
<td>Charlesworth et al.</td>
<td>Exo: ( \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} )</td>
<td>Catalytic wall</td>
<td>✓</td>
<td></td>
<td></td>
<td>Combustion and reforming in small channels are investigated independently</td>
</tr>
<tr>
<td>Kaminsky et al.</td>
<td>Exo: Methane oxidative coupling</td>
<td>Catalytic wall</td>
<td>✓</td>
<td></td>
<td></td>
<td>Patent for a dual-flow chemical reactor containing catalytic heat transfer wall that allows the oxidative coupling of methane into higher hydrocarbons and cracking of hydrocarbon compounds in separate gas streams.</td>
</tr>
</tbody>
</table>

**INDIRECT AUTOETHERMAL COUPLING**

*Exo*: Endothermic reaction 
*Endo*: Exothermic reaction
<table>
<thead>
<tr>
<th>Authors</th>
<th>Reaction system</th>
<th>Reactor Type</th>
<th>E</th>
<th>T</th>
<th>P</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ioannides and Verykios (1997, 1998) Piga and Verykios (2000)</td>
<td>CH₄ + 0.5O₂ → CO + H₂ (via an indirect reaction mechanism in which part of the methane is initially combusted to CO₂ and H₂O and the remaining methane is then converted by steam/CO₂ reforming - see also 4)</td>
<td>Catalytic wall</td>
<td>☑</td>
<td></td>
<td></td>
<td>Heat integrated catalytic wall reactor in counter-current flow arrangement</td>
</tr>
<tr>
<td>Frauhammer et al. (1999)</td>
<td>Exo: CH₄ + 2O₂ → CO₂ + 2H₂O Endo: CH₄ + H₂O → CO + 3H₂ CH₄ + 2H₂O → CO₂ + 4H₂ CO + H₂O → CO₂ + H₂</td>
<td>Monolith</td>
<td>☑</td>
<td>☑</td>
<td></td>
<td>Counter-current flow arrangement</td>
</tr>
<tr>
<td>Polman et al. (1999)</td>
<td>Exo: CH₄ + 2O₂ → CO₂ + 2H₂O Endo: CH₄ + H₂O → CO + 3H₂</td>
<td>Catalytic wall</td>
<td>☑</td>
<td></td>
<td></td>
<td>Co-current flow arrangement</td>
</tr>
<tr>
<td>Mulvaney and Dandekar (2000)</td>
<td>Exo: catalytic combustion Endo: Any catalytic endothermic process</td>
<td>Catalysts disposed in narrow channels</td>
<td></td>
<td></td>
<td>☑</td>
<td>Patent for an apparatus that coupled exothermic and endothermic processes by means of indirect heat transfer containing also a recuperative section to used the product for feed preheating.</td>
</tr>
<tr>
<td>Authors</td>
<td>Reaction system</td>
<td>Reactor Type</td>
<td>E</td>
<td>T</td>
<td>P</td>
<td>Comments</td>
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<td>------------------</td>
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<td>--------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Ismagilov et al.</td>
<td>Exo: CH₄+2O₂ $\rightarrow$ CO₂+2H₂O</td>
<td>Tubular</td>
<td>✓</td>
<td></td>
<td></td>
<td>Catalyst were synthesised on a heat conducting metal foam support applied by plasma spraying</td>
</tr>
<tr>
<td>(2001)</td>
<td>Endo: CH₄ +H₂O $\rightarrow$ CO +3H₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO + H₂O$\rightarrow$CO₂ +H₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₄+H₂O →CO +3H₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO +H₂O$\rightarrow$CO₂ +H₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kolios et al.</td>
<td>Exo: CH₄+2O₂ $\rightarrow$ CO₂+2H₂O</td>
<td>Parallel</td>
<td></td>
<td>✓</td>
<td></td>
<td>Theoretical investigation of thermal behaviour for counter current flow arrangement and different catalyst distribution along the reactor</td>
</tr>
<tr>
<td>(2001)</td>
<td>Endo: CH₄+H₂O →CO +3H₂</td>
<td>channels</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₄+2H₂O →CO₂ +4H₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO+H₂O$\rightarrow$CO₂ +H₂</td>
<td></td>
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</tr>
</tbody>
</table>
2.4 Catalytic Combustion of Methane

2.4.1 Catalytic versus Homogeneous Combustion

Interest in a process, which reduces combustion pollutant emissions and also improves thermal efficiency, generated by catalytic combustion dates from early seventies (Pfefferle 1975, Blazowski 1975). Extensive reviews (Trimm 1983, Prasad et al. 1984, Pfefferle and Pfefferle 1987, Zwinkels et al. 1993, Hayes and Kolaczkowski 1997) discuss the advantages and disadvantages of catalytic combustion against the homogeneous combustion, together with challenges faced for its application. The use of catalyst provides lower activation energy for the heterogeneous reaction in comparison to the homogeneous one. Consequently, significant reaction rates can be achieved for much lower temperatures and wider fuel concentration range. Being a flameless process, catalytic combustion leads to significant reactor volume reduction. The decrease of the reaction temperature from 1500-2000°C, characteristic to flame combustion, to much lower values, around 980 °C, (Hayes and Kolaczkowski 1997) diminishes the chances for nitrogen oxides, and carbon monoxide formation. Fewer constraints for the equipment materials and reactor design are active at lower temperatures. Thus, metallic materials can replace the refractory bricks, usually used in furnaces, leading not only to a lower capital cost, but also to a better heat transfer. By comparison to conventional combustion, catalytic combustion allows better control of oxidation over wider [fuel : air] ratios outside the flammability range, produces less pollutants and improves the energy efficiency. In spite of this, several limitations come from the fact that the catalysts are expensive and have a finite life. They may be subject to poisoning and deactivation, when operating at high temperatures the sintering of metal or the support may be important, or they may even melt.
2.4.2 Applications of Catalytic Combustion

The wide variety of applications for catalytic combustion is categorised into primary and secondary processes (Hayes and Kolaczkowski 1997). Although, the lower emissions aspect is the dominant concern in all applications for catalytic combustion, the principal objective is different. In the primary combustion applications, the aim is to produce heat for use in a process by combusting a suitable fuel, while in the secondary applications it is desired to purify a stream of harmful or undesirable substances.

Examples of primary applications are combustor for gas turbine, radiant heater, and process heater. Gas turbine combustors try to maximise the amount of energy in the hot gaseous stream fed to the turbine, at a temperature level that prevent NOx formation and turbine blade destruction (Kolaczkowski 1995, Dalla Betta and Rostrup-Nielsen 1999, Cutrone et al. 1999). For catalytic heaters and boilers, the use of catalytic combustion aims to maximise the radiant heat flux (Emonts 1999, Forzatti 2000, Redenius et al. 2001). Commercially achievable heat fluxes are in the range of 10-30 kW/m² (Hayes and Kolaczkowski 1997). The applications of process heater consist of heat exchange between the exothermic combustion reaction and a heat sink, which may be a cold fluid or an endothermic reaction. Different options for autothermal coupling of exothermic and endothermic reactions have been discussed in the previous sections.

The secondary applications of catalytic combustion are environmental applications related to oxidation of volatile organic compounds (VOC). VOCs emission into the atmosphere from motor vehicle exhausts, evaporation of fuels, solvent usage, landfill waste and agricultural activities are exposed nowadays to stringent environmental regulations, which require suitable technologies to reduce their level (Spivey 1987, Hodnett 2000).
2.4.3 Catalysts and Kinetics for Methane Combustion

Typical catalysts used for catalytic combustion are the transitional metals and their oxides on a variety of support materials. Among all hydrocarbon, methane is the most difficult to oxidise (Trimm 1983). The kinetics for catalytic combustion has complex mechanism and usually the description of heterogeneous processes requires the coupling of the reactive flow with the catalytic surface. Deutschmann et al. (1998) investigated numerically for a transient one dimensional flow configuration on catalytic foil and catalytic wire, the catalytic combustion of methane. The analysis included detailed reaction mechanisms in the gas phase and on the surface as well as a detailed transport model. A set of 14 elementary surface reactions was used in order to describe the chemical mechanism. Although these approaches are useful in order to elucidate the limiting step from the mechanism, they become difficult to apply within a more complex reactor model giving rise to computational difficulties. A more appropriate approximation is to obtain an overall expression for the reaction rate, usually power law or Langmuir-Hishelwood, which can be easily used further for reactor modelling.

Lee and Trimm (1995) summarised the most representative kinetics of methane catalytic combustion on noble metals including Palladium, Platinum, and Rhodium, as given in Table 2.2. Cullis and Willatt (1983) determined experimentally the orders of reaction with respect to methane and oxygen for various supported catalysts at temperature range 300-440 °C using reactant mixtures CH\textsubscript{4} : O\textsubscript{2} ratios varying from 1:10 to 10:1. With both Palladium and Platinum catalyst, the order in oxygen tended toward zero, whereas the order in methane was usually about unity. However, as shown in Table 2.2 fractional orders are also reported by different authors. Negative fractional reaction order with respect to oxygen for Pt catalyst have been reported by Yao (1980).
<table>
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</tr>
</thead>
<tbody>
<tr>
<td>Pd/Al₂O₃</td>
<td>260-440</td>
<td>Excess O₂</td>
<td>Microcalorimetric technique</td>
<td>&lt;290°C: 138</td>
<td>1.0</td>
<td>-</td>
<td>Firth and Holland (1969)</td>
</tr>
<tr>
<td>Pt/Al₂O₃</td>
<td>400-500</td>
<td></td>
<td></td>
<td></td>
<td>199</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>295</td>
<td>0.37</td>
<td>Pulse flow reactor</td>
<td>94.5</td>
<td>0.5</td>
<td>0</td>
<td>Cullis et al. (1971)</td>
</tr>
<tr>
<td>Pd wire</td>
<td>350-500</td>
<td>0.1-0.7</td>
<td>Continuous flow reactor</td>
<td>71.1</td>
<td>0.8</td>
<td>0.1</td>
<td>Yao (1980)</td>
</tr>
<tr>
<td>Rh wire</td>
<td>450-550</td>
<td>0.1-0.7</td>
<td>Continuous flow reactor</td>
<td>100</td>
<td>0.6</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Pt wire</td>
<td>475-550</td>
<td>0.25-1</td>
<td>Continuous flow reactor</td>
<td>87.8</td>
<td>1.0</td>
<td>-0.6</td>
<td></td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>400</td>
<td>0.25</td>
<td>Continuous flow reactor</td>
<td>71.1</td>
<td>0.7</td>
<td>0</td>
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<td>Rh/Al₂O₃</td>
<td>500</td>
<td>0.25</td>
<td>Continuous flow reactor</td>
<td>92.0</td>
<td>0.45</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Pt/Al₂O₃</td>
<td>500</td>
<td>0.25</td>
<td>Continuous flow reactor</td>
<td>100</td>
<td>1.2</td>
<td>-0.5</td>
<td></td>
</tr>
<tr>
<td>Pt/Al₂O₃ porous</td>
<td>&lt;540</td>
<td>0.5-1.7</td>
<td>Continuous flow reactor</td>
<td>188</td>
<td>1.0</td>
<td>0.75</td>
<td>Trimm and Lam (1980)</td>
</tr>
<tr>
<td>Pt/Al₂O₃ porous</td>
<td>&gt;540</td>
<td>0.5-1.7</td>
<td>Continuous flow reactor</td>
<td>83.8</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Pt/Al₂O₃ non-porous</td>
<td>&lt;550</td>
<td>0.3-2</td>
<td>Continuous flow reactor</td>
<td>167</td>
<td>1.0</td>
<td>0.75</td>
<td></td>
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<tr>
<td>Pt/Al₂O₃</td>
<td>&gt;550</td>
<td>0.3-2</td>
<td>Continuous flow reactor</td>
<td>75.2</td>
<td>1.0</td>
<td>1.0</td>
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<tr>
<td>2% wt Pt/Al₂O₃</td>
<td>450</td>
<td>0.5</td>
<td>Continuous flow reactor</td>
<td>123</td>
<td>0.9</td>
<td>0</td>
<td>Niwa et al. (1983)</td>
</tr>
<tr>
<td>Pt/γAl₂O₃</td>
<td>350-450</td>
<td>0.02-0.4</td>
<td>Recirculation batch reactor</td>
<td>Pt loading</td>
<td>1.0</td>
<td>0</td>
<td>Otto et al. (1989)</td>
</tr>
</tbody>
</table>

Pt loading  
<5 wt %: 147  
5-30 wt %: 115
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$T\ ^\circ\text{C}$</th>
<th>Rate Expression</th>
<th>Activation Energy</th>
<th>Notes</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Al$_2$O$_3$</td>
<td>390-450</td>
<td>$\frac{k_i K_{CH_4} P_{CH_4} \sqrt{K_{O_2} P_{O_2}}}{(1 + K_{CH_4} P_{CH_4} + \sqrt{K_{O_2} P_{O_2}})^2}$</td>
<td>34.7</td>
<td></td>
<td>Ma et al. (1996)</td>
</tr>
<tr>
<td>Pt/MgO</td>
<td>$&gt;$600</td>
<td>$\frac{k^0 \exp \left(-\frac{E_A}{R_g T}\right) P_{CH_4} P_{O_2}}{(1 + K_{CH_4} P_{CH_4} + K_{O_2} P_{O_2} + K_{CO_2} P_{CO_2} + K_{H_2O} P_{H_2O})^2}$</td>
<td>55.2</td>
<td>$k_i^0 = 1.2 \times 10^{15}, \text{Pa}^3 \text{m}^3 \text{kg}^{-1} \text{s}^{-1}$</td>
<td>Wolf et al. (1997)</td>
</tr>
<tr>
<td>Pd</td>
<td>377-397</td>
<td>$\frac{k^0 \exp \left(-\frac{E_A}{R_g T}\right) (Y_{CH_4})^{0.07}}{1 + k_e (Y_{H_2O})^{0.38}}$</td>
<td>58</td>
<td>$k_v^0 = 39.924 \times 10^6, \text{mol m}^3 \text{s}^{-1}$</td>
<td>Hayes et al. (1999)</td>
</tr>
<tr>
<td>PdO/Al$_2$O$_3$</td>
<td>400-600</td>
<td>$\frac{K_r \cdot C_{CH_4}}{1 + K_{H_2O} C_{H_2O}}$</td>
<td>63.6</td>
<td>at 773 K, $K_r = 1.2 \text{ m}^3/(\text{kg s})$, $K_{H_2O} = 5 \text{ m}^3/\text{mol}$</td>
<td>Groppi et al. (2001)</td>
</tr>
</tbody>
</table>
Reported orders in water (Giezen et al. 1999) are negative pointing to a mechanism involving competition between water and one of the reactants for adsorption sites. Negative reaction orders point forward Langmuir Hinshelwood type kinetics. Several expressions of this type for methane total oxidation are summarised in Table 2.3.

Cullis and Willatt (1983) showed in their experimental study that for both Pt and Pd catalysts, the value of activation energy suddenly changes with temperature. The transition temperature depends on catalyst, support, and composition of the methane-oxygen mixture. Several examples from their study are given in Table 2.4. Values of the activation energy below the transition temperature, for platinum catalysts are generally higher than those for palladium catalysts but above this temperature the reverse is true. Platinum catalysts underwent a sudden increase in activation energy, while Palladium catalysts show a more gradually transition.

<table>
<thead>
<tr>
<th>Supported Catalyst</th>
<th>Activation energy kJ/mol</th>
<th>Transition point K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low temp region</td>
<td>High temp region</td>
</tr>
<tr>
<td>2.7 wt% Pd on TiO$_2$</td>
<td>83</td>
<td>35</td>
</tr>
<tr>
<td>2.7 wt% Pd on γ-Al$_2$O$_3$</td>
<td>84</td>
<td>23</td>
</tr>
<tr>
<td>2.7 wt% Pd on α-Al$_2$O$_3$</td>
<td>89</td>
<td>45</td>
</tr>
<tr>
<td>2.7 wt% Pt on TiO$_2$</td>
<td>116</td>
<td>19</td>
</tr>
<tr>
<td>2.7 wt% Pt on γ-Al$_2$O$_3$</td>
<td>114</td>
<td>24</td>
</tr>
</tbody>
</table>

Lee and Trimm (1995) concluded that oxidation of methane is dependent on several factors such as: feed ratio CH$_4$ /O$_2$, catalyst loading and particle size, water presence, and type of support. Under oxygen rich conditions, methane is oxidised only to carbon dioxide, while under oxygen deficient conditions, the formation of carbon monoxide is possible. For Pt and Pd, at low metal concentrations an increase of the loading increases the reaction rate, as the loading was increased further, a rate maximum was achieved.
before the reaction rate decreased (Lee and Trimm 1995, Cullis and Willatt 1983). It has been shown experimentally that the catalyst activity and the activation energy depend not only on the catalyst type but also on its structure and particle size. Large particles are more active than small ones (Briot et al. 1990, Ribeiro et al. 1994, Muller et al. 1999). Changes of catalyst activity under reaction conditions are attributed to structural rearrangements of the precious metal under reaction conditions (Baldwin and Burch 1990, Burch and Loader 1995). Lee and Trimm (1995) showed that the presence of water in the reaction feed increases the formation of carbon dioxide. For a Palladium catalyst, Ribeiro et al (1994) found that water has a strong inhibiting effect on the reaction rate. Typical support materials for catalytic combustion are porous alumina, dense alumina, aluminium titanate, silica, silicon carbone, silicone nitride, mullite, zircon mullite, cordierite, fecralloy. The role of support or washcoat is primarily to ensure good distribution of catalyst and to inhibit sintering, especially if the catalyst is used in thin layer (Trimm 1983). The major factors responsible for catalyst deactivation are sintering and sulphur poisoning. The thermal stability of the catalyst is strongly dependent on the support. The sintering of supports and catalysts is accelerated at higher temperatures. The sulphur presence on the catalysts can either inhibit the adsorption or the dissociation of molecular species and the surface reaction between adsorbed species. (Lee and Trimm 1995).

The scatter of published kinetic data implies that methane catalytic combustion is strongly system dependent, and is influenced by various factors. Comparing the kinetic data published in the literature for supported Pd, Lyubovsky and Pfefferle (1999) emphasised that in spite of the intensive research of the system there is still a lack of agreement among researchers. The activation energy for the reaction rate reported in
different work varies by a factor of 3 and the pre-exponential coefficient varies by orders of magnitude.

2.4.4. Specific Behaviour of Pd-based Catalyst

Since the early studies of methane combustion, Palladium supported on alumina was identified as the most promising catalytic system (Anderson et al. 1961). Nevertheless the behaviour of this important catalytic system is still not well understood. Depending on the reaction conditions (temperature, pressure, gas mixture, composition), palladium can easily undergo oxidation/reduction, $\text{Pd} + 0.5\text{O}_2 \leftrightarrow \text{PdO}$, during the reaction. Farrauto et al. (1995) studied a number of supported Pd catalysts. During the heating cycle PdO is decomposed to metallic Pd at a temperature $T_D$ that depend on the support material. Upon a cooling cycle the metallic Pd is reformed at a temperature $T_R$. Their results, as reproduced in Figure 2.1, show a large hysteresis in the Pd oxidation/reduction cycle. Depending on the support type, the decomposition temperature, $T_D$, has values in the range $955 - 1083$ K, while the difference between the decomposition and the reformation temperature was reported between $45 - 212$ K.

![Figure 2.1 Thermogravimetric cycle in air for the composition of supported PdO to Pd metal during heating in air and its partial reformation on cooling in air. (Farrauto et al. 1995)](image-url)
The authors argue that at high temperature the metallic Pd state of the catalyst is formed and upon cooling it transforms into a more active PdO state. The inactivity of the metallic Pd was attributed to its supposed inability to absorb oxygen from the gas phase. Similar behaviour has been confirmed experimentally by McCarty (1995) who identified during the cooling cycle a region between 150 – 570 °C when the conversion of methane increases with the decrease of temperature. The authors refer to the observed phenomenon as “negative activation energy”. The complex nature of PdOₓ<→Pd equilibrium has been demonstrated in the work of Lyubovsky and Pfefferle (1998) from which a typical Arrhenius plot for methane combustion is presented in Figure 2.2.

![Arrhenius plot](image)

Figure 2.2 Arrhenius plot for the combustion of methane over palladium catalyst supported on alumina. The catalyst was first heated to 1073 K, and data were collected as the temperature was decreased in stages (Lyubovsky and Pfefferle, 1998)

In this work, the apparent activation energy for methane oxidation for the oxidised PdO state was claimed to be much lower than over the metallic Pd (40-45 kcal/mol and 16-18 kcal/mol respectively) and the pre-exponential factor for Pd is 5-6 order of magnitude higher (depending on many factors such as particle size, faceting, metal-support interaction). The “negative activation” phenomenon was attributed to the thermodynamic shift in Pd/PdO equilibrium towards oxidised state, which leads to formation of small PdO crystallites dispersed over the previously formed metallic Pd.
surface. This mixed PdO/Pd state is likely the most active form of the catalyst, and its structural changes have been also confirmed experimentally by Datye et al. (2000). To conclude, the studies presented in the literature so far suggest that although Pd-based catalysts are very active at low temperatures, their use in the higher temperature range should be treated with care. The mechanism of the catalyst activation/deactivation can cause strong instabilities in the application of catalytic combustion in practical systems (Lyubovsky and Pfefferle 1998).

2.5 Steam Reforming of Methane

2.5.1 Conventional Process of Steam Reforming

Steam reforming of methane is well known as the main process for hydrogen and synthesis gas production for large-scale processes such as methanol or ammonia synthesis. Extensive reviews about the steam reforming of hydrocarbons, (Van Hook 1980, Rostrup-Nielsen 1984, Ridler and Twigg 1989, Kochloefl 1997) show that the conventional process is carried out on supported Ni catalysts in multitubular reactors operated at temperatures varying from 500 to 800 °C, pressures ranging from 20 to 40 bar and molar steam-to-carbon ratios in the feed 2 - 4. The main chemical reactions involved in the process are

- steam reforming: \( \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \) \( \Delta H = +206.1 \text{ kJ/mol} \) (2.4-1)
- water gas-shift: \( \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \) \( \Delta H = -41 \text{ kJ/mol} \) (2.4-2)
- reverse methanation: \( \text{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 4\text{H}_2 \) \( \Delta H = +164 \text{ kJ/mol} \) (2.4-3)

Side reactions may involve carbon deposition

- thermal cracking: \( \text{CH}_4 \leftrightarrow \text{C} + 2\text{H}_2 \) \( \Delta H = +74.9 \text{ kJ/mol} \) (2.4-4)
- Boudouard reaction: \( 2\text{CO} \leftrightarrow \text{C} + \text{CO}_2 \) \( \Delta H = -173 \text{ kJ/mol} \) (2.4-5)
- CO reduction: \( \text{CO} + \text{H}_2 \leftrightarrow \text{C} + \text{H}_2\text{O} \) \( \Delta H = +132 \text{ kJ/mol} \) (2.4-6)
Carbon formation is undesirable because it can lead to partial or total blockage of the reformer tubes. It can be suppressed by using an excess of steam at minimum molar ratio steam: methane of 1.7 (Ridler and Twigg 1989).

The overall process is highly endothermic and the necessary heat to drive the endothermic reactions is provided by heating up the catalyst tubes in a fired furnace. A typical reformer may contain between 40 and 400 tubes. The internal diameter is in the range 70 -160 mm with a tube thickness 10 –20 mm. Large multiple burners are mounted along the inside walls of the fire box, their arrangement depends on the furnace type. The process is heat transfer limited, 50% of the heat of combustion is used for the reaction, and a great deal of effort is spent to recover the waste heat by preheating feeds and steam generation (Armor 1999). The reactions are equilibrium limited and show a strong internal mass transfer resistances (De Deken et al. 1982, Xu and Froment 1989b).

2.5.2 Catalysts and Kinetics for Methane Steam Reforming

Industrial catalysts used for steam reforming are exclusively based on supported nickel. Because of the severe conditions for primary steam reforming, the requirements placed on steam reforming catalysts such as high activity, a high mechanical strength and the thermoresistance are in conflict (Rostrup-Nielsen, 1989). The most thermoresistant carriers utilised are α-alumina, magnesium aluminum spinel or zirconia. Carriers with good mechanical properties usually achieve poor Ni dispersion that gives low catalyst activity. Therefore, a compromise is made using carriers with moderate mechanical and thermal properties but a specific surface area around 20 m² g⁻¹, (e.g MgAl₂O₄). In such cases higher Ni dispersions (2-5%) can be obtained with Ni crystallite sizes in the range 20-50 nm (Kochloefl 1997). The activity per gram catalyst increases by increasing Ni
content, but the Ni dispersion or Ni utilisation decreases. The Ni content in industrial catalysts is usually between 7–15% (Rostrup-Nielsen, 1989). The catalyst performances are affected mainly due to growth of Ni crystallites by sintering during reaction, carbon formation and sulphur poisoning.

A large number of kinetic rate expressions for the steam reforming of methane is reported in the literature from which a selection is given in Table 2.5, where $K_{e,1}$, $K_{e,2}$, $K_{e,3}$ are the equilibrium constants for steam reforming, water gas shift and reverse methanation respectively. Their dependence on temperature as calculated from thermodynamic data (Elnashaie et al. 1990) is

\[
K_{e,i} = \exp(-\frac{26830}{T} + 30.114), \text{ bar}^2 \quad (2.4-7)
\]
\[
K_{e,2} = \exp(\frac{4400}{T} - 4.036), - \quad (2.4-8)
\]
\[
K_{e,3} = \exp(-\frac{22430}{T} + 26.078), \text{ bar}^2 \quad (2.4-9)
\]

Most of these rate equations are either empirically based power law kinetics or are obtained by applying a large number of assumptions on the proposed mechanisms, making their use limited for a certain range of reaction conditions. This kind of approaches has led to contradictions among the literature data such as the disappearance of certain reactant and/or product concentrations from the rate equations. One of the most interesting contradictions is the prediction of positive, as well as negative effective reaction order with respect to steam. Elnashaie et al. (1990) finds this as a strong indication for the existence of non-monotonic dependence of the rate of reaction upon a specific reactant. They analysed by comparison the reaction rates of Bodrov et al. (1964), which contain a negative order dependency on steam, De Deken (1982), which contain a positive order dependency on steam, and Xu and Froment (1989a), which developed a general rate equation based on Langmuir-Hinshelwood-Hougen-Watson (LHHW) approach. Their study showed that despite the quantitative difference between
Table 2.5 Steam Reforming Kinetics.

<table>
<thead>
<tr>
<th>Supported catalyst</th>
<th>Experimental conditions</th>
<th>Kinetic expression</th>
<th>Notes</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Reduced nickel</td>
<td>336 - 637 °C, 1 atm, H₂O:CH₄ 2.5 - 10</td>
<td>steam reforming: ( k \cdot p_{CH₄}, \text{ mole/(kg-cat s)} ) ( k = 0.078 \exp\left(\frac{-20417}{R_gT}\right), \text{ mole/(kg-cat s atm)} )</td>
<td>Akers and Camp (1955)</td>
<td></td>
</tr>
<tr>
<td>2. Ni foils</td>
<td>800 - 900 °C, 1 atm, H₂O:CH₄ 2.5 - 10</td>
<td>steam reforming: ( \frac{k \cdot p_{CH₄}}{1 + a \cdot p_{H₂O}/p_{H₂} + b \cdot p_{CO}}, \text{ mol} / m^2 \cdot \text{Ni} \cdot \text{h} ) ( k = 1.1 \cdot 10^9 \exp\left(\frac{-130000}{R_gT}\right) ) ( T=800 \text{ °C}, a=0.5; b=2 \text{ bar} ) ( T=900 \text{ °C}, a=0.2; b=0 \text{ bar} )</td>
<td>Bodrov et al. (1964)</td>
<td></td>
</tr>
<tr>
<td>3. Ni/Al₂O₃ 75% Ni</td>
<td>500-680 °C, 1 atm, H₂O:CH₄ 3:1</td>
<td>steam reforming: ( k \cdot p_{CH₄}p_{H₂O}^{-0.5}, \text{ mole/(m}^2 \text{ s)} ) ( k = 2.96 \cdot 10^{-7} \exp\left(\frac{-29000}{R_gT}\right), \text{ mole/(m}^2 \text{ s torr}^{-0.5}) )</td>
<td>Ross and Steel (1973)</td>
<td></td>
</tr>
<tr>
<td>4. Ni/Al₂O₃ 350-450 °C, 1 atm</td>
<td>reverse methanation: ( k = 2.14 \cdot 10^8 \exp\left(\frac{-130290}{R_gT}\right), \text{ mol} / g_{cat} \cdot \text{h} \cdot \text{atm} ) ( K_{CH₄} = 2.16 \cdot 10^9 \exp\left(\frac{-88706}{R_gT}\right), \text{ atm}^{-1} )</td>
<td>Quach and Rouleau (1975)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Ni/Al₂O₃ 550-680 °C, 5-15 atm</td>
<td>carbon monoxide production ( k_{CO} (p_{CH₄} \cdot p_{H₂O}/p_{H₂}^2 - p_{CO}/K_{e,1}) \frac{\text{kmol}}{(1 + K_{CO}p_{CO})^2}, \text{ kg}<em>{cat} \cdot \text{h} ) ( k</em>{CO} = 1.13 \cdot 10^{21} \exp\left(\frac{-364000}{R_gT}\right), \text{ kmol/kg}_{cat} \cdot \text{h} \cdot \text{bar} )</td>
<td>De Dekken et al. (1982)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>carbon dioxide production ( k_{CO}<em>2 (p</em>{CH₄} \cdot p_{H₂O}/p_{H₂}^2 - p_{CO}<em>2/K</em>{e,3}) \frac{\text{kmol}}{(1 + K_{CO}p_{CO})^2}, \text{ kg}<em>{cat} \cdot \text{h} ) ( k</em>{CO}<em>2 = 3.68 \cdot 10^{18} \exp\left(\frac{-317000}{R_gT}\right), \text{ kmol/kg}</em>{cat} \cdot \text{h} \cdot \text{bar} )</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>( K_{CO}_2 = 3.5 \cdot 10^{-8} \exp\left(\frac{137000}{R_gT}\right), \text{ bar}^{-1} )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2.5 Steam Reforming Kinetics (continued).

<table>
<thead>
<tr>
<th>Supported catalyst</th>
<th>Experimental conditions</th>
<th>Kinetic expression</th>
<th>Notes</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>6. Ni/Al₂O₃</td>
<td>400-890 °C</td>
<td>steam reforming: ( k_1 \left( p_{\text{CH}<em>4} - p</em>{\text{eq}} \right) \cdot \frac{p_{\text{H}_2 \text{O}}^{0.596}}{(\text{cat bed}) m^3 \cdot h} )</td>
<td>( k_1 = 9.286 \cdot 10^8 \exp \left( \frac{-106870}{R_g T} \right) \cdot \frac{\text{mol}}{(\text{cat bed}) m^3 \cdot h \cdot \text{bar}} )</td>
<td>Numaguchi and Kikuchi (1988)</td>
</tr>
<tr>
<td>8.7 % Ni</td>
<td>1-25 atm</td>
<td>water shift: ( k_2 \left( p_{\text{CO}} - p_{\text{eq}} \right) \cdot \frac{\text{mol}}{(\text{cat bed}) m^3 \cdot h} )</td>
<td>( k_2 = 8.688 \cdot 10^5 \exp \left( \frac{-54531}{R_g T} \right) \cdot \frac{\text{mol}}{(\text{cat bed}) m^3 \cdot h \cdot \text{bar}} )</td>
<td></td>
</tr>
<tr>
<td>7. Ni/Al₂O₃</td>
<td>527-677 °C</td>
<td>steam reforming: ( k_1 p_{\text{CH}<em>4} \left( 1 - \frac{p</em>{\text{CO}} \cdot p_{\text{H}<em>2 \text{O}}^{3}}{K</em>{e,1} \cdot p_{\text{CH}<em>4} \cdot p</em>{\text{H}<em>2 \text{O}}} \right) \cdot \frac{\text{mol}}{g</em>{\text{cat}} \cdot s} )</td>
<td>( k_1 = 8.82 \cdot 10^{-2} \exp \left( \frac{-53326}{R_g T} \right) \cdot \frac{\text{mol}}{g_{\text{cat}} \cdot s \cdot \text{kPa}} )</td>
<td>Richardson et al. (1988)</td>
</tr>
<tr>
<td>14 % Ni</td>
<td>1 atm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O:CH₄</td>
<td>2.5-5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. Ni/MgAl₂O₄</td>
<td>500-575 °C</td>
<td>steam reforming: ( \frac{k_1 p_{\text{CH}<em>4} \left( p</em>{\text{CH}<em>4} \cdot p</em>{\text{H}<em>2 \text{O}} - p</em>{\text{CO}} \cdot p_{\text{H}<em>2 \text{O}}^{3} \right)}{K</em>{e,1} \cdot p_{\text{H}<em>2 \text{O}}} \cdot \frac{\text{kmol}}{(\text{Den})^2 \cdot \text{kg}</em>{\text{cat}} \cdot \text{h}} )</td>
<td>( k_1 = 4.255 \cdot 10^{15} \exp \left( \frac{-240100}{R_g T} \right) \cdot \frac{\text{kmol} \cdot \text{bar}^{0.5}}{\text{kg}_{\text{cat}} \cdot \text{h}} )</td>
<td>Xu and Froment (1989)</td>
</tr>
<tr>
<td>15.2 % Ni</td>
<td>3 atm</td>
<td>water gas shift: ( \frac{k_2 p_{\text{CO}} \cdot p_{\text{H}<em>2 \text{O}} - p</em>{\text{CO}} \cdot p_{\text{H}<em>2 \text{O}}^{2}}{K</em>{e,2} \cdot p_{\text{H}<em>2 \text{O}}} \cdot \frac{\text{kmol}}{(\text{Den})^2 \cdot \text{kg}</em>{\text{cat}} \cdot \text{h}} )</td>
<td>( k_2 = 1.955 \cdot 10^{6} \exp \left( \frac{-67130}{R_g T} \right) \cdot \frac{\text{kmol}}{\text{kg}_{\text{cat}} \cdot \text{bar}} )</td>
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<tr>
<td></td>
<td>H₂O:CH₄</td>
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<td>3-5</td>
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<td>2.5-5</td>
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</tr>
<tr>
<td>8. Ni/MgAl₂O₄</td>
<td>500-575 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.2 % Ni</td>
<td>3 atm</td>
<td>reverse methanation: ( \frac{k_3 p_{\text{CH}<em>4} \left( p</em>{\text{CH}<em>4}^{2} \cdot p</em>{\text{CO}}^{3} \right)}{K_{e,3} \cdot p_{\text{H}<em>2 \text{O}}} \cdot \frac{\text{kmol}}{(\text{Den})^2 \cdot \text{kg}</em>{\text{cat}} \cdot \text{h}} )</td>
<td>( K_{\text{CO}} = 8.23 \cdot 10^{-4} \exp \left( \frac{70650}{R_g T} \right) \cdot \text{bar}^{-1} )</td>
<td></td>
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<tr>
<td></td>
<td>H₂O:CH₄</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>3-5</td>
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<td>2.5-5</td>
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<tr>
<td>Supported catalyst</td>
<td>Experimental conditions</td>
<td>Kinetic expression</td>
<td>Notes</td>
<td>Reference</td>
</tr>
<tr>
<td>---------------------</td>
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<td>--------------------</td>
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<td>-----------</td>
</tr>
<tr>
<td>Ni/Al₂O₃ 21% Ni</td>
<td>600-700 °C 1 atm H₂O:CH₄ 1-10</td>
<td>( r_{\text{CH}<em>4} = kP</em>{\text{CH}<em>4}^{0.044}P</em>{\text{H}_2\text{O}}^{-0.9577} ), mole/(g_cat h)</td>
<td>( K_{\text{H}_2\text{O}} = 1.77 \cdot 10^4 \exp \left( \frac{-88680}{R_g T} \right) ), bar⁻¹</td>
<td>Ko et al. (1995)</td>
</tr>
<tr>
<td>Ni/Al₂O₃ 9.7-11% Ni</td>
<td>475-555 °C 12 atm H₂O:CH₄ 1-4</td>
<td>steam reforming: ( k_1 = 5.922 \cdot 10^8 \exp \left( \frac{-209200}{R_g T} \right) ), kmol/kg_cat s·kPa⁰·²⁵</td>
<td>( k_1 = 5.922 \cdot 10^8 \exp \left( \frac{-209200}{R_g T} \right) ), kmol/kg_cat s·kPa⁰·²⁵</td>
<td>Hou and Hughes (2001)</td>
</tr>
<tr>
<td>Ni</td>
<td>475-555 °C 12 atm H₂O:CH₄ 1-4</td>
<td>water gas shift: ( k_2 = 6.028 \cdot 10^{-4} \exp \left( \frac{-154000}{R_g T} \right) ), kmol/kg_cat s·kPa⁰·²⁵</td>
<td>( k_2 = 6.028 \cdot 10^{-4} \exp \left( \frac{-154000}{R_g T} \right) ), kmol/kg_cat s·kPa⁰·²⁵</td>
<td>Hou and Hughes (2001)</td>
</tr>
<tr>
<td>Ni</td>
<td>475-555 °C 12 atm H₂O:CH₄ 1-4</td>
<td>reverse methanation: ( k_3 = 1.093 \cdot 10^7 \exp \left( \frac{-109400}{R_g T} \right) ), kmol/kg_cat s·kPa⁰·²⁵</td>
<td>( k_3 = 1.093 \cdot 10^7 \exp \left( \frac{-109400}{R_g T} \right) ), kmol/kg_cat s·kPa⁰·²⁵</td>
<td>Hou and Hughes (2001)</td>
</tr>
<tr>
<td>Ni</td>
<td>475-555 °C 12 atm H₂O:CH₄ 1-4</td>
<td>( K_{\text{CO}} = 5.127 \cdot 10^{-13} \exp \left( \frac{140000}{R_g T} \right) ), kPa⁻¹</td>
<td>( K_{\text{CO}} = 5.127 \cdot 10^{-13} \exp \left( \frac{140000}{R_g T} \right) ), kPa⁻¹</td>
<td>Hou and Hughes (2001)</td>
</tr>
<tr>
<td>Ni</td>
<td>475-555 °C 12 atm H₂O:CH₄ 1-4</td>
<td>( K_{\text{H}_2\text{O}} = 9.251 \exp \left( \frac{-159000}{R_g T} \right) ), bar⁻¹</td>
<td>( K_{\text{H}_2\text{O}} = 9.251 \exp \left( \frac{-159000}{R_g T} \right) ), bar⁻¹</td>
<td>Hou and Hughes (2001)</td>
</tr>
<tr>
<td>Ni</td>
<td>475-555 °C 12 atm H₂O:CH₄ 1-4</td>
<td>( K_{\text{H}_2} = 5.68 \cdot 10^{-10} \exp \left( \frac{93400}{R_g T} \right) ), kPa⁰·⁵</td>
<td>( K_{\text{H}_2} = 5.68 \cdot 10^{-10} \exp \left( \frac{93400}{R_g T} \right) ), kPa⁰·⁵</td>
<td>Hou and Hughes (2001)</td>
</tr>
</tbody>
</table>
the values of the reaction rates due to different catalyst type used, the qualitative trends express by Bodrov and De Deken expressions are found in the LHHW expression of Xu and Froment. The latter is obviously a more general form predicting well both negative and positive effective reaction orders with respect to steam, while the former two are valid in a narrower range due to limited reaction conditions used for their determination.

The effectiveness factors for steam reforming and reverse methanation calculated by diverse authors (Van Hook 1980, Rostrup-Nielsen 1984, De Deken 1982, Xu and Froment 1989b) are of the order 0.02-0.04, for particle size between 10 –17 mm. Xu and Froment (1989b) noticed that these low effectiveness factors could explain why many authors obtained activation energies for steam reforming of approximately half the intrinsic values.

2.6. Light Alkanes Dehydrogenation

2.6.1. General Considerations

Although the main industrial route for light alkanes dehydrogenation is by thermal cracking, the catalytic dehydrogenation represents an attractive alternative (Buonomo et al. 1997). Despite the apparent simplicity of its chemistry, catalytic dehydrogenation is one of the most complex catalytic process due to two basic characteristics that strongly affect the choice in its technological implementations: the thermodynamic equilibrium limits the conversion per pass and the reactions are highly endothermic. The theoretical dehydrogenation equilibrium for alkanes to alkenes, \( C_nH_{2n+2} \leftrightarrow C_nH_{2n} + H_2 \), for several alkanes is given in Table 2.6 (Weckhuysen and Schoonheydt 1999).

<table>
<thead>
<tr>
<th>Conversion, %</th>
<th>Ethene</th>
<th>Propene</th>
<th>1-Butene</th>
<th>1-Pentene</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>555</td>
<td>456</td>
<td>460</td>
<td>450</td>
</tr>
<tr>
<td>30</td>
<td>660</td>
<td>540</td>
<td>545</td>
<td>535</td>
</tr>
<tr>
<td>50</td>
<td>725</td>
<td>595</td>
<td>600</td>
<td>585</td>
</tr>
<tr>
<td>70</td>
<td>790</td>
<td>660</td>
<td>670</td>
<td>650</td>
</tr>
<tr>
<td>90</td>
<td>900</td>
<td>750</td>
<td>753</td>
<td>730</td>
</tr>
</tbody>
</table>
In order to supply the heat necessary to achieve this high temperature, it is necessary to overhear the reactant or the catalyst or the reactor walls, with potential loss of selectivity due to the side reactions catalysed by the hot contact surfaces. The achievable selectivities are in the range of 75-95% depending on the alkane to be dehydrogenated and the selected operating conditions. Carbonaceous residue is formed and irreversible adsorbed on the catalyst, this forces frequent regeneration to restore the initial activity. The available commercial dehydrogenation processes are summarised in Table 2.7 (Stitt et al. 1999). They are characterised by different choices concerning the system catalyst-heat-supply mode catalyst-regeneration mode.

<table>
<thead>
<tr>
<th>Process</th>
<th>Oleflex</th>
<th>STAR</th>
<th>Catofin or Houndry</th>
<th>Snamprogetti-Yarsintez</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>supported Pt supported Pt supported Cr₂O₃ supported Cr₂O₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactor</td>
<td>moving bed fixed bed fixed bed fluidised bed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat supply</td>
<td>Heating of the feed Heating of the catalyst tubes in furnaces Heat stored in the catalyst bed during regeneration step Heat stored in the catalyst by direct combustion of the fuel during regeneration step</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>License</td>
<td>UOP Inc. Phillips Air Products and Chemicals Snamprogetti-Yarsintez</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**2.6.2. Catalysts and Kinetics for Ethane and Propane Dehydrogenation**

The main catalyst types used for catalytic dehydrogenation are supported noble metals, mainly platinum promoted with tin, or chromium oxides on alumina or zirconia. They differ in terms of the quality of some by-products and the treatment they require when reactivated after coke burn-off, and gives similar selectivities (Buonomo et al. 1997). Champagnie et al. (1992) studied ethane dehydrogenation on platinum supported catalysts and developed a rate expression for ethane dehydrogenation as:

\[
\dot{r}_{C_2H_6} = 4.56 \cdot 10^4 \exp \left( \frac{-86274}{R_e T} \right) \cdot \left( \frac{P_{C_2H_6} - P_{C_2H_2}}{K_e} \right), \frac{\text{mol}}{\text{cm}^3 \text{s}}
\]  

(2.5-1)
where $K_e$ is the equilibrium constant, and its dependence on temperature is given by:

$$K_e = 1.096 \cdot 10^7 \exp\left(-\frac{17250}{T}\right), \text{ atm} \quad (2.5-2)$$

A similar expression was found also by Gobina et al. (1995) for a palladium catalyst, with activation energy of 75580 kJ/mol and a pre-exponential factor of 4.39 mol/(gcat s atm). Wan and Chu studied propane dehydrogenation over partially reduce zinc oxide supported on silicalite. Their reaction rate expression follows a LHHW expression as:

$$r_{C_3H_8} = \frac{k_iC_i\left(p_{C_3H_8} - p_{C_2H_4} \cdot p_{H_2}/K_e\right)}{1 + p_{C_3H_8}/K_3} \quad (2.5-3)$$

where $k_iC_i = 417 \exp\left(-\frac{121783}{R_g T}\right), \text{ mol} \quad (2.5-4)$

$$K_3 = 8.52 \cdot 10^{17} \exp\left(\frac{36250}{T}\right), \text{ atm} \quad (2.5-5)$$

$$K_e = 1.09 \cdot 10^7 \exp\left(-\frac{15270}{T}\right), \text{ atm} \quad (2.5-6)$$

Stitt et al. (1999a) determined the propane dehydrogenation kinetics of an alumina supported chromia catalyst, including the reaction for deactivation due to carbon formation. They compared further the performances of a deactivating propane dehydrogenation catalytic reactor (Stitt et al. 1999b). The best design for abatement of deactivation was found to be nearly isothermal with a gentle increase in temperature through the reactor.
2.7 Modelling of Catalytic Wall Reactors

2.7.1 Catalytic Wall versus Fix Bed Reactors

The catalytic wall reactor (CWR), mainly used with a tubular geometry, also known as Tubular Wall Reactor (TWR), consists of a reacting stream flowing in a cylindrical tube, which has the wall covered with a thin catalyst layer. Such reactor design attracted attention since early '50s due to the fact that it can handle highly exothermic reactions with good temperature control (Baron et al. 1952, Chambre et al. 1956, Katz 1959, Hudson 1965, Solomon and Hudson 1967). Smith and Carberry (1974) and later Huang and Varma (1980) highlighted that there are several advantages of the CWRs compared to the conventional fixed-bed reactors (FBR). The latter are usually heat transfer limited due to large gas-solid thermal resistances, subject at the same time to significant intraphase mass resistances. Within CWRs, the heat is generated at the wall eliminating the large gas-solid thermal resistances, thus much higher heat generation rates are achievable without excessive temperature rise. Since the catalyst is used in a thin layer its efficiency is much higher and the amount of catalyst required is significantly reduced. For complex reaction systems, the diffusion of intermediate desired product from the catalytic wall to the bulk gas phase is faster than from a catalyst pellet, resulting in shorter residence time and potentially enhanced yield. In contrast to FBR where high gas velocities are required to minimise the gas film around the pellet, CWRs can make use of lower velocities. Consequently, lower pressure drops are achieved. Finally, the parametric sensitivity of CWRs is minimal providing a higher degree of stability than FBR (Smith and Carberry 1975), which in turn leads to better temperature control. Thus, catalyst destruction and deactivation due to hot spots is minimised and the catalyst life extended.
2.7.2 Applications of Catalytic Wall Reactors

The application of catalyst-coated wall reactors has been investigated for various exothermic reactions such as oxidation of sulphur dioxide (Baron et al. 1952), hydrogenation of carbon monoxide (Goyal et al. 1982, 1983; Dalai et al. 1992a, 1992b), oxidation of naphthalene over $\text{V}_2\text{O}_5$ catalysts (Smith and Carberry 1975, 1976, Parent et al. 1983), conversion of synthesis gas to gaseous and liquid fuel via Fischer-Tropsch synthesis (Goyal et al. 1984, 1988), hydrogenation of nitrobenzene to aniline (Amon et al. 1999). Extensive attention has been dedicated to catalytic combustion in monoliths which are considered a specific catalytic wall reactor (Young and Finlayson 1976a, 1976b; Kolaczkowski 1995, 1999; Groppi et al. 1995a, 1995b; Hayes et al. 1992, 1996; Cominos and Gavriilidis 2001).

![Figure 2.3 Reaction and transport processes in catalytic wall reactors](image)

2.7.3 General Form of Governing Equations

The mathematical formulation of an adequate model for a chemical reactor consists of equations of momentum, mass, and energy balances at a degree of complexity that is most of the time a compromise between the accuracy of the model and the solving effort and time (Froment and Bischoff 1990). The complexity of the physical and chemical phenomena present in catalytic wall reactors is characteristic to heterogeneous chemical
reactors. An illustrative summary is given in Figure 2.3. The movement of the reacting stream in the reactor is usually coupled with heat and mass transfer phenomena, and chemical reactions. Heterogeneous reaction takes place in the catalyst layer and at the surface, at the same time homogeneous reactions are possible in the gas phase. Momentum, mass, and heat transfer by convection, diffusion, and conduction characterise the gas-phase. For the catalyst layer, the predominant transport phenomena are mass diffusion in the catalyst pores and heat transfer by conduction and radiation. The complexity of the system arises due to strong interactions between these phenomena. The general form of the governing equations is presented below.

**Momentum balance.** This balance is obtained by application of Newton's second law on a moving fluid element as presented in the classical work of Bird et al. (1960), where usually only pressure drops and friction forces has to be considered (Froment and Bischoff 1990).

\[
\frac{\partial}{\partial t} \rho v = -[\nabla \cdot \rho v v] - \nabla p - [\nabla \cdot \tau] \tag{2.7-1}
\]

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
<th>Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Momentum Rate</td>
<td>Per unit volume</td>
<td></td>
</tr>
<tr>
<td>Convection</td>
<td>Contribution</td>
<td></td>
</tr>
<tr>
<td>Pressure force</td>
<td>Contribution</td>
<td></td>
</tr>
<tr>
<td>Viscous force</td>
<td>Contribution</td>
<td></td>
</tr>
</tbody>
</table>

Most of the time, the computational effort for solving a reactor model that includes the motion equation besides the equations of mass and energy balance is quite demanding. Rather than solving the momentum balance, the velocity profiles are approximated according to the reactor geometry and flow regime (i.e. flat velocity profile for turbulent flow, parabolic velocity profile for laminar flow). Pressure drop can be estimated using empirical correlations (Geankoplis 1993).

**Mass balance.** For a reacting multicomponent mixture the mass conservation for each species i present in the mixture (Bird et al. 1960), is given by
\[
\frac{\partial \rho_i}{\partial t} = -[\nabla \cdot \rho_i \nabla] - \nabla J_i - \sum_j v_{ij} r_j
\] (2.7-2)

Rate of increase of mass concentration of species \( i \) per unit volume

Convection contribution
Diffusion contribution
Chemical reaction contribution

In general terms, the diffusion mass flux, \( J_i \), consists of contribution of concentration, pressure, forced, and thermal diffusion. When the flow is laminar or perfectly ordered the term \( \nabla J_i \), results from molecular diffusion only. It can be written more explicitly as an extension of Fick's law for diffusion in a binary system (Froment and Bischoff 1990):

\[
J_i = \rho \cdot D_{i,m} \nabla \omega_i
\] (2.7-3)

\( D_{i,m} \) is the effective binary diffusivity for the diffusion of the species \( i \) in the multicomponent mixture, and \( \omega_i \) the mass fraction. Using more specific multicomponent diffusion law, such as Stefan-Maxwell can increase the model accuracy, but the computational effort increases.

**Energy Balance.** The rigorous equation of energy balance for a multicomponent system given by Bird et al. (1960) as applied by Forment and Bischoff (1990) in chemical reactors is

\[
\sum_i \rho_i c_{pi} \frac{\partial T}{\partial t} = -\sum_i \rho_i c_{pi} \nabla \cdot \nabla T + \nabla \cdot (\lambda \nabla T) + \sum_j \left( \Delta H_j \right) r_j - \sum_i J_i \Delta H_i + Q_{\text{rad}} \] (2.7-4)

Energy Rate per unit volume
Convection contribution
Conduction contribution
Reaction heat contribution
Molecular diffusion (mixing) contribution
Radiation contribution

The radiative term is significant only at high temperature, and even then it can be lumped with the conductive term by using an effective conductivity for \( \lambda \). The contribution of the molecular diffusion term, \( \sum_i J_i \Delta H_i \), where \( H_i \) are the partial mass enthalpies, is negligible for gaseous mixtures at low pressures that have an almost ideal behaviour (Sandler 1989).
**Continuity equation.** In a closed system the fundamental property of mass conservation needs to be fulfilled.

\[
\frac{\partial \rho}{\partial t} + \nabla \rho v = 0
\]  
(2.7-5)

### 2.7.4 Models for Catalytic Wall Reactors

The modelling and design of CWRs is based on the utilisation of conservation equations discussed in the previous section for gas phase and catalyst layer with appropriate boundary conditions. Several relevant modelling studies published in the literature are summarised in Table 2.8. The number of space dimensions must accommodate an optimal description of the problem. **3D models** require significant computational effort, and are used when a complicated geometry is associated to the reactor (Roduit et al. 1998). In most of the cases, CWRs have a symmetrical geometry and a **2D model** represents a good compromise between the model accuracy and the degree of difficulty required solving it. The lumped **1D models** use average values for the system variables (concentrations, temperature, velocity) instead of cross-sectional distributions, and transverse diffusive transport of heat and mass is estimated by means of global coefficients. Their simplicity brings the advantage of easy solving, but the choice of proper correlation to evaluate the transfer coefficients remains critical. Several modelling studies for catalytic combustor emphasised the discrepancy between the Nu and Sh numbers calculated using a 2D model and the empirical correlation utilised to approximate the interphase resistance (Hayes et al. 1992, 1996; Hayes and Kolaczkowski 1994; 1999; Groppi et al. 1995a, 1995b; Wanker et al. 2000). Another important aspect in modelling CWRs is related to estimation of the intraphase diffusion. For single reactions, with simple kinetics usually first order, intraphase resistance is considered by means of an expression of the effectiveness factor based on Thiele
modulus (Groppi et al. 1995b, Cominos and Gavriilidis 2000). However, for a more complex reaction system and kinetics, the estimation of the intraphase resistances must be obtained by coupling the model of the catalyst layer with the one of gas-phase (Mihail and Teodorescu 1982; Leung et al. 1996; Kolaczkowski and Serbetcioglu 1996; Hayes et al. 1999). Although, neglecting the catalyst thickness is tempting since the computing time can be dramatically reduced (Wanker et al. 2000), this may be a non-realistic assumption especially for fast reactions such as catalytic combustion, when the effectiveness factor have values of the order $10^2$ (Kolaczkowski and Serbetcioglu 1996). The geometry of the catalyst layer may become another error source if a Thiele modulus expression is used. Wanker et al. (2000) presented a fully distributed model for the simulation of a catalytic combustor. Their 2D model describe the laminar flow for propane combustion and includes the conservation equations for momentum, mass and energy. The non-isothermal reaction/diffusion problem is solved for the thin annular shell washcoat geometry. The authors showed that an estimation of the effectiveness factor based on flat plate geometry was misleading. Thus, reactor performance is overestimated at high temperatures, while at low temperature it can lead to an underestimation.
<table>
<thead>
<tr>
<th>Authors</th>
<th>Reaction system</th>
<th>Reactor type</th>
<th>Space Dim.</th>
<th>Interphase resistances</th>
<th>Intraphase resistance</th>
<th>Reaction Homogeneous</th>
<th>Type</th>
<th>Thermal Operation</th>
<th>Solving Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Katz (1959)</td>
<td>1st order</td>
<td>Tubular</td>
<td>2D</td>
<td>-</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>I</td>
<td>A</td>
</tr>
<tr>
<td>Hudson (1965)</td>
<td>1st order</td>
<td>Tubular</td>
<td>2D</td>
<td>-</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>I</td>
<td>A</td>
</tr>
<tr>
<td>Solomon and Hudson (1967)</td>
<td>1st order</td>
<td>Tubular</td>
<td>2D</td>
<td>-</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>I</td>
<td>A</td>
</tr>
<tr>
<td>Smith and Carberry (1975a, 1975b)</td>
<td>Naphthalene oxidation</td>
<td>Tubular</td>
<td>2D</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>EHT</td>
<td>N</td>
</tr>
<tr>
<td>Votruba et al. (1975)</td>
<td>Catalytic combustion</td>
<td>Monolith</td>
<td>1D</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Ad</td>
<td>N</td>
</tr>
<tr>
<td>Young and Finlayson (1976a, 1976b)</td>
<td>CO oxidation</td>
<td>Monolith</td>
<td>2D</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Ad</td>
<td>N</td>
</tr>
<tr>
<td>Mihail and Teodorescu (1982)</td>
<td>Porous Wall</td>
<td>1D-gas</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Ad</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>Chang et al. (1986 a, 1986b)</td>
<td>Consecutive n-th order</td>
<td>Tubular/Parallel Plate</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Ad</td>
<td>N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Goyal et al. (1988)</td>
<td>Fischer Tropsch</td>
<td>Annular</td>
<td>2D</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Ad</td>
<td>A</td>
</tr>
</tbody>
</table>
Table 2.6 Models for Catalytic Wall Reactors (continued). A-analytical; N-numerical.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Reaction system</th>
<th>Reactor type</th>
<th>Space Dim.</th>
<th>Interphase resistances</th>
<th>Intraphase resistance</th>
<th>Reaction</th>
<th>Type</th>
<th>Thermal Operation</th>
<th>Solving Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hayes et al. (1992)</td>
<td>Propane combustion</td>
<td>Monolith</td>
<td>2D</td>
<td></td>
<td>Yes</td>
<td>Yes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hayes and Kolaczkowski (1994)</td>
<td>Propane and CO combustion</td>
<td>Monolith</td>
<td>2D</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Ad</td>
<td>N</td>
</tr>
<tr>
<td>Groppi et al. (1995a, 1995b)</td>
<td>Catalytic combustion</td>
<td>monolith</td>
<td>1D, 2D</td>
<td>Yes, No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Ad</td>
<td>N</td>
</tr>
<tr>
<td>Lawal (1996a, 1996b)</td>
<td>1-st order consecutive</td>
<td>Tubular</td>
<td>2D</td>
<td></td>
<td>Yes</td>
<td>Yes</td>
<td>I</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>Leung et al. (1995)</td>
<td>Propane CO methane combustion</td>
<td>Monolith</td>
<td>2D</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Ad</td>
<td>N</td>
</tr>
<tr>
<td>Wanker et al. (2000)</td>
<td>Propane combustion</td>
<td>Monolith</td>
<td>2D</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Ad</td>
<td>N</td>
</tr>
<tr>
<td>Balakotaiah et al. (2000)</td>
<td>1-st order</td>
<td>Monolith</td>
<td>1D, 2D</td>
<td>Yes, No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Ad</td>
<td>A</td>
</tr>
<tr>
<td>Cominos and Gavrilidis (2001)</td>
<td>Methane combustion</td>
<td>Monolith</td>
<td>2D</td>
<td></td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Ad</td>
<td>N</td>
</tr>
</tbody>
</table>
Most of the methods employed for solving the mathematical models for CWR are numerical, using finite difference or finite element methods (Hayes and Kolaczkowski 1997). Nevertheless, several published papers find analytical solutions for these type of problems (Katz 1959, Hudson 1965, Solomon and Hudson 1967, Dang 1984, Lawal 1996a, 1996b, Balakotaiah 2000). The disadvantages of conventional numerical methods are underlined by Lawal (1996), which showed that the accuracy of numerical solving requires small integral steps and consequently excessive demands on computer storage and CPU time. In addition, numerical solution techniques have to contend with numerical difficulties such as convergence and stability. The analytical solution brings the advantage of an explicit expression for concentration and temperature field with a higher predictive capability of the solution. However, the analytical solution can be obtained only for simple first order kinetics and negligible intraphase resistance.

2.8 Parametric Sensitivity Analysis

2.8.1 Applications for Parametric Sensitivity Analysis

Parametric Sensitivity Analysis (PSA) has various applications in chemical engineering, such as model discrimination, optimisation, control system design, parameter estimation, model simplification, process sensitivity and multiplicity and experimental design (Takamatsu et al. 1970; Rabitz et al. 1983, Ungureanu 1989; Curteanu and Ungureanu 1995, Varma et al. 1999; Kelkar and Ng 1998, 2000). The implementation of PSA for chemical reactors was first identified by Bilous and Amundson (1956). They defined that a chemical reactor operates in the parametric sensitivity region when, for given small variations of some of the input parameters of the reactor, one or more of the outputs undergo large variations.
Historically, most of research on PSA for chemical reactors is related to exothermic reactions and deals with the magnitude of the temperature peak, or hot spot, which almost inevitably develops. Alder and Enig (1964) studied reaction runaway in thermal explosion theory and their work represents one of the early developments in parametric sensitivity approach. Criteria were developed to predict the ignition temperature. Froment and co-workers (Van Welsenaere and Froment 1970, Hosten and Froment 1986) introduced criteria for runaway in fixed bed tubular reactors based on geometrical properties of the temperature profile along the reactor to predict critical values for operation variables. They showed that if there is a positive second derivative of temperature with respect to reactor length before the temperature reaches its maximum, then the approach to maximum temperature is more sudden than when the second derivative is negative. Thus, avoiding positive second derivative could mean avoiding runaway. McGreavy and Adderley (1973) developed a similar criterion based on a heterogeneous model of a fixed bed reactor. The authors underlined the importance of intraphase resistances, especially for cases having the effectiveness factor greater than unity, when the criteria for the quasi-homogeneous models can be misleading. Morbidelli and Varma (1982) provided a necessary and sufficient condition for reactor runaway based on the method of isoclines. For all positive-order exothermic reactions, using the full Arrhenius temperature dependence of the reaction rate, critical values of the heat of reaction and heat transfer parameters beyond which runaway was encountered were derived. The authors concluded that runaway is more likely as the reaction order decreases, the reaction activation energy increases, or as the inlet temperature of the reaction mixture increases.

Although the geometry-based criteria give a fundamentally correct description of thermal runaway, they do not give any measure of runaway intensity. For this purpose
sensitivity-based criteria can be employed. The normalised objective sensitivity is defined as the scaled derivative of the maximum temperature with respect to a certain reactor inlet condition or physico-chemical parameter. Morbidelli and Varma (1988) defined criticality as the situation where the normalised objective sensitivity of the temperature maximum to any of the physico-chemical parameters of the model is a maximum. This criterion was utilised to study a variety of reacting systems. Morbidelli and Varma (1986, 1987) identified parametrically sensitive regions for heterogeneous plug flow reactors. Chemburkar et al. (1986) showed for non-adiabatic CSTRs that if operating conditions are chosen so that to avoid the possibility of parametric sensitivity then steady-state multiplicity is automatically avoided. Tjahjadi et al. (1987) applied the same sensitivity criterion to tubular polymerisation reactors to find design constraints for various operating parameters. Morbidelli and Varma (1989) studied tubular reactors where multiple reactions take place and analysed the connection between thermal runaway and runaway of yield and selectivity. Wu et al. (1998) demonstrated that if one uses reactant conversion instead of reactor axial co-ordinate as independent variable to identify the critical conditions, more conservative runaway boundaries are predicted.

In an attempt to reduce the sensitivity of a catalytic reactor where an exothermic reaction takes place van der Vaart and van der Vaart (1991, 1992), introduced an endothermic reaction in the system. Using various parametric sensitivity criteria they calculated the proportion of the two catalysts to provide insensitive reactor operation.

Apart from run-away criteria, the application of PSA in chemical reactor study is related to quantitatively prediction of the effect of parameter uncertainty on the reactor model. Priestley and Agnew (1975) analysed the catalytic hydrochlorination of acetylene to vinyl chloride in a fixed bed reactor. The authors made use of the temperature variance
concept by the statistical theory as the sum of squares of temperature deviations from its
nominal value due to perturbations in the transport and kinetic parameters. They
calculated further the fractional contribution to the total variance in the system
performance produced by a single parameter. The results of sensitivity calculations
showed that the contribution of the heat transfer parameters to total variance of
temperature is 53% followed by the kinetic parameters by 46%, while the fluid-particle
heat and mass transfer contribution is low, namely 1%. Skilivaniotis et al. (1988)
examined the sensitivity behaviour of a fixed-bed heat exchanger showing that during
experimental measurements the contours of the sensitivity in axial and radial direction
can be used as a guide to locate the sensors at near optimal location. Ungureanu et al.
(1994) employed a quasi-homogeneous two-dimensional mathematical model for a
reactor where the endothermic ethyl-benzene dehydrogenation takes place. Parameters
affecting radial heat transfer such as reactor radius had the greater impact on reactor
sensitivity. Quina et al. (1999) studied the partial oxidation of methanol to
formaldehyde in a fixed bed reactor with two distinct zones: at the entrance the catalyst
is diluted with inert, followed by a region with pure catalyst. It was found that the
system was particularly sensitive to the wall temperature and almost insensitive to mass
transfer parameters.

2.8.2. Sensitivity Concepts and their Computation

Sensitivity analysis general concepts are fully explained in several available text books
(Ungureanu 1988, 1989; Varma et al. 1999). Let us consider a single-variable system
described by a mathematical model specified by the following general differential
equation:

\[
\frac{dy}{dt} = f(y, \Phi, t)
\]  

(2.8-1)
with initial condition:

\[ y(0) = y_0 \]  \hspace{1cm} (2.8-2)

The function \( f \) is assumed to be continuous and continuously differentiable in all its arguments. The first-order local sensitivity, \( s(y; \Phi_j) \), or simply local sensitivity of a dependent variable, \( y \), with respect to the input parameter, \( \Phi_j \), is defined as

\[ s(y; \Phi_j) = \frac{\partial y(t, \Phi_j)}{\partial \Phi_j} \]  \hspace{1cm} (2.8-3)

where \( t \) is the independent variable. "s" is also known as absolute sensitivity. Another quantity commonly used in sensitivity analysis, is the normalised sensitivity, \( S(y; \Phi_j) \) defined as (Rabitz et al. 1983, Varma et al. 1999):

\[ S(y; \Phi_j) = \frac{\Phi_j}{y} \cdot \frac{\partial y}{\partial \Phi_j} = \frac{\Phi_j}{y} \cdot s(y; \Phi_j) \]  \hspace{1cm} (2.8-4)

It can be deduced from its definition that:

\[ S(y; \Phi_j) = \frac{\Phi_j}{y} \cdot \frac{\partial y}{\partial \Phi_j} = \frac{\Phi_j}{y} \lim_{\Delta \Phi_j \to 0} \frac{y(\Phi_j + \Delta \Phi_j) - y(\Phi_j)}{\Delta \Phi_j} = \lim_{\Delta \Phi_j \to 0} \frac{\Delta y}{\Delta \Phi_j} \Rightarrow \]

\[ \frac{\Delta y}{y} = S(y; \Phi_j) \cdot \frac{\Delta \Phi_j}{\Phi_j} \quad (\Delta \Phi_j \to 0) \]  \hspace{1cm} (2.8-5)

In other words, for small enough variation of the input parameter \( \Phi_j \), the percentage variation of the dependent variable can be predicted by multiplying the normalised sensitivity with the corresponding percentage variation of the parameter of interest (Quina et al. 1999). The sign of sensitivity can be positive or negative. When a sensitivity coefficient is positive an increase in the model parameter leads to an increase in the corresponding state variable, and when it is negative the opposite is true.

One of the most common methods for computing sensitivities, is the direct differential method (Varma et al. 1999). It consists of solving simultaneously model and sensitivity
equations for computing local sensitivities. In a single-variable system as described by equation (2.8-1) for the computation of the local sensitivity of $y$ with respect to the $j$th input parameter, $\Phi_j$, one needs to differentiate both sides of the equation (2.8-1) with respect to $\Phi_j$. Then considering the definition (2.8-3) for the local sensitivity one obtains

$$\frac{d(y/\Phi_j)}{dt} = \frac{\partial f}{\partial y} \cdot \frac{\partial y}{\partial \Phi_j} + \frac{\partial f}{\partial \Phi_j}$$

Eq. (2.8-6) represents the local sensitivity equation. Its initial condition can be obtained similarly by differentiating the initial condition (2.8-2). Depending on which input parameter, $\Phi_j$, is chosen the initial condition becomes

$$s(y;\Phi_j)_{t=0} = \begin{cases} 0, & \Phi_j \neq y_0 \\ 1, & \Phi_j = y_0 \end{cases} \quad (2.8-7)$$

By solving simultaneously the model equation (2.8-1) and the sensitivity equation (2.8-6), along with ICs (2.8-2) and (2.8-6) both the dependent variable $y$ and the corresponding local sensitivity $s(y;\Phi_j)$ are obtained as a function of the independent variable $t$. The method can be extended to a multivariable system, by utilisation of the sensitivity matrix $[s^y]$, where $Y$ is the vector dependent variable and $\Phi$ is the vector of input parameters, is calculated.

It is worth noting that the dependent variable, $y$, can be reactant conversion, magnitude of the maximum/minimum temperature, time needed for a reactant to reach a certain conversion, concentration maximum for an intermediate product, or selectivity of a desired product. The input parameter, $\Phi_j$, can be an operating parameter (inlet temperature, composition, flowrates etc), kinetic parameter (pre-exponential factor,
activation energy, reaction order etc), or *geometrical parameter* (reactor volume, diameter etc).
CHAPTER 3

MODELLING OF A CATALYTIC PLATE REACTOR FOR DEHYDROGENATION–COMBUSTION COUPLING

3.1 Introduction.

Large-scale production of ethylene is carried out by pyrolysis (cracking) of hydrocarbon feedstocks in the presence of steam in large, pyrolysis furnaces and subsequent separation of the resultant gas mixture through a complex sequence of unit operations (Sundaram et al. 1994). Steam is added to the feed in order to avoid coke formation. The temperature of the hydrocarbon and steam mixture entering the reactor is 500 - 700 °C. Depending on residence time and feed composition, the reactor outlet temperature is typically between 775 and 950 °C, while the outlet pressure is 150-375 kPa. The heat necessary for the highly endothermic cracking reaction is supplied by firing fuel gas and/or fuel oil using side-wall or floor burners. Only 35 - 50 % of the fire duty is absorbed by the reactor. The remaining heat of the flue gases is used to preheat the feed and generate steam. In addition to ethylene, a wide range of by-products are formed. However, catalytic dehydrogenation can lead to higher selectivity towards ethylene (Buonomo et al., 1997).

In this chapter catalytic ethane dehydrogenation combined with catalytic methane combustion in a Catalytic Plate Reactor (CPR) is modelled utilising a two-dimensional numerical model with “zero catalytic thickness”. The influence of several parameters is investigated in order to gain insight in reactor behaviour and identify suitable ranges of operating conditions.
3.2 Description of the Reacting System

The reaction system consists of the endothermic catalytic ethane dehydrogenation coupled with catalytic combustion in a CPR.

\[ C_2H_6 \leftrightarrow C_2H_4 + H_2 \quad \Delta H = 137 \text{kJ/mol} \quad (3.2-1) \]

\[ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H = -800 \text{kJ/mol} \quad (3.2-2) \]

The intrinsic kinetics used for ethane dehydrogenation is the one determined by Gobina et al. (1995) for a palladium catalyst

\[ r_{C_2H_6} = 4.39 \cdot \exp\left( \frac{-75580}{R_g \cdot T} \right) \cdot \frac{P_{C_2H_6} - P_{C_2H_4} \cdot P_{H_2}}{K_e} \cdot \frac{\text{mol}}{g_{\text{cat}} \cdot \text{s}} \quad (3.2-3) \]

The equilibrium constant, \( K_e \), is given by:

\[ K_e(T) = 1.096 \cdot 10^7 \cdot \exp\left( -\frac{143410}{R_g \cdot T} \right), \text{atm} \quad (3.2-4) \]

The heat required by the endothermic reaction is provided by catalytic methane combustion Depending on the operation conditions and especially at high temperatures (usually above 800 °C) homogeneous reactions may also take place (Pfefferle et al. 1989, Kolaczkowski 1995). In this study reaction temperature is kept below this limit and hence homogeneous reactions are neglected. As discussed in section 2.3.3, where a review of methane oxidation kinetics over supported precious metal catalysts was presented, catalytic combustion of methane usually follows first order kinetics with respect to methane and zero order with respect to oxygen (Cullis et Willatt 1983). These kinetics are adopted in the model, along with a value of 88 kJ/mol for the activation energy.
3.3 Mathematical Model of CPR

A comprehensive 2-D model has been developed for a CPR in order to determine the concentration and temperature distributions inside the reactor. Under the assumption of overall adiabaticity, only the representation of a single plate as shown in Figure 3.1 needs to be utilised, due to symmetry conditions at the centreline of the channels. Thus, three different domains could be identified: channel 1, where the endothermic reaction takes place, channel 2, where catalytic combustion occurs and the solid wall.

![Figure 3.1 Single-plate geometry within the catalytic plate reactor](image)

The model includes heat and mass balances for gas and solid phases. The transport mechanisms considered are convection for axial direction while conduction and diffusion occur in both directions. Assumptions made are as follows: steady state is considered for reactor operation in a co-current flow arrangement; fully developed laminar flow characterises the hydrodynamics in both channels; ideal gas behaviour is assumed; chemical reactions on both sides were considered to take place only on the catalytic walls; catalyst layers were considered thin enough to neglect intraphase transport resistances; heat transfer by radiation and pressure drop along reactor channels are negligible; diffusive mass flux and conductive heat flux at reactor outlet are assumed to be zero.
Table 3.1 Mathematical Model

### GAS PHASE

#### Material Balances:
\[
\rho_j u_{zj} \frac{\partial \omega_{ij}}{\partial z} = \frac{\partial}{\partial x_j} \left( \rho_j D_{j_{i-mixj}} \frac{\partial \omega_{ij}}{\partial x_j} \right) + \frac{\partial}{\partial z} \left( \rho_j D_{j_{i-mixj}} \frac{\partial \omega_{ij}}{\partial z} \right)
\]

#### Energy Balances:
\[
\rho_j u_{zj} c_{pj} \frac{\partial T_j}{\partial z} = \frac{\partial}{\partial x_j} \left( k_j \frac{\partial T_j}{\partial x_j} \right) + \frac{\partial}{\partial z} \left( k_j \frac{\partial T_j}{\partial z} \right)
\]

#### Continuity Equation:
\[
\frac{\partial \rho_j u_{zj}}{\partial z} = 0
\]

#### Equation of State for Ideal Gas
\[
\rho_j = \frac{P_j}{R_j T_j \left( \sum \omega_{ij} \right)^{-1}}
\]

### Boundary Conditions

1. **Inlet conditions:** \( z = 0; \ \forall x_j \)
   - inlet composition: \( \omega_{ij} = \omega_{ij}^0 \)
   - inlet temperature: \( T_j = T_j^0 \)
   - parabolic inlet velocity profile \( u_{zj} = 1.5 \cdot u_{zj}^0 \left[ 1 - \left( x_j / R_j \right)^3 \right] \)

2. **Outlet conditions:** \( z = L; \ \forall x_j \)
   - zero flux \( \frac{\partial \omega_{ij}}{\partial z} = \frac{\partial T_j}{\partial z} = \frac{\partial u_{zj}}{\partial z} = 0 \)

3. **Symmetry conditions at channel centre:** \( \forall z; \ x_j = 0 \)
   - zero flux \( \frac{\partial \omega_{ij}}{\partial x_j} = \frac{\partial T_j}{\partial x_j} = \frac{\partial u_{zj}}{\partial x_j} = 0 \)

4. **Wall conditions:** \( \forall z; \ x_j = R_j \)
   - reacting wall
     \[
     \rho_j D_{j_{i-mixj}} \frac{\partial \omega_{ij}}{\partial x_j} = v_{gj} r_j M_{ij}
     \]
     \[
     j=1, \ k_1 \left. \frac{\partial T_1}{\partial x_1} \right|_{x_1=R_1} = r_1 ( - \Delta H_1 ) + \lambda_s \left. \frac{\partial T_s}{\partial x_s} \right|_{x_s=0}
     \]
     \[
     j=2, \ k_2 \left. \frac{\partial T_2}{\partial x_2} \right|_{x_2=R_2} = r_2 ( - \Delta H_2 ) - \lambda_s \left. \frac{\partial T_s}{\partial x_s} \right|_{x_s=-5}
     \]
   - no slip conditions
     \( u_{zj} = 0 \)
Table 3.1. Mathematical Model (cont.)

### Reaction Rates:

\[
egin{align*}
    r_1 &= k_1^0 \exp \left( -\frac{E_1}{R_s T} \right) \left[ p_{C_2H_6} - p_{C_2H_4} p_{H_2} \right] \\
    r_2 &= k_2^0 \exp \left( -\frac{E_2}{R_s T} \right) c_{CH_4}
\end{align*}
\]

### SOLID WALL:

Laplace’s equation
\[
\frac{\partial^2 T_s}{\partial z^2} + \frac{\partial^2 T_s}{\partial x_s^2} = 0
\]

Boundary conditions:

1. Inlet condition
   \[ z = 0; \quad \forall x_s; \quad \frac{\partial T_s}{\partial z} = 0 \]

2. Outlet condition
   \[ z = L; \quad \forall x_s; \quad \frac{\partial T_s}{\partial z} = 0 \]

3. Dehydrogenation wall
   \[ \forall z; \quad T_s|_{x\_s=0} = T_{1s|x\_s=R_1} \]

4. Combustion wall
   \[ \forall z; \quad T_s|_{x\_s=L} = T_{2s|x\_s=R_2} \]

### j – channel:

1. dehydrogenation;
2. combustion;

### i – chemical species:

- \( i_1 : C_2H_6, C_2H_4, H_2 \);
- \( i_2 : CH_4, O_2, CO_2, H_2O \);

s – solid wall.

The velocity variation in the reactor takes into account the influence of temperature and composition changes so that the global mass balance is satisfied.

\[
\left. \int_0^{R_j} \rho_j u_{z_j} dx_j \right|_{L_z=0} = \left. \int_0^{R_j} \rho_j u_{z_j} dx_j \right|_{L_z=V_z} \quad (3.3-1)
\]

The inlet velocity profile is for fully developed laminar flow between two parallel infinite plates (Coulson et al. 1990). The dependence of the physical properties of chemical species on temperature is accounted for, via the following expressions:

- heat capacity:
  \[
  c_p=a+bT+cT^2+dT^3, \quad (3.3-2)
  \]
  (Hayes and Kolaczkowski, 1997)

- thermal conductivity:
  \[
  k = k_0 \left( \frac{T}{T_0} \right)^{0.75} \quad (3.3-3)
  \]
Modelling of a CPR for Dehydrogenation-Combustion Coupling

- diffusion coefficient: \( D = D_0 \left( \frac{T}{T_0} \right)^{1.75} \)  

\[(3.3-4)\]

(Groppi et al. 1995).

The diffusion coefficients have been calculated for a binary mixture between component \( i \) and \( N_2 \) (dehydrogenation channel) or air (combustion channel). The heat capacity and thermal conductivity of the reaction mixtures are calculated based on local composition.

The mathematical formulation of CPR model is given in Table 3.1, and it consists of mass balances of ethane, ethylene and hydrogen in channel 1, mass balance of methane, oxygen, carbon dioxide and water in channel 2 and heat balances in the two channels and solid phase. Reactor performance is evaluated by means of conversion, which is calculated by integrating the local mass flowrate

\[
X_j(z) = 1 - \frac{\int_{0}^{R_j} \rho_j u_j \omega_{LR_j} \, dx_j}{\int_{0}^{R_j} \rho_j u_j \omega_{LR_j} \, dx_j} \right|_{z=0}
\]

\[(3.3-5)\]

where, \( \omega_{LR} \) is the mass fraction of the limiting reactant, ethane for dehydrogenation channel and methane for combustion channel respectively. After solving the model, concentration and temperature profiles are obtained along axial and radial directions. The influence of catalyst loading, inlet flowrates and wall thermal conductivity is studied.

As shown in Table 3.1, the mathematical model formulated consists of a system of partial differential equations (PDEs). It is solved utilising the general PROcess Modelling System (gPROMS) simulation package (Oh and Pandelides, 1996). gPROMS is a software designed for modelling and simulating processes with both
discrete and continuous characteristics. It allows model developers to write the detailed mathematical equations using a sophisticated natural language. It distinguishes two fundamental types of modelling entity. MODELs describe the physical and chemical laws that govern the intrinsic behaviour of a system, while TASKs are descriptions of the external actions and disturbances imposed on such system. A third type of entity, the PROCESS is formed by a TASK driving a MODEL, thereby defining a complete simulation of the process. The gPROMS input file is given in Appendix A1. The system of integral, partial differential, ordinary differential, and algebraic equations (IPDAEs) defined within gPROMS MODELs are normally solved using the method-of-lines family methods (Oh 1995). This involves discretisation of the distributed equations with respect to all spatial domains, which reduces the problem to the solution of a set of differential algebraic equations (DAEs). The gPROMs language allows the user to specify the type of spatial discretisation method such as for example finite difference methods or orthogonal collocation on finite elements method, order of approximation for partial derivatives and integrals in finite difference methods, and the degree of polynomials used in finite element method, and the number of discretisation intervals/element. The specification of the numerical method is done separately for each distribution domain. Based on the previous experience using gPROMS (Oh 1995, Cominos 2001) to simulate tubular or catalytic wall reactors, orthogonal collocation on finite elements is adopted for the radial direction as the model is predominantly dispersive in that direction (Finlayson 1980). Third-order polynomials over three finite elements are used. Satisfactory convergence is achieved with overall ten grid points. Increasing the total number of grid points increased significantly computational time yet made no significant difference for the temperature and concentration profiles obtained. The backward finite difference method is adopted for the axial direction. Twenty one points are found to be sufficient to achieve satisfactory convergence.
3.4 Results and Discussion

3.4.1 Base Case

In order to establish a reference point, so that the influence of various parameters can be evaluated, calculations are first carried out for a “base case”, for which typical conditions for ethane dehydrogenation are considered, and are given in Table 3.2. On the methane combustion side, for efficiency purposes, an almost stoichiometric methane-air mixture is utilised. Catalyst loading was adjusted by means of pre-exponential factors, in order to keep the reactor temperature below 800 °C, thus avoiding homogeneous reactions. The values of the pre-exponential factors considered for the base case are $A_1=800 \text{ mol/(m}^2\text{s.atm)}$ for the dehydrogenation channel and $A_2=375 \text{ m/s}$ for the combustion channel.

Table 3.2. Data used for base case calculations

<table>
<thead>
<tr>
<th>Operating Conditions</th>
<th>Channel</th>
<th>Ethane Dehydrogenation</th>
<th>Methane Combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet Temperature, °C</td>
<td></td>
<td>650</td>
<td></td>
</tr>
<tr>
<td>Pressure,</td>
<td></td>
<td>atmospheric</td>
<td></td>
</tr>
<tr>
<td>Inlet Composition</td>
<td></td>
<td>C$_2$H$_6$ - N$_2$ mixture</td>
<td>CH$_4$ - Air mixture</td>
</tr>
<tr>
<td>(%(vol.))</td>
<td></td>
<td>50 % C$_2$H$_6$</td>
<td>9.1% CH$_4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 % N$_2$</td>
<td>19.1% O$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>71.8 % N$_2$</td>
</tr>
<tr>
<td>Inlet Average Velocities, m/s</td>
<td></td>
<td>5</td>
<td>4.31</td>
</tr>
<tr>
<td>Flowrate, Nl/s</td>
<td></td>
<td>2.96</td>
<td>2.55</td>
</tr>
<tr>
<td>Reactor Geometry</td>
<td></td>
<td>• parallel plates of 1m x 1m</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• plate thickness: 2 mm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• distance between plates: 2 mm</td>
<td></td>
</tr>
</tbody>
</table>
One of the first issues to examine is the isothermality of the system. For this purpose, radial temperature profiles between channel centrelines, at various axial locations are shown in Figure 3.2. A temperature difference of 8 °C is observed at the channel entrance, between the gas phase and the wall. The gas is at the inlet temperature specified, 650 °C, while the wall becomes hotter due to heat conducted axially from downstream through the wall. As we move along the reactor the radial profiles become less symmetrical and eventually no sharp temperature gradients exist in the cross section. In addition, the highest temperature is observed at the combustion channel wall, since this is where heat is generated. Part of this heat (ca 75 %) is used to drive the endothermic reaction and the rest to heat the reaction mixtures in both channels. The
temperature in the centreline of the dehydrogenation channel is always lower than that of the combustion channel, and this is due to higher flowrate and gas stream heat capacity of the former as compared to the latter. Along the reactor length, temperature increases smoothly and no hot spots develop as demonstrated in Figure 3.3 which shows axial temperature profiles in the middle of the channels. It can be seen that temperature values in the two channels are close to each other, especially towards the end of the reactor where they are almost the same. This demonstrates the efficient thermal communication between channels, which is due to high solid wall conductivity and the relatively small channel height.

![Figure 3.3 Variation of temperature at channel centrelines along the reactor for the base case](image)
For a more detailed examination of reactor thermal behaviour, it is useful to present the evolution of various radial temperature differences as defined in Figure 3.4. The dependence of these differences ($\Delta T_m$, $\Delta T_w$, $\Delta T_1$, $\Delta T_2$) on reactor axial coordinate is shown in Figure 3.5. It is interesting to note that even though the temperature difference between channel centrelines do not exceed 5.1 °C, the temperature difference between centreline and wall for the dehydrogenation channel can reach 8 °C at the entrance (see also Figure 3.2) and ca. 9 °C in the channel interior ($z = 0.3$ m). For the combustion channel $\Delta T_2$ is also 8 °C at the entrance, but in the interior it does not go beyond 4 °C, (see Figure 3.5d). As shown in Figure 5b, radial temperature differences in the solid phase are negligible as a result of high solid thermal conductivity even though large amounts of heat are produced and consumed on the two sides of the wall.
In Figure 3.6a, conversions in both channels and dimensionless temperature in the middle of the solid wall along the reactor length are shown. Methane reaches 89.5 % conversion and ethane 62.2 % conversion which is close to the equilibrium value ($X_e = 74.8 \%$). Figure 3.6b shows the variation of the generated and consumed heat flux from the exothermic and the endothermic reactions respectively, along the reactor length. Combustion proceeds faster than dehydrogenation and as a result more heat is produced by the exothermic reaction than consumed by the endothermic one. The excess heat raises the temperature of the system in the first half of the reactor as illustrated by the temperature profile in Figure 3.6a. In the second half, the difference between heat generated and heat consumed becomes smaller, and as a result solid as well as gas phase temperatures stabilise at approximately 780 °C. It is worth noting that radial concentration gradients were found to be insignificant, indicating efficient mass transfer across the small channels, and are not shown for brevity.
Figure 3.6. Variation of (a) wall dimensionless temperature and conversions for both channels (reference temperature 923 K) and (b) generated and consumed heat fluxes along the reactor for the base case.
Overall, the operating and design parameters chosen for the base case lead to efficient coupling of the two reactions, with a moderate temperature increase of 130 °C along the reactor and with a generated heat flux of ca 3.75 kW/m$^2$.

3.4.2 Influence of Catalyst Loading

The relation between heat generation and heat consumption is important for efficient performance of the CPR. In order to gain further insight into reactor behaviour, the pre-exponential factors have been varied one at a time, keeping all the other parameters constant at their base case values. The pre-exponential factor is a direct measure of catalyst loading or activity, which in turn affects reaction rates and indirectly rate of heat generation or consumption. The ratio of catalyst loading, $K_j$ defined as

$$K_j = \frac{k_j}{(k_j)_{\text{base case}}}$$

(3.4-1)

is used to express the influence of catalyst loading as compared to the base case. Figures 3.7a, b show the changes in reactor behaviour in terms of axial wall temperature profiles and reactant outlet conversions, when the catalyst loading in the combustion channel, $K_2$, is varied. As $K_2$ decreases from the base case to a lower value, catalytic combustion slows down and lower methane conversion is obtained. Consequently, the amount of heat generated is smaller and the temperature at every point along the reactor drops, compared with the base case. Dehydrogenation reaction rate and equilibrium conversion decreases, and as a result lower outlet ethane conversion is obtained. If $K_2$ decreases further to a value of 0.5, heat generated is so small that dehydrogenation makes use of sensible heat available in the gases and a cold spot develops. The reactor cools down until it reaches axial position $z = 0.35$ m, and then the situation reverses. The amount of heat generated becomes larger than heat consumed and temperature starts to increase. When $K_2$ increases, the amount of heat generated is higher and both exit conversions increase. At the same time, a hot spot develops due to the fact that
combustion is faster than the endothermic reaction, heat generation overcomes heat consumption and both streams are heated up. The rise in temperature accelerates the endothermic reaction, which in turn results to an increase of heat consumption so that eventually the temperature drops. These situations may not be desired since hot spots could damage the catalyst on both sides.

Figure 3.7. Wall temperature profiles and outlet conversions in both channels as a function of catalyst loading in combustion side (a, b) and in dehydrogenation side (c,d).

Figures 3.7c, d show results for the case of catalyst loading variation in the dehydrogenation channel, $K_1$, keeping all other parameters at their base case value. Higher values of $K_1$ do not improve performance, on the contrary as the endothermic reaction rate initially increases heat removal rates also increase. Consequently temperature drops and this in turn constrains combustion rate, which is slowed down at
the reactor entrance. In certain cases ($K_i > 1.75$), this cooling effect is so strong that cold spots develop. Overall, $K_i$ increase above its base value, results in lower outlet temperature and concomitant lower conversions. On the other hand, $K_i$ decrease below the base case value, results to hot spots (see Figure 3.7c) and thus larger conversions for both reactants are obtained (see Figure 3.7d). Eventually, when $K_i$ reaches a sufficiently low value, ethane conversion will start decreasing, due to insufficient catalyst activity.

The role played by the ratio of heat generated over heat consumed in the formation of hot or cold spots is illustrated in Figure 3.8, which shows the variation of generated and consumed heat fluxes [calculated by (heat of reaction) x (reaction rate)], for two representative cases. Thus, Figure 3.8a is for $K_i=1.75$ when a cold spot is generated, while Figure 3.8b is for $K_i=0.5$, when a hot spot occurs (all the other parameters are at their base case value). If the consumed heat flux is higher than the generated one, the system starts to cool down resulting to low temperature, which in turn decreases both reaction rates; however the decrease of the endothermic rate is more significant. At a certain location along the reactor ($z=0.15$ in Figure 3.8a) the generated heat flux becomes larger than the consumed one and the system heats up. This results to a minimum in temperature along the reactor (see also Figure 3.7c). The opposite situation occurs when at the reactor entrance, the generated heat flux is higher than the consumed one. The system heats up and both reaction rates increase. Most of the heat available is released in the first half of the reactor where a peak in both heat fluxes is observed. Afterwards though, the generated heat flux decreases rapidly, mainly due to fuel depletion and results to an increase in the endothermic reaction rate and consequently of heat consumption. Thus, after a certain position along the reactor ($z=0.45$ in Figure 8b) the generated heat flux becomes lower than the consumed one, which coincides with a hot spot development (see Figure 3.7c). These results indicate that a balance between heat generation and heat removal is required to avoid excessive temperature gradients.
Figure 3.8. Generated and consumed heat fluxes along the reactor for (a) $K_1=1.75, K_2=1$ and (b) $K_1=0.5, K_2=1$
Figure 3.9 Wall dimensionless temperatures and conversions along the reactor for both channels: (a) inlet velocities 2 times higher than the base case values and (b) inlet velocities and pre-exponential factors 2 times higher than the base case values. Reference temperature, 923 K.
3.4.3 Influence of Flowrates

The influence of the flowrates could be considered through variation of the average inlet velocities. When reactor geometry, inlet operating conditions and catalyst loading are fixed, then variations of flowrates result in corresponding variations of fluid velocities and residence times. Figure 3.9a illustrates how the reactor behaves when both velocities are increased by 100% as compared to the base case. Axial temperature variation becomes smoother (see also Figure 6a), while conversions are significantly decreased to 0.35 for dehydrogenation and 0.54 for combustion compared with 0.62 and 0.89 respectively, for the base case. This is an obvious consequence of the fact that the amount of catalyst on both sides is not enough for these higher flowrates. In order to achieve high conversions one can decrease the inlet velocities (decrease to 50% of their base case values results to $X_{1\text{ outlet}}=0.72$ and $X_{2\text{ outlet}}=1.0$), or increase pre-exponential factors to compensate for higher flowrates. For example, as shown in Figure 9b, a 2 times increase of catalyst loading as compared to Figure 9a, results to $X_{1\text{ outlet}}=0.62$ and $X_{2\text{ outlet}}=0.90$.

3.4.4 Influence of Wall Thermal Conductivity

The thermal conductivity of the wall is an important design parameter, since it influences heat communication between channels as well as along the reactor. Calculations presented so far are based on typical metallic wall thermal conductivity. In the following, reactor behaviour is studied for the case where thermal conductivity is 50 times lower than the base case, keeping everything else constant. This ratio of thermal conductivities is typical of metal/ceramic materials. Figure 3.10 presents channel centreline dimensionless temperature profiles along the reactor for both sides. It can be seen that significant radial temperature differences appear. In addition, hot spots in the axial profiles are observed, while these are not present for the base case calculations.
Modelling of a CPR for Dehydrogenation-Combustion Coupling

(see Figure 3.3). The above behaviour is due to the fact that heat conduction is not efficient enough to transport the large amount of heat generated by the catalytic combustion axially downstream the reactor, as well as radially to the endothermic reaction location. Combustion rate becomes higher and gas temperature increases.

![Graph showing temperature variation at channel centrelines along the reactor. Solid thermal conductivity in 50 times smaller than that of the base-case.](image)

**Figure 3.10.** Variation of temperature at channel centrelines along the reactor. Solid thermal conductivity in 50 times smaller than that of the base-case.

Temperature differences between specific location across the radial direction, as defined in Figure 3.4, are shown in Figure 3.11. Several aspects can be identified by comparing with the base case results of Figure 3.5. Large temperature difference between the two sides of the wall is observed, and reaches a maximum of 22 °C (see Figure 3.11 b). For the base case though, the corresponding maximum does not exceed 0.4 °C (see Figure 3.5b). This is consistent with increased heat transport resistance across the wall. The most significant temperature difference is observed between channel centrelines, as opposed to the base case, where the highest temperature difference is obtained between the gas phase and the channel wall of the dehydrogenation side (compare Figures 3.5
and 3.11). This is due to the shift of the principal heat transfer resistance from the gas phase to the solid phase. Slower axial heat conduction results not only to hot spots as mentioned above, but also it reduces the difference between gas and wall temperatures at the entrance of the reactor, particularly for the dehydrogenation channel (compare Figures 3.5c and 3.11c). An interesting feature is that the gas temperatures can exceed wall temperatures in the second half of the reactor (see Figures 3.11c and 3.11d), something that was not observed for the base case, which indicates the increased contribution of convection as compared to solid phase conduction for heat transport.

![Graphs showing temperature differences](image)

Figure 3.11 Variation of temperature differences (for definitions see Figure 3.4) along the reactor. Solid thermal conductivity is 50 times lower than that of base case.
3.5 Conclusions

Catalytic Plate Reactors (CPRs) represent a novel reactor design (Reay 1993, Charlesworth 1996) that despite its attractiveness has not been implemented in practice yet. Its feasibility is demonstrated from the theoretical point of view by means of the present work. It is proved that such reactors combine reaction with heat exchange in an intensified manner. Although, the autothermal coupling of the exothermic and endothermic reactions by means of indirect heat transfer has been previously presented in the literature (Frauhammer et al 1999, Kolios et al 2001) such approach refers to monolith channels rather than alternate plates. The model is based on a simplified 1D approach and is limited to study mainly the axial temperature profile for a counter-current flow arrangement. Therefore, the features of the present model represent an element of novelty not only due to its formulation based on a 2D-approach, but also due to parametric studies performed. The 2D-approach makes the model more realistic by increasing its capability to capture significant parameters design (i.e. wall thickness, channel gap) and by eliminating the uncertainties introduced by heat and mass transfer coefficients used in a 1D model. The parametric studies performed are valuable to provide guidance for CPR design for a different reaction system than before in a counter-current flow arrangement.

In this work, the endothermic catalytic ethane dehydrogenation in a CPR was modelled and the reactor operation was simulated. Heat required for the reaction was supplied by catalytic combustion of methane. The feasibility of using a CPR for the above reaction system was demonstrated utilising a 2-dimensional theoretical model. By adjusting the ratio of heat generation to heat consumption on the two sides of the reactor smooth axial temperature profiles can be obtained and hot spots avoided. The metallic wall, due to its high thermal conductivity made possible efficient heat transfer between endothermic and exothermic catalyst locations even for small temperature differences. If a wall with low thermal conductivity is employed, not only significantly radial temperature gradients appear but also poor heat transport along axial direction gives rise to hot spots. The ratio of catalyst loadings for the two reactions is a key variable and must be carefully adjusted in order to avoid hot spots or insufficient reactant conversion.
CHAPTER 4

MODELLING OF A CATALYTIC PLATE REACTOR FOR STEAM REFORMING–COMBUSTION COUPLING

4.1 Introduction

Among all potential applications for CPR, small-scale hydrogen production is favoured due to an increasing demand of hydrogen for fuel cells. A small reactor enables the placement of the hydrogen generation unit near the point of use. Methane is a convenient feedstock because the existing natural gas pipeline infrastructure makes it readily available and accessible at any point along the distribution chain. Availability of highly compact hydrogen generators will make possible electrical power generation by fuel cells at central stations, substations, or residences. Currently, hydrogen is industrially produced from methane steam reforming by fixed-bed technology. In order to supply the heat for the overall endothermic steam reforming reaction, the process is carried out inside a furnace equipped with burners (Ridler and Twigg 1989). Replacing conventional combustion by catalytic one eliminates the presence of flame and burners, leading to a significant size reduction.

Hydrogen production in compact reformer for hydrogen production has been studied experimentally by Polman et al. (1999) and Frauhammer et al. (1999). Modelling of autothermal coupling of steam reforming of methane with methane catalytic combustion has been addressed by Kolios and al. (2000). The authors used a one-dimensional model and did not consider intraphase transfer resistances.
In order to fully understand, the CPR behaviour for the system steam reforming / methane combustion, a complex mathematical model, which describes the interactions between the physico-chemical phenomena in the gas phases and catalyst layer is required.

In the present chapter a comprehensive 2D model for a CPR for methane steam reforming coupled with methane catalytic combustion is formulated and solved for two different kinetics of the reaction system. Model complexity is discussed and some simplifications are proposed to reduced the computation effort but at the same time to maintain reasonable accuracy. A comparison to the conventional reformer is made. In addition the influence of several design parameters such as catalyst thickness, catalyst loading, and channel height on reactor thermal behaviour and performance is investigated.

4.2. Model Formulation and Preliminary Studies Based on Simplified Kinetics

4.2.1 Description of the Reaction System

The reaction system considered in this section is the endothermic catalytic steam reforming of methane coupled with catalytic combustion by means of indirect heat transfer in a CPR.

\[ \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3 \text{H}_2 \quad \Delta H = 206 \text{ kJ/mole} \quad (4.2-1) \]
\[ \text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad \Delta H = -803 \text{ kJ/mole} \quad (4.2-2) \]
To model the reaction system, the water gas shift reaction from the steam reforming process and all other secondary reactions (e.g. carbon deposition) are neglected. The overall kinetics for steam reforming is considered to follow a first order dependence on methane concentration modified to account for the reverse reaction (Richardson et al. 1995).

\[
r_{\text{CH}_4} = k_1^0 \exp \left( -\frac{E_1}{R_\text{g} T} \right) \left[ p_{\text{CH}_4} - \frac{\frac{P_{\text{CO}} \cdot P_{\text{H}_2}^3}{K_p \cdot P_{\text{H}_2}\text{O}}} \right] \tag{4.2-3}
\]

For methane catalytic combustion the kinetics has a first order dependence on methane concentration and zero order on oxygen concentration, (Cullis and Willatt 1983).

\[
r_{\text{CH}_4} = k_2^0 \exp \left( -\frac{E_2}{R_\text{g} T} \right) c_{\text{CH}_4} \tag{4.2-4}
\]

### 4.2.2. Formulation of the Mathematical Model

A comprehensive 2-D model has been developed in order to determine the concentration and temperature distributions inside the reactor. Under the assumption of overall adiabaticity, only the representation of a single plate as shown in Figure 4.2.1 needs to be utilised, due to symmetry conditions at the centreline of the channels. Thus, five different domains could be identified: reforming channel, catalyst layer for reforming, the solid wall, catalyst layer for catalytic combustion, and combustion channel. The coordinate system attached to each domain is represented in appendix B1. The model includes heat and mass balances for gas and solid phases. The transport mechanisms considered in channels and the solid wall are convection for axial direction while conduction and diffusion occur in both directions. The distribution of the catalyst and washcoat is assumed uniform along the reactor, so that the catalyst layers may be modelled as a slab of thickness $\delta$, using a one-dimensional approach.
Modelling of a CPR for Steam Reforming - Combustion Coupling

Figure 4.2.1. Single plate geometry within the Catalytic Plate Reactor

The transport mechanisms in the catalyst layer are diffusion and conduction in radial direction. Assumptions made are as follows: steady state is considered for reactor operation in a co-current flow arrangement; fully developed laminar flow for two infinite plates characterise the hydrodynamics in both channels; ideal gas behaviour is assumed; variation of physical properties and velocities with temperature and composition change is accounted for; homogeneous reactions are neglected; heat transfer by radiation and pressure drop along reactor channels are negligible. The equations of the mathematical model are displayed in Table 4.1 for gas phase, catalyst layer and solid wall. The dependence of physical properties and velocity on temperature and composition is similar to the one discussed in section 3.3. The velocity variation in the reactor takes into account the influence of temperature and composition changes so that the global mass balance is satisfied.

\[ \int_{z=0}^{1} \rho_j \mu_{z, j} \, dx \bigg|_{z=0} = \int_{z=0}^{1} \rho_j \mu_{z, j} \, dx \bigg|_{z=2} \]  
(4.2-5)
Table 4.2.1. Mathematical model

**GAS PHASE**

**Material Balances:**

\[ \rho_j \frac{\partial \omega_{i,j}}{\partial z} = \frac{\partial}{\partial \chi_j} \left( \rho_j D_{i,mix,j} \frac{\partial \omega_{i,j}}{\partial \chi_j} \right) + \frac{\partial}{\partial z} \left( \rho_j D_{i,mix,j} \frac{\partial \omega_{i,j}}{\partial z} \right) \]

**Energy Balances:**

\[ \rho_j c_{pj} \frac{\partial T_j^g}{\partial z} = \frac{\partial}{\partial \chi_j} \left( k_j \frac{\partial T_j^g}{\partial \chi_j} \right) + \frac{\partial}{\partial z} \left( k_j \frac{\partial T_j^g}{\partial z} \right) \]

**Continuity Equation:**

\[ \frac{\partial \rho_j u_{z,j}}{\partial z} = 0 \]

**Equation of State for Ideal Gas**

\[ \rho_j = \frac{P_j}{R_g T_j^g} \cdot \frac{1}{\sum_i \frac{\omega_{i,j}}{M_{i,j}}} \]

**Boundary Conditions**

1. Inlet conditions: \( z = 0; \ \forall x_j^g \)
   - inlet composition: \( \omega_{i,j} = \omega_{i,0}^0 \)
   - inlet temperature: \( T_j^g = T_j^0 \)
   - parabolic inlet velocity profile \( u_{z,j} = 1.5 \cdot u_{j,0}^0 \left[ 1 - \left( \frac{x_j^g}{R_j} \right)^2 \right] \)

2. Outlet conditions: \( z = L; \ \forall x_j^g \)
   - zero flux \( \frac{\partial \omega_{i,j}}{\partial z} = \frac{\partial T_j^g}{\partial z} = \frac{\partial u_{z,j}}{\partial z} = 0 \)

3. Symmetry conditions at channel centre: \( \forall z; \ x_j^g = 0 \)
   - \( \frac{\partial \omega_{i,j}}{\partial x_j^g} = \frac{\partial T_j^g}{\partial x_j^g} = \frac{\partial u_{z,j}}{\partial x_j^g} = 0 \)

4. Catalyst surface conditions: \( \forall z; \ x_j^g = R_j \)
   - \( \rho_j D_{i,mix,j} \frac{\partial \omega_{i,j}}{\partial \chi_j^g} \bigg|_{x_j^g = R_j} = -\rho_j D_{eff,j} \frac{\partial \omega_{i,j}^{cat}}{\partial \chi_j^g} \bigg|_{x_j^g = \delta_{cat}} \)
   - \( k_j \frac{\partial T_j^g}{\partial \chi_j^g} \bigg|_{x_j^g = R_j} = -\lambda_{eff,j} \frac{\partial T_j^{cat}}{\partial \chi_j^g} \bigg|_{x_j^g = \delta_{cat}} \)
   - no slip conditions \( u_{z,j} = 0 \)
Table 4.2.1. Mathematical model (cont.)

**CATALYST LAYER**

### Mass Balance

\[
\frac{\partial}{\partial x^\text{cat}} \left( \rho_j D_{\text{eff},i,j} \frac{\partial C_{\text{cat}}}{\partial x^\text{cat}} \right) = -v_{i,j} \cdot r_j \cdot M_{i,j}
\]

### Energy Balance

\[
- \frac{\partial}{\partial x^\text{cat}} \left( \lambda_{\text{eff},i,j} \frac{\partial T^\text{cat}}{\partial x^\text{cat}} \right) = r_j (\Delta H_j)
\]

### Equation of State for Ideal Gas

\[
\rho_j = \frac{P_j}{R_g T^\text{cat}_j} \cdot \frac{1}{\sum_i \omega_{i,j}^{\text{cat}}} \frac{\partial u_{i,j}^{\text{cat}}}{\partial M_{i,j}}
\]

### Boundary Conditions

1. **Inlet conditions:** \( z = 0; \) \( \forall x^\text{cat}_j \)
   - zero flux \( \frac{\partial C_{\text{cat}}}{\partial z} = \frac{\partial T^\text{cat}_j}{\partial z} = 0 \)

2. **Outlet conditions:** \( z = L; \) \( \forall x^\text{cat}_j \)
   - zero flux \( \frac{\partial C_{\text{cat}}}{\partial z} = \frac{\partial T^\text{cat}_j}{\partial z} = 0 \)

3. **Wall conditions:** \( \forall z; \) \( x^\text{cat}_j = 0 \)
   - zero mass flux \( \frac{\partial C_{\text{cat}}}{\partial x^\text{cat}_j} = 0 \)
   - effectiveness factor \( \lambda_{\text{eff},i,j} \frac{\partial T^\text{cat}_j}{\partial x^\text{cat}_j} \bigg|_{x^\text{cat}_j = \delta^\text{wall}} = (-1)^i \cdot \lambda \frac{\partial T^\text{cat}_j}{\partial x^\text{cat}_j} \bigg|_{x^\text{cat}_j = \delta^\text{wall}} \)

4. **Catalyst surface conditions:** \( \forall z; \) \( x^\text{cat}_j = \delta^\text{cat}_j \)
   - mass fraction \( \omega^\text{cat}_j \bigg|_{x^\text{cat}_j = \delta^\text{cat}_j} = \omega^\text{cat}_j \bigg|_{x^\text{cat}_j = \delta^\text{wall}} \)
   - temperature \( T^\text{cat}_j \bigg|_{x^\text{cat}_j = \delta^\text{cat}_j} = T^\text{cat}_j \bigg|_{x^\text{cat}_j = \delta^\text{wall}} \)

### Effectiveness Factor

\[
\eta_j = \frac{D_{\text{eff},i,j}}{\delta^\text{cat}_j \cdot r_j} \bigg|_{x^\text{cat}_j = \delta^\text{cat}_j}
\]

### Heat Flux

\[
H_j = (-\Delta H_j) \cdot \eta_j \cdot r_j^i
\]
### SOLID WALL

Table 4.2.1. Mathematical model (cont.)

<table>
<thead>
<tr>
<th>SOLID WALL</th>
<th>Laplace's equation</th>
<th>( \frac{\partial^2 T_s}{\partial z^2} + \frac{\partial^2 T_s}{\partial x_i^2} = 0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Boundary conditions:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Inlet condition</td>
<td>( z = 0; \ \forall x_i; \ \frac{\partial T_s}{\partial z} = 0 )</td>
<td></td>
</tr>
<tr>
<td>2. Outlet condition</td>
<td>( z = L; \ \forall x_i; \ \frac{\partial T_s}{\partial z} = 0 )</td>
<td></td>
</tr>
<tr>
<td>3. Reforming wall</td>
<td>( \forall z; \ T_{s</td>
<td><em>{x_i=0}} = T</em>{1</td>
</tr>
<tr>
<td>4. Combustion wall</td>
<td>( \forall z; \ T_{s</td>
<td><em>{x_i=\delta</em>{wall}}} = T_{2</td>
</tr>
</tbody>
</table>

Conversion is calculated by integrating the local mass flowrate

\[
X_j(z) = 1 - \frac{\int_{0}^{R_j} \rho_j u_j \omega_{CH_4} \, dx_i}{\int_{0}^{R_j} \rho_j u_j \omega_{CH_4} \, dx_i \bigg|_{z=0}} \quad \text{(4.2-6)}
\]

The averaged diffusivity of a species \( i \), \( D_{M,i} \), has been calculated based on diffusion in the gas phase \( D_{g,i} \) and Knudsen diffusion \( D_{K,i} \) (Hayes and Kolaczkowski 1997) as:

\[
\frac{1}{D_{M,i}} = \frac{1}{D_{g,i}} + \frac{1}{D_{K,i}} \quad \text{(4.2-7)}
\]

The bulk diffusion coefficient was calculated for each species, as a binary mixture air – \( i \) for combustion channel and water – \( i \) for reforming channel, while the Knudsen diffusion coefficient was calculated based on pore radius as:

\[
D_{K,i} = 97 \tau_p \left( \frac{T}{M_i} \right)^{0.5} \quad \text{(4.2-8)}
\]

The effective diffusion coefficient in the catalyst layer is then obtained from the parallel pore model from the equation:

\[
D_{eff} = \frac{\varepsilon}{\tau} D_M \quad \text{(4.2-9)}
\]
The model was solved using gPROMS environment. The gPROMS code formulation is similar with the one used in chapter 2, and is given in Appendix B2.

4.2.3. Results and Discussion

4.2.3.1 Base Case.

In order to establish a reference point, so that the influence of various parameters can be evaluated, calculations are first carried out for a “base case”, for which typical conditions for steam reforming are considered, and are given in Table 4.2.2. The starting point for model parameters selection was based on the experimental work developed at the University of Newcastle, Department of Chemical Engineering (Charlesworth 1996). Individual experimental studies of methane catalytic combustion and steam reforming of methane in small channels with thin film catalyst coated on the wall revealed the achievable ranges for the overall heat flux generated and consumed. Thus, for channels with height up to 2.5 mm and 0.3 m length, having the wall coated with specific catalyst with thickness between 5-20 µm, it was demonstrated that an overall heat flux of 10 kW/m² for combustion and 20 kW/m² for reforming are achievable.

The inlet conditions for steam reforming corresponding to methane: steam molar ratio of 1:3, while the inlet composition for combustion corresponds to a 5 % excess air. The geometry of the channel was fixed at 2 mm channel height and a 0.3 m length. The first main target was to establish a base case where steam reforming of methane can run in almost isothermal conditions using the heat supplied by the catalytic combustion. The industrial temperature rage for steam reforming is typically 770 –1100 K. Experimental observations suggested that temperatures higher than 1100 K may destroy the thin catalyst layer on both combustion and reforming side. Consequently, an inlet
Modelling of a CPR for Steam Reforming - Combustion Coupling

temperature of 1000 K was considered suitable in order to achieve high conversion and to avoid the catalyst destruction. The inlet flowrate and thus the inlet velocities have been estimated by assuming that for 95 % outlet reforming conversion and 100 % combustion conversion an approximately overall heat flux of 8.6 kW/m² can be achieved.

Table 4.2.2 Model parameters used in the calculations

<table>
<thead>
<tr>
<th>Gas Phase</th>
<th>Reforming</th>
<th>Combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inlet conditions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition % (vol)</td>
<td>25 % CH₄, 75 % H₂O</td>
<td>9.1 % CH₄, 90.9 % Air</td>
</tr>
<tr>
<td>Temperature</td>
<td>1000 K</td>
<td></td>
</tr>
<tr>
<td>Pressure</td>
<td>1.1 bar</td>
<td></td>
</tr>
<tr>
<td>Velocity</td>
<td>4 m/s</td>
<td>2.7 m/s</td>
</tr>
<tr>
<td><strong>Geometry</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Length</td>
<td>0.3 m</td>
<td></td>
</tr>
<tr>
<td>Channel Height</td>
<td>2 mm</td>
<td></td>
</tr>
<tr>
<td><strong>Catalyst layer</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness</td>
<td>20 µm</td>
<td></td>
</tr>
<tr>
<td>Pore radius</td>
<td>10 nm</td>
<td></td>
</tr>
<tr>
<td>Porosity</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Tortuosity</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.4 W/mK</td>
<td></td>
</tr>
<tr>
<td><strong>Kinetics</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-exponential factor</td>
<td>222 mol m³·s·kPa</td>
<td>0.82 x 10⁸ s⁻¹</td>
</tr>
<tr>
<td>Activation energy</td>
<td>53326 J/mol</td>
<td>90000 J/mol</td>
</tr>
<tr>
<td><strong>Solid wall</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness</td>
<td>0.5 mm</td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>25 W/m K</td>
<td></td>
</tr>
</tbody>
</table>

After solving the mathematical model, axial and radial temperature and concentration profiles are obtained for all domains. One of the first issues to examine is the thermal behaviour of the system. For this purpose, the temperature profile along radial and axial dimensionless co-ordinates is given in Figure 4.2.2a, while the heat flux generated in the combustion channel together with the heat consumed in the reforming channel along the reactor are given in Figure 4.2.2b. It can be seen that at the reactor entrance the heat
consumed is higher than the heat generated, thus the reaction mixtures cool below the entrance temperature till the heat fluxes equalise at the dimensionless position $\zeta=0.1$, ($\zeta=z/L$), when a minimum in temperature of 990 K occurs. Between the axial dimensionless positions $\zeta=0.1$ and 0.6, the generated heat flux becomes higher than the heat consumed and the temperature starts to increase reaching a maximum of 1017 K. From the axial dimensionless position $\zeta=0.6$ the temperature decreases again so that at the exit the gas phases are only 9 K above the inlet temperature. It is worth noticing that radial temperature gradients are not significant. The radial temperature gradient in the catalyst layers and the solid wall do not exceed 0.5 K.

Figure 4.2.3a and 4.2.3.b show methane concentration profiles in the reforming side and combustion side respectively for gas phase and catalyst layer. It can be seen that concentration radial gradients in gas phase are smaller than the ones of the solid phase. Conversions in both channels calculated by averaging the methane concentration in the cross section are displayed in Figure 4.2.4 together with the effectiveness factors along the reactor dimensionless axial co-ordinate. Reforming outlet conversion is 0.88 while for combustion is 0.93. The results showed that the effectiveness factor was in the range 0.77 – 0.79 for combustion channel, and 0.65 – 0.67 for reforming channel.

The results for the base case suggest that the heat resistances in the catalyst layers are very small, while the mass intraphase resistances are substantial even for thin catalyst layer thickness of the order of micrometers. Thus, in order to decrease the model complexity, it is justified to neglect the temperature gradients in the catalyst layer, while neglecting the mass intraphase resistances can be misleading, resulting in overestimation of the CPR performance.
Figure 4.2.2. CPR thermal behaviour for base case
a. Temperature profile; b. Heat flux consumed and generated along the reactor
Figure 4.2.3. Methane concentration profiles channel and its catalyst layer for base case 
a. reforming side; b. combustion side
Figure 4.2.4. Conversions and effectiveness factors along the reactor for base case

4.2.3.2 Influence of Catalyst Thickness for Constant Overall Catalyst Loading.

The catalyst thickness was increased by a factor of 2 and 3 relative to the base case, keeping constant the overall catalyst activity per unit area (the pre-exponential factors were decreased accordingly). Figure 4.2.5 shows the main changes in reactor performance and thermal behaviour for different thickness. An increase of catalyst thickness is expected to lower the outlet conversions due to higher mass intraphase resistance (see Figure 4.2.5c). This is indeed the case for the reforming side. However, for the combustion side a doubled catalyst thickness results in higher conversion. Increasing further the thickness leads to a slightly lower conversion (Figure 4.2.5a). The changes of intraphase resistance alter the ratio between heat produced and heat consumed which in turn affects the temperature profiles along the channels, as can be seen in Figure 4.2.5b. Higher catalyst temperatures can compensate the lower reactant concentrations for the exothermic reaction, which has large activation energy, but not for the endothermic one.
Figure 4.2.5. Changes in CPR performance and thermal behaviour with variation of catalyst layer thickness for constant overall catalyst loading: a. Outlet reactor conversions; b. Wall dimensionless temperature profiles; c. Effectiveness factors along reactor
Since the difference between outlet conversions is enlarged with the increase of catalyst thickness, the corresponding outlet temperature is also higher, namely 55 K for 40 μm and 76 K for 60 μm above the inlet temperature compared to only 9 K for the base case (20 μm). This once again suggests the influence of intraphase resistances not only on the final conversions but also on the thermal behaviour.

4.2.3.3 Influence of Catalyst Loading

The catalyst loading was varied by increasing the catalyst thickness without altering the pre-exponential factors. The CPR performance and thermal behaviour are illustrated in Figure 4.2.6, in terms of conversion (Figure 4.2.6.a), wall temperature profiles (Figure 4.2.6.b) and effectiveness factors (Figure 4.2.6.c).

As expected an increase in the amount of catalyst increases the CPR conversions in both channels (Figure 4.2.6.a) despite lowering the effectiveness factors (Figure 4.2.6.c). In addition, a temperature increase is observed compared to the base case along the channel. This indicates a stronger effect of changes in catalyst loadings in the first third of the reactor on combustion reaction rate, where both reaction mixtures contain high reactant concentrations. However, due to a higher amount of catalyst also in the reforming channel, it is possible to consume the additional heat produced in the system and obtain higher reforming outlet conversions. This though is achieved at the expense of more significant hot spots.
Figure 4.2.6. Changes in CPR performance and thermal behaviour with variation of catalyst loading: a. Outlet reactor conversions; b. Wall dimensionless temperature profiles; c. Effectiveness factors along reactor.
4.3 Model Refinement and Simulation

The reforming kinetics used in the previous section neglect both reverse methanation and water gas shift reaction and is thus a simplification of the reaction system involved in the steam reforming process. Therefore, in the present section, these two reactions are considered along with the steam reforming reaction. In addition, same simplifications are applied to the CPR model presented in section 4.2, in order to reduce the computational effort. A base case has been generated considering the same inlet average velocity for the reforming channel as in the previous section. Inlet composition and temperature were considered similar to the industrial process (Xu and Froment 1989b). It has been aimed to investigate the situation when combustion is used not only to provide the heat for the endothermic process but also to heat up both reaction mixtures. After solving the model, concentration and temperature profiles are obtained along axial and radial directions. The influence of channel height, and catalyst thickness for constant residence time is investigated. The performance of steam reforming of methane in a CPR is compared to the conventional process.

4.3.1. Description of Reacting System

As discussed in section 2.5, steam reforming of methane is based on a complex reaction system, consisting of three main reactions

- methane steam reforming \( \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \) \( \Delta H = +206.1 \text{kJ/mol} \) (4.3-1)
- water gas-shift \( \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \) \( \Delta H = -41 \text{kJ/mol} \) (4.3-2)
- reverse methanation \( \text{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 4\text{H}_2 \) \( \Delta H = +164 \text{kJ/mol} \) (4.3-3)
Side reactions may involve carbon deposition that can be suppressed by using an excess of steam at minimum molar ratio steam: methane of 1.7 (Ridler and Twigg 1989). The composition adopted in this study refers to a molar ratio steam: methane higher than 1.7, consequently the reactions leading to carbon deposition have been neglected.

A large number of kinetic rate expressions for steam reforming of methane is reported in the literature, and most of them have been revised in section 2.5.2, Table 2.5. A study by Elnashaie et al. (1990) shows that the general rate equation based on Langmuir-Hinshelwood-Hougen-Watson (LHHW) approach, developed by Xu and Froment (1989a) describes the process most accurately for a wide range of parameters. Consequently, these kinetics are used in the present work to describe the steam reforming process. The rate equations characteristic to the chemical reactions (4.3-1), (4.3-2), and (4.3-3) are:

\[
\begin{align*}
    r_1 &= \frac{k_1}{p_{H_2}^{0.5}} \left( \frac{p_{CH_4} \cdot p_{H_2O} - p_{H_2}^3 \cdot p_{CO}}{K_{e,1}} \right) \left( \text{Den} \right)^2, \text{ kmol/kg}\_\text{cat}/h \quad (4.3-4) \\
    r_2 &= \frac{k_2}{p_{H_2}^2} \left( \frac{p_{CO} \cdot p_{H_2O} - p_{H_2}^2 \cdot p_{CO_2}}{K_{e,2}} \right) \left( \text{Den} \right)^2, \text{ kmol/kg}\_\text{cat}/h \quad (4.3-5) \\
    r_3 &= \frac{k_3}{p_{H_2}^{3.5}} \left( \frac{p_{CH_4} \cdot p_{H_2O}^2 - p_{H_2}^4 \cdot p_{CO_2}}{K_{e,3}} \right) \left( \text{Den} \right)^2, \text{ kmol/kg}\_\text{cat}/h \quad (4.3-6)
\end{align*}
\]

where: \( \text{Den} = 1 + K_{CO}p_{CO} + K_{H_2}p_{H_2} + K_{CH_4}p_{CH_4} + K_{H_2O}p_{H_2O}/p_{H_2} \) \quad (4.3-7)

The values of the pre-exponential factor, activation energies, heats of chemisorption, and equilibrium constants are given in section 2.5.2.
The advantages of catalytic combustion of methane along with representative kinetics have been discussed in section 2.4.1. For the current calculations, first order kinetics with respect to methane, and zero order with respect to hydrogen were utilised in the calculation along with activation energy of 90 kJ/mol and pre-exponential factor of $4 \times 10^8$ s$^{-1}$.

4.3.2. Mathematical Model

The results obtained in the previous section suggest that certain simplifications can be made to the mathematical model without affecting the model accuracy. Thus, it was shown that the temperature radial gradients in the catalyst layer are not significant, consequently both catalyst layers have been considered isothermal. The boundary conditions for the energy balance have been modified accordingly. The heat flux generated or consumed along the reactor have been calculated as

$$H_j = \sum_k \left( - \Delta H_{k,j} \cdot \int_0^{\delta_{c,0}} \frac{r_{k,j} dx_{j,cat}}{} \right)$$ (4.3-8)

where $\Delta H_{k,j}$ and $r_{k,j}$ are the heat and rate of reaction $k$, in channel $j$. The values of heat fluxes were used in the boundary condition related to the interface between each channel and the solid wall.

The effectiveness factor has been calculated for each reaction by integrating the reaction rate across the catalyst layer:

$$\eta_{\text{eff},k,j} = \frac{1}{\delta_{\text{cat},j}} \int_0^{\delta_{\text{cat},j}} \frac{dx_{j,\text{cat}}}{r_{k,j}(x_{j,\text{cat}})}$$ (4.3-9)
Table 4.3.1. Mathematical model

**GAS PHASE**

**Material Balances:**

\[
\rho_j u_{jz} \frac{\partial \omega_{i,j}}{\partial z} = \frac{\partial}{\partial x_j} \left( \rho_j D_{i-\text{mix}} \frac{\partial \omega_{i,j}}{\partial x_j} \right) + \frac{\partial}{\partial z} \left( \rho_j D_{i-\text{mix}} \frac{\partial \omega_{i,j}}{\partial z} \right)
\]

**Energy Balances:**

\[
\rho_j u_{jz} c_{pj} \frac{\partial T_j^g}{\partial z} = \frac{\partial}{\partial x_j} \left( k_j \frac{\partial T_j^g}{\partial x_j} \right) + \frac{\partial}{\partial z} \left( k_j \frac{\partial T_j^g}{\partial z} \right)
\]

**Continuity Equation:**

\[
\frac{\partial \rho_j u_{jz}}{\partial z} = 0
\]

**Equation of State for Ideal Gas**

\[
\rho_j = \frac{P_j}{R_g T_j^g} \frac{1}{\sum_i \omega_{i,j}^g M_{i,j}}
\]

**Boundary Conditions**

1. Inlet conditions: \( z = 0; \ \forall x_j^g \)
   - inlet composition: \( \omega_{i,j}^g = \omega_{i,j}^0 \)
   - inlet temperature: \( T_j^g = T_j^0 \)
   - parabolic inlet velocity profile \( u_{jz} = 1.5 \cdot u_j^0 \left[ 1 - \left( \frac{x_j^g}{R_j} \right)^2 \right] \)

2. Outlet conditions: \( z = L; \ \forall x_j^g \)
   - zero flux \( \frac{\partial \omega_{i,j}^g}{\partial z} = \frac{\partial T_j^g}{\partial z} = \frac{\partial u_{jz}}{\partial z} = 0 \)

3. Channel centre: \( \forall z; \ x_j^g = 0 \)
   - symmetry \( \frac{\partial \omega_{i,j}^g}{\partial x_j^g} = \frac{\partial T_j^g}{\partial x_j^g} = \frac{\partial u_{jz}}{\partial x_j^g} = 0 \)

4. Catalyst surface conditions: \( \forall z; \ x_j^g = R_j \)

\[
\rho_j D_{i-\text{mix}} \left. \frac{\partial \omega_{i,j}^g}{\partial x_j} \right|_{x_j^g=R_i} = -\rho_j D_{\text{eff-}j} \left. \frac{\partial \omega_{\text{cat}}}{\partial x_j} \right|_{x_j^g=R_i}
\]

\[
\begin{align*}
\text{j=1,} \quad k_1 \left. \frac{\partial T_j^g}{\partial x_j^g} \right|_{x_j^g=R_i} = & H_1 + \lambda_s \left. \frac{\partial T_s}{\partial x_s} \right|_{x_s=0} \\
\text{j=2,} \quad k_2 \left. \frac{\partial T_j^g}{\partial x_j^g} \right|_{x_j^g=R_s} = & H_2 - \lambda_s \left. \frac{\partial T_s}{\partial x_s} \right|_{x_s=0}
\end{align*}
\]

- no slip conditions \( u_{jz} = 0 \)
Table 4.3.1. Mathematical model (cont.)

**CATALYST LAYER**

**Isothermal in Radial Direction** \( T_{j}^{\text{cat}} = T_{j}^{g} \big|_{x_{j} = l} \)

**Mass Balance**

\[
\frac{\partial}{\partial x_{j}^{\text{cat}}} \left( \rho_{j} D_{n,i,j} \frac{\partial \omega_{i,j}^{\text{cat}}}{\partial x_{j}^{\text{cat}}} \right) = -\sum_{k} \left( v_{i,k,j} \cdot r_{k,j} \cdot M_{i,j} \right)
\]

**Equation of State for Ideal Gas**

\[
\rho_{j} = \frac{P_{j}}{R_{g} T_{j}^{\text{cat}}} \cdot \frac{1}{\sum_{i} \omega_{i,j}^{\text{cat}}} M_{i,j}
\]

**Boundary Conditions**

1. Inlet conditions: \( z = 0 \); \( \forall x_{j}^{\text{cat}} \)
   - zero flux \( \frac{\partial \omega_{i,j}^{\text{cat}}}{\partial z} = 0 \)

2. Outlet conditions: \( z = L \); \( \forall x_{j}^{\text{cat}} \)
   - zero flux \( \frac{\partial \omega_{i,j}^{\text{cat}}}{\partial z} = 0 \)

3. Wall conditions: \( \forall z \); \( x_{j}^{\text{cat}} = 0 \)
   - zero flux \( \frac{\partial \omega_{i,j}^{\text{cat}}}{\partial x_{j}^{\text{cat}}} = 0 \)

4. Catalyst surface conditions: \( \forall z \); \( x_{j}^{\text{cat}} = \delta_{\text{cat}j} \)
   \( \omega_{i,j}^{\text{cat}} \big|_{x_{j} = R_{j}} = \omega_{i,j}^{\text{cat}} \big|_{x_{j} = 0} \)

**Effectiveness Factor**

\[
\eta_{\text{eff};k,j} = \frac{\frac{1}{\delta_{\text{cat}j}} \cdot \int_{0}^{\delta_{\text{cat}j}} r_{k,j}^{\text{cat}} dx_{j}^{\text{cat}}}{\int_{0}^{\delta_{\text{cat}j}} r_{k,j}^{\text{cat}} dx_{j}^{\text{cat}}} = 0
\]

**Heat Flux**

\[
H_{j} = \sum_{k} \left( -\Delta H_{k,j} \cdot \left[ r_{k,j}^{\text{cat}} \right]_{0}^{\delta_{\text{cat}j}} \right)
\]

**SOLID WALL**

**Laplace's equation**

\[
\frac{\partial^{2} T_{j}^{s}}{\partial z^{2}} + \frac{\partial^{2} T_{j}^{s}}{\partial x_{s}^{2}} = 0
\]

**Boundary conditions:**

1. Inlet condition \( z = 0 \); \( \forall x_{s} \); \( \frac{\partial T_{j}^{s}}{\partial z} = 0 \)

2. Outlet condition \( z = L \); \( \forall x_{s} \); \( \frac{\partial T_{j}^{s}}{\partial z} = 0 \)

3. Reforming wall \( \forall z \); \( T_{j}^{s} \big|_{x_{s} = 0} = T_{j} \big|_{x_{s} = R_{1}} \)

4. Combustion wall \( \forall z \); \( T_{j}^{s} \big|_{x_{s} = d} = T_{j}^{s} \big|_{x_{s} = R_{2}} \)
Table 4.3.1. Mathematical model (cont.)

<table>
<thead>
<tr>
<th>Subscripts:</th>
</tr>
</thead>
<tbody>
<tr>
<td>i – chemical species</td>
</tr>
<tr>
<td>j – reaction mixture</td>
</tr>
<tr>
<td>k – reaction</td>
</tr>
<tr>
<td>s – solid wall</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>j=1 Reforming</th>
</tr>
</thead>
<tbody>
<tr>
<td>i= CH₄, H₂O, CO, CO₂, H₂, N₂;</td>
</tr>
<tr>
<td>k=1 methane steam reforming reaction</td>
</tr>
<tr>
<td>CH₄+H₂O ⇄ CO+3H₂</td>
</tr>
<tr>
<td>k=2 water gas shift reaction</td>
</tr>
<tr>
<td>CO+H₂O ⇄ CO₂+H₂</td>
</tr>
<tr>
<td>k=3 reverse methanation reaction</td>
</tr>
<tr>
<td>CH₄+2H₂O ⇄ CO₂+4H₂</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>j=2 Combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td>i= CH₄, O₂, CO₂, H₂O, N₂;</td>
</tr>
<tr>
<td>k=1 methane catalytic combustion</td>
</tr>
<tr>
<td>CH₄+ 2O₂ → CO₂+2H₂O</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Superscripts:</th>
</tr>
</thead>
<tbody>
<tr>
<td>g – gas phase</td>
</tr>
<tr>
<td>cat – catalyst layer</td>
</tr>
</tbody>
</table>

The mathematical formulation of CPR model is given in Table 4.3.1, and it consists of mass balances of all species in the gas phase and the catalyst layers and heat balances in the both reforming and combustion channel, and solid wall. The corresponding gPROMs code used to solve the model is given in Appendix B3.

4.3.3 Results and Discussion

4.3.3.1 Base Case

The conditions used in the calculations for the base case are given in Table 4.3.2. The inlet conditions, for the reforming side, are similar to the ones used by Xu and Froment (1989b), except for the total pressure. The present calculations use a value close to the atmospheric pressure, while calculations presented by Xu and Froment (1989a) use a 29 bar pressure characteristic to industrial operation. CPRs are expected to operate at low pressure due to their specific application for fuel cell or small-scale production. The
inlet reforming composition is typical for an industrial reforming, it correspond to a steam : methane ratio of 3.358 having small amounts of CO₂, H₂ and N₂. On the methane combustion side, an almost stoichiometric air-methane mixture was used. An inlet temperature of 793 K is typical for industrial steam reforming. Thus, the base case aims to investigate the situation when catalytic combustion is used simultaneously to provide heat for the endothermic process and to heat up both reaction mixtures, reproducing an increasing temperature profile between 793 – 1060 K which is representative for the conventional steam reforming process. This may allow comparing the CPR and conventional reformer for the same thermal behaviour. The inlet average velocity in the reforming channel has been fixed at 4 m/s, as in the previous section, while the inlet velocity, and consequently the inlet flowrate, in the combustion channel has been approximated based on an overall heat balance. The data for reforming catalyst used in the calculations are the ones presented by Xu and Froment (1989a) and correspond to a catalyst containing 15.2 % Ni, supported on magnesium spinel. The catalyst layer density was considered 2 355 kg/m³. The pre-exponential factor of the catalytic combustion was adjusted in order to obtain a temperature profile similar to the one characteristic to the conventional reformer. For both catalysts layer a pore radius of 10 nm, together with a porosity of 0.4 and a tortuosity factor of 4 were considered. These values are typical for both combustion and reforming catalysts. (Xu and Froment 1989, De Deken et. al. 1982; Groppi et al. 1994). After solving the mathematical model the temperature and concentration profiles are obtained as a function of axial and radial co-ordinate of the reactor.
Table 4.3.2. Data used for base case calculations

<table>
<thead>
<tr>
<th>Gas Phase</th>
<th>Reforming</th>
<th>Combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inlet conditions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition % (vol)</td>
<td>21.28 % CH₄, 71.45 % H₂O, 1.19 % CO₂, 2.60 % H₂, 3.48 % N₂</td>
<td>9.1 % CH₄, 90.9 % Air</td>
</tr>
<tr>
<td>Temperature</td>
<td>793 K</td>
<td></td>
</tr>
<tr>
<td>Pressure</td>
<td>1.1 bar</td>
<td></td>
</tr>
<tr>
<td>Velocity</td>
<td>4 m/s 3.2 m/s</td>
<td></td>
</tr>
<tr>
<td><strong>Geometry</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Length</td>
<td>0.3 m</td>
<td></td>
</tr>
<tr>
<td>Channel Height</td>
<td>2 mm</td>
<td></td>
</tr>
<tr>
<td><strong>Catalyst layer</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness</td>
<td>20 μm</td>
<td></td>
</tr>
<tr>
<td>Pore radius</td>
<td>10 nm</td>
<td></td>
</tr>
<tr>
<td>Porosity</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Tortuosity</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.4 W/mK</td>
<td></td>
</tr>
<tr>
<td><strong>Kinetics</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-exponential factor</td>
<td>See Table 2.5</td>
<td>4 x 10⁸ ¹/s</td>
</tr>
<tr>
<td>Activation energy</td>
<td>See Table 2.5</td>
<td>90000 J/mol</td>
</tr>
<tr>
<td><strong>Solid wall</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness</td>
<td>0.5 mm</td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>25 W/m K</td>
<td></td>
</tr>
</tbody>
</table>

**Thermal behaviour and heat transfer efficiency.** The first issue to examine is the effect of the thermal coupling of steam reforming with catalytic combustion in terms of evolution of both exothermic and endothermic conversion. The wall temperature along the reactor is shown in Figure 4.3.1a. It can be seen that it increases from its inlet value of 793 K to 1058 K at the outlet. This axial temperature profile is similar to the temperature profile along a tube filled with catalyst within a conventional reformer obtained by Xu and Froment (1989b). An outlet conversion of 98 % for combustion and 95 % for reforming together with a molar ratio CO₂/CO = 0.579 are achieved. Figure 4.3.1b shows the absolute values of the heat fluxes generated in the combustion reaction.
and consumed in the reforming ones along the reactor. Thus, an adequate catalyst loading in the combustion channel provides the necessary heat flux to heat up both reaction mixtures and to drive the endothermic process at the same time. The maximum in the heat flux generated and consumed are located at the same axial position, namely 0.35. A decrease in the heat flux consumed is observed near the reactor entrance as a consequence of the trends in the reaction rates of the endothermic process that follow a LHHW behaviour, see also Figure 4.3.3 b.

In order to estimate how much from the heat generated in the endothermic side has been consumed strictly by the endothermic process, a thermal efficiency is defined as:

$$
\eta_{\text{thermal}} = \frac{\text{Heat consumed in the endothermic process}}{\text{Heat generated in the exothermic process}}
$$

(4.3-10)

For the base case a thermal efficiency of 66.7 % is obtained corresponding to the heat generated by methane catalytic combustion, which is used by the exothermic process while the rest is necessary to heat up both reaction streams.
Figure 4.3.1 CPR behaviour
a. Conversions and wall dimensionless temperature; b. Heat fluxes generated and consumed in combustion and reforming process respectively.
Next issue to examine is the magnitude of the radial temperature gradients. Figure 4.3.2a shows the wall temperature gradient, defined as the difference between the temperature of the combustion wall and reforming wall, \( \Delta T_w = T_{\text{combustion, wall}} - T_{\text{reforming, wall}} \), along the axial dimensionless co-ordinate. The high thermal conductivity of the metallic wall makes possible an efficient heat transfer at a temperature difference lower than 0.5 K. Further, in Figure 4.3.2b the temperature gradient in the gas phase, defined as the difference between the temperature of the gas phase at wall and the channel centre, \( \Delta T_g = T_{\text{wall}} - T_{\text{channel, centre}} \), is shown for combustion and reforming channel. As long as the heat flux generated is higher than the heat flux consumed, the wall temperature is higher than the gas phase temperature. The maximum temperature radial gradient is 35 K for reforming and 41 K for combustion. It can be seen that the radial temperature gradients are similar for the first 20% of the reactor length, while afterwards the temperature gradients in the reforming channel are lower than the ones in the combustion one. This can be explained by the fact that hydrogen generation in the reforming channel increases significantly the thermal conductivity of the reforming gas mixture compared to the combustion gas mixture, resulting in a more efficient heat transfer across the channel. Towards the end of the channel, axial position 0.8, the gradients change sign which means that the wall temperature becomes lower than the gas phase temperature. The consumed heat fluxed in the endothermic channel becomes slightly higher than the heat flux generated by combustion around the reactor exit, see also Figure 4.3.1b, thus the wall is slightly cooler than the gas phase.
Figure 4.3.2 Radial Temperature Gradients

a. in the solid wall $\Delta T_w = T_{combustion \_ wall} - T_{ref \_ wall}$

b. in the gas phase $\Delta T_g = T_{wall} - T_{channel \_ central}$
Mass transfer and chemical reactions. One important aspect to determine is the significance of the intraphase resistance. The effectiveness factors for all reactions involved have been calculated as shown in Table 4.3.1 and they are plotted in Figure 4.3.3a, while Figure 4.3.3b shows the reaction rates at the catalyst surface. Near the reactor entrance due to low hydrogen concentration both reforming and reverse methanation are fast, so that the effectiveness factors of these reactions have a minimum at the reactor inlet. They reach the maximum values of 0.62 and 0.49 respectively at the dimensionless axial position of 0.15, afterwards their value decrease up to 0.32 for both reforming and reverse methanation. The effectiveness factor of water gas shift reaction has a very high value at the reactor inlet, due to the fact that the CO is not present in the inlet mixture. Consequently the water gas shift rate is nearly zero at the catalyst surface giving an infinite large number for the effectiveness factor. Within the catalyst layer while the steam reforming is taking place the CO is generated and the rate of water gas shift is higher in the catalyst layer than at the catalyst surface. Along the reactor, the effectiveness factor for this reaction is maintained between 2 and 0.9. Comparing the values for the reaction rates present in the reforming channel, Figure 4.3.3b, it can be seen that the predominant reaction is steam reforming of methane, however neither water gas shift nor reverse methanation can be neglected, their contribution being significant. The effectiveness factor range of 0.9 – 0.35 for the combustion indicates also a significant intraphase resistance in the exothermic channel.
Figure 4.3.3 Mass resistances and chemical reaction in CPR
a. effectiveness factors along reactor; b. reaction rates at the catalyst surface along reactor
4.3.3.2 Comparison between the isothermal and non-isothermal operation

Although the cases presented in the section 4.2 and 4.3 use different kinetics expression for steam reforming side, several aspects can be discussed in order to compare the CPR behaviour for almost isothermal and non-isothermal operation (see Figures 4.2.2a and 4.3.1a). So far, it has been shown that during the autothermal coupling in a CPR, the catalytic combustion can be used to supply simultaneously the heat necessary to drive the endothermic process and to heat up both reaction mixtures provided that the necessary amount of fuel is made available and at the same time the catalyst loading provide an adequate local rate of heat generation (see also section 3.4.2). The theoretical investigation showed that for the non-isothermal operation a pre-exponential factor for the combustion kinetics approximately 5 times higher than for the isothermal operation would be necessary. A successful practical implementation of CPR requires the availability of suitable catalysts to meet such demand.

For isothermal operation the local heat fluxes (see figure 4.2.2b) are very close to each other and have a decreasing profile from the inlet towards the outlet mainly due to reactants depletion. Moreover, during the non-isothermal operation (see figure 4.31b) the heat flux generated is higher than the heat flux consumed along most part of the reactor length, the difference being used to heat up both the reaction mixtures. In addition, both heat fluxes have a maximum as a result of the opposite effect of increasing temperature and reactant depletion on the reaction rates along the reactor.

The magnitude of radial temperature gradients across the solid wall is similar (see figure 4.2.2a and 4.3.2a) namely below 0.5 K. However, the radial temperature gradients in the gas phase are larger for the non-isothermal operation. Thus, for isothermal operation the
absolute values of the difference between the wall temperature and the gas phase temperature at the channel centre do not exceed 4.6 K for reforming and 3 K for combustion (see Figure 4.2.2a), while for non-isothermal operation these are 35 K for reforming and 41 K for combustion occur (see Figure 4.3.2 b). The values of the Peclet number defined as the ratio of transversal conduction resistance $\delta/k_f$ and the axial convection resistance $1/\rho c_p u_z$, is $Pe = u_z \delta/\alpha > 10$ for both channels, meaning that the convection in the axial direction is the dominant heat transfer mechanism (Kaviany 2002). Thus, the excess heat flux generated at the wall rather flows downwards the channel rather than penetrating by conduction across it. For non-isothermal operation when the fluid has lower temperature at the inlet, this generates radial temperature gradients whose magnitude is proportional to the magnitude of excess of the heat flux generated at wall.
4.3.3.3 Influence of Channel Gap

4.3.3.3.1 Influence of Channel Gap at Constant Catalyst Residence Time.

The catalyst residence time, defined as the ratio between the amount of catalyst and the inlet molar flowrate of methane is directly proportional to catalyst thickness and reactor length and inverse proportional to inlet velocity and channel gap:

$$\tau_w \propto \frac{\delta_{ext} \cdot L}{u_z^0 \cdot R} \quad (4.3-11)$$

The influence of channel gap, expressed in the mathematical model by the parameter $R$, on CPR behaviour was studied by keeping constant the product $u_z^0 \cdot R_j$, thus the inlet methane molar flowrate was kept constant. The CPR operation was simulated for values of the half channel height, $R$, of 0.5, 0.67, 1, 1.5, 2 mm modifying accordingly the inlet velocities and keeping all the other parameters at their base case value. Alterations have been made simultaneously for both endothermic and exothermic channel. Although, the changes in the channel gap, do not affect significantly the outlet conversions and outlet reactor temperature, there are notable changes in the reactor thermal behaviour, radial temperature gradients, and mass fraction radial gradients especially in the first half of the reactor. Figure 4.3.4a shows the axial temperature profile in the middle of the solid wall along the reactor. It can be seen that for higher channel gap the axial temperature increase is faster. For example, at the axial dimensionless position, $\zeta=0.3$, the wall temperature has a value of 985 K for a $R=2$ mm, while for $R=0.5$mm, the wall temperature is only 908 K. Towards the end of the channel, dimensionless position $\zeta=0.7$, the wall temperature reaches a maximum of about 1063 K for all cases and drops towards the exit, reaching an outlet value of 1057 K, 1058 K, and 1060 K for half channel height of 0.5 mm, 1 mm, and 2 mm respectively.
Figure 4.3.4 Influence of channel gap for constant catalyst residence time
a. Wall temperature; b. Generated and consumed heat fluxes.
Figure 4.3.4b indicates that the decrease in the channel gap moves towards the reactor exit the axial location where the maximum of the heat flux occurs.

Strong influences on the mass and temperature radial gradients are shown at changes in channel gap. The temperature radial gradients defined as the difference between the wall temperature and the gas phase temperature at the channel centre are shown in Figure 4.3.5a and 4.3.5b for reforming and combustion channel respectively. A lower channel gap results in a more efficient heat transfer and lower temperature gradients. For R=0.5 mm, the maximum temperature difference between the gas phase and the wall is 18 K for reforming and 21 K for combustion, while at R=2 mm, it has the values 68 K for reforming and 76 K for combustion. Similar effects are shown on the mass fraction radial gradients. Figure 4.3.6a and 4.3.6b shows the difference between the methane mass fraction at the channel centre and the reacting wall for reforming and combustion channel. It can be seen that the smaller the channel gap the smaller are the radial mass fraction gradients.

The conversion of methane for three different axial positions has been plotted for various values of half channel height, in Figure 4.3.7a and 4.3.7b for reforming and combustion respectively. In the first half of the reactor, for example at axial dimensionless axial co-ordinate $\zeta=0.5$, the increase in the channel gap has as effect the increase of conversion mainly due to higher temperature achieved. Around the axial position $\zeta=0.7$ for reforming and $\zeta=0.65$ for combustion, the conversion has the same value for all channel gaps investigated. At higher conversion towards the reactor exist, a decrease in the channel gap improves the exit conversion due to the decrease of external mass resistances.
Figure 4.3.5 Influence of channel gap at constant catalyst residence time. Radial temperature gradients between wall and channel centre in a. reforming channel; b. combustion channel
Figure 4.3.6 Influence of channel gap at constant catalyst residence time. Mass fraction gradients in a. reforming channel; b. combustion channel.
Figure 4.3.7 Influence of channel gap at constant catalyst residence time. Conversion dependence on channel gap at different axial dimensionless position for: a. reforming channel; b. combustion channel.
The influence of channel gap can be discussed based on mass Fourier number defined hereby as the ratio between the local space time $\tau_s$ and a radial diffusion time, $\tau_d$. The local space-time $\tau_s$ represents the time needed for a small element of the fluid at the axial position $z$ at the channel centre to exit the reactor (see Figure 4.3.8).

$$\tau_s = \frac{L - z}{u_z(z,0)} \quad \text{(4.3-12)}$$

The radial diffusion time $\tau_d$ is defined as the time necessary for the reactant to reach the reacting wall, from the channel centre by diffusion.

$$\tau_d = \frac{R^2}{D_{\text{CH}_4}(z)} \quad \text{(4.3-13)}$$

Thus, the Fourier number can be calculated as (see also Figure 4.3.8):

$$F_{\text{m}} = \frac{\tau_s}{\tau_d} = \frac{L - z}{u_z(z,0)} \cdot \frac{D_{\text{CH}_4}(z)}{R^2} \quad \text{(4.3-14)}$$

![Diagram](image)

Figure 4.3.8 Definition of local space-time $\tau_s$ and radial diffusion time, $\tau_d$.

The mass Fourier number is a function of the axial co-ordinate, and can be used to estimate if the reactant molecules from the channel centre have enough time to reach the reacting wall before they exit the reactor. Thus,
- if $F_{om} > 1$ (or $\ln [F_{om}] > 0$) there is potential for the reactant molecules from the channel centre to reach the reacting wall;
- if $F_{om} < 1$ (or $\ln [F_{om}] < 0$) there is a high probability that the reactant molecules from the channel centre cannot reach the reacting wall before they exit the reactor.

The $\ln(F_{om})$ is represented along the reactor length for different channel gap in Figure 4.3.9. The smallest the channel gap the shortest the position where $\ln(F_{om}) < 0$. This again justifies higher outlet conversions for small channel gap.

Figure 4.3.9. Logarithm of the mass Fourier number, $F_{om} = \frac{L-z}{u_z(z,0)} \frac{D_{CH_4}(z)}{R^2}$, for combustion and reforming side, for different half channel size.
It is interesting to compare the mass Fourier numbers in both channels. For this purpose
the ratio between the combustion mass Fourier number, \( F_{m}^{\text{combustion}} \), and the reforming
mass Fourier number \( F_{m}^{\text{reforming}} \) has been calculated and plotted in Figure 4.3.10 along
the reactor.

First, it can be seen that this ratio keeps increasing along the reactor. This can be
explained by the fact that it depends on the ratio of the methane diffusion coefficients
and the inverse ratio of the gas velocity.

\[
\frac{F_{m}^{\text{combustion}}}{F_{m}^{\text{reforming}}} = \frac{u_{\text{reforming}}^{\text{gas}}}{u_{\text{combustion}}} \times \frac{D_{\text{CH}_4}^{\text{combustion}}}{D_{\text{CH}_4}^{\text{reforming}}} 
\]  

(4.3-14)

The ratio between the diffusion coefficients does not change much along the reactor
since they have the same temperature dependence, however the ratio of the velocities
changes mainly due to the increasing of the number of the moles as the reforming
process progresses. Thus, the methane from the channel centre in the combustion
channel has better chances to reach the wall and react before to exit the channel than the
methane in the reforming channel. In addition, it can be seen that the ratio of the mass
Fourier numbers increases with channel gap, for the most part of the reactor length.
Thus, for higher channel gap the methane in the combustion channel has better chances
to reach the catalyst layer and react relatively to the methane in the reforming channel.
This can provide an excess heat that explains the faster increase in temperature (see
Figure 4.3.4a) and the location of the maximum of the local heat fluxes towards the
reactor entrance (see Figure 4.3.4b), for higher channel gap.
4.3.3.3.2 Influence of Channel Gap for Constant Space Time

The space-time is hereby defined as the ratio between the CPR length and inlet velocity of the gas phase.

\[ \tau_s = \frac{L}{u_{z0}} \] \hspace{1cm} (4.3-16)

The reactor thermal behaviour and performance has been studied for different half channel height, \( R \), and constant space-time. The variation range for \( R \) was (0.5-4 mm). All the other parameters are kept at their base case value. Keeping constant the space-time and altering the channel gap results in modifying the inlet flowrate in the CPR. Therefore, an increase in the channel gap leads to lower conversions as can be seen in Figure 4.3.11a.

Decreasing the channel gap from its base case value (1 mm) to 0.5 mm, reduces the reactant flowrates by half. Since the catalyst amount is the same, both conversions are driven towards their upper limit. Similar conversions to the outlet conversions to the base case are achieved at the axial dimensionless position 0.45. In the first part of the reactor, the increase of temperature is faster (see Figure 4.3.11b). At the dimensionless axial position \( \zeta = 0.3 \), due to fuel depletion the heat flux generated becomes slightly smaller than the heat flux consumed and consequently a maximum in temperature occur. The increase in the endothermic conversion is slightly higher than for the exothermic one, therefore the heat consumed increases accordingly and the outlet temperature is lower than for the base case (see Figure 4.3.11b).
Figure 4.3.11 Influence of channel gap at constant space-time
a. Outlet conversions as a function of half channel height; b. wall temperature along the reactor
By increasing the channel gap from its base case value (1mm), on one hand the catalyst amount becomes insufficient for the amount of reactants fed in the reactor, on the other hand the external mass resistances may start to play a stronger role. Both aspects lead to conversion reduction as the channel gap increases. In addition, the amount of heat generated is lower, consequently as the channel gap increases the outlet temperature also decreases, as shown in Figure 4.3.11b.

The ln(Fo_m) for the cases studied in this sections are plotted in Figure 4.3.12, for both reforming and combustion side.

\[ \text{Fo}_m = \frac{L - z}{u_z(z,0)} \cdot \frac{D_{CH_4}(z)}{R^2}, \]

for combustion and reforming side, for different half channel size.

It can be seen that an increase of the channel gap for constant space time \( (\tau_s = \frac{L}{u_z^0}) \) lowers the mass Fourier number so that for a half channel size of 4 mm, \( \text{Fo}_m<1 \) for both reforming and combustion channel for the whole reactor length. This diminishes the
chances for the reactant molecules to reach the reacting wall from the centre of the channel. At small channel gap (R=0.5 mm), for almost the entire reactor length the conditions, $F_{om} > 1$ is fulfilled, consequently external mass transfer resistances are minimised. Comparing Figures 4.3.9 and 4.3.12 it can be seen that the influence of channel gap for constant catalyst resident time and constant space time has similar trends, but the differences among the cases is more significant for the latter. This may indicate that the flowrates and the catalyst amount in channels has to be correlated carefully.

An interesting aspect can be observed by comparing the ratio between the combustion mass Fourier number, $F_{om}^{combustion}$ and the reforming mass Fourier number $F_{om}^{reforming}$, as plotted in Figure 4.3.13.

Figure 4.3.13. Ratio of the mass Fourier numbers in combustion and reforming channel along the reactor, for constant space-time ($\tau_s = L/u_0$), for different values of half channel size
The variation of the channel gap has an opposite effect on the ratio $\frac{F_{0m}^{\text{combustion}}}{F_{0m}^{\text{reforming}}}$ at constant space-time than at constant catalyst residence time (see Figure 4.3.10). For constant space-time (Figure 4.3.13) a decrease of the channel gap results in a higher ratio of mass Fourier numbers. This corresponds to higher conversions and thus more significant changes of reforming gas velocity (see equation 4.3-13). In addition, the outlet conversions are much different among the cases, therefore the difference in the ratio of the mass Fourier number is more significant than for constant catalyst residence time (see also Figure 4.3.10). This is in agreement with the temperature profiles represented in Figure 4.3.11 b, where it can be seen that the smallest channel gap corresponds to the highest ratio of mass Fourier number and gives the sharpest temperature rise.

These results emphasise that for CPR design the channel gap choice has to be correlated with care with the flowrates and the amount of catalyst necessary to achieve a desired outlet conversion. Modifications in channel gap disturbs the local heat balance leading to perturbations in CPR thermal behaviour. The effect of such perturbations are system dependent and need to be analysed for each particular case.
4.3.3.4 Influence of Catalyst Thickness.

The influence of catalyst thickness, expressed in the mathematical model by the parameter $\delta_{\text{cat},i}$, on CPR behaviour was studied by keeping constant the ratio $\frac{\delta_{\text{cat},i}}{u_{z,i}}$. The CPR operation was simulated for values of catalyst thickness, of 10, 20, 40 and 60 $\mu$m modifying accordingly the inlet velocities and keeping all the other parameters at their base case value. This corresponds to alteration of total catalyst amount in the reactor keeping catalyst residence time constant. Alterations have been made simultaneously for both endothermic and exothermic channels. Changes in the catalyst thickness influence considerably both thermal behaviour and outlet conversions. Figure 4.3.14a shows the wall temperature along the reactor, while figure 4.3.14b shows the exit conversions in reforming and combustion channel as a function of catalyst thickness. The values of the effectiveness factors are shown in Figure 4.3.15a for steam reforming reaction (see equation 4.3-1) and in Figure 4.3.15b for combustion.

Higher conversions correspond to thinner catalyst layer. For 10 $\mu$m catalyst thickness the outlet reforming conversion is 98.95 % and the outlet combustion conversion is 99.95%, while for a catalyst thickness of 60 $\mu$m the reforming conversion is 59.5 % and the combustion conversion is 66.84 %. The drop in outlet conversions is a consequence of higher intraphase resistance at thicker catalyst layer (see Figure 4.3-15). The increase of the catalyst layer from 10 $\mu$m to 60 $\mu$m decreases the reforming effectiveness factor by 4-4.5 times, and the combustion effectiveness factor by 2.1-4. The decrease in the reforming effectiveness factor is more pronounced than for combustion, therefore the decrease in the reforming conversion is more significant than the combustion one.
Since the changes in the effectiveness factors are different for combustion and reforming process, the local heat balance has characteristic features for each case determining a specific axial temperature profile. Near the reactor entrance, the endothermic reactions rates have high values due to low $\text{H}_2$ concentration (see also Figure 4.3.3) and thus for the base case (20 $\mu$m) the heat flux consumed is slightly higher than the heat flux generated (see also Figure 4.3.1 b). Decreasing the catalyst thickness to 10 $\mu$m increases the effectiveness factor more for the endothermic reactions than for combustion (at reactor entrance), therefore the heat difference between the heat flux consumed and the heat flux generated becomes even higher, therefore the wall temperature is lower compared to the base case. At low catalyst thickness the intraphase resistances are also lower and both processes progress faster, which explains why for a catalyst thickness of 10 $\mu$m the increase in the axial temperature profile is the sharpest among the cases studied. In addition, the fact that the endothermic and the exothermic conversions are more close to each other than for the base case (20 $\mu$m), see also Figure 4.3.14 b, lead to less excess heat in the system. Thus, the outlet temperature for 10 $\mu$m is 1046 K, lower than for 20 $\mu$m, 1059 K. This makes a thinner catalyst layer to have a slightly higher thermal efficiency, for example 68.2 % for 10 $\mu$m and 66.7 % for 20 $\mu$m.

For thicker catalyst layer, the intraphase resistances act as a diffusion barrier having a significant effect especially near the reactor inlet in the reforming channel. Thus, the rate of heat consumption at this location is moderated resulting in a higher wall temperature at the reactor entrance compared to the base case (20 $\mu$m) see also Figure 4.3.-14a. Downstream the wall temperature becomes lower than for the base case, due to less heat generated in the system related to the inlet flowrates (lower conversions, see also Figure 4.3-14 b). The thermal efficiency, as defined by equation 4.3-10, decreases for thicker
catalyst layer, thus for 40 μm the thermal efficiency is 62.61 %, while for 60 μm the thermal efficiency is 60.52 %. This means that from the heat generated less amount is used by the endothermic process, which explains why increasing the catalyst thickness at constant catalyst residence time widens the difference between the conversion of the exothermic and the endothermic side. Higher catalyst thickness corresponds also to higher inlet flowrates. The decrease in conversions (see Figure 4.3.14b) can be a consequence not only of higher intraphase resistances (see Figure 4.3.15), but also of the fact that the gas-solid interface remains the same.

The effectiveness factors values (Figure 4.3.15a and 4.3.15b) indicate that for both reforming and combustion processes, although the catalyst thickness is of order of micrometers, intraphase resistances are significant. Neglecting the intraphase resistance can lead to error not only regarding the necessary amount of catalyst, but also regarding the reactor thermal behaviour and performance. During the investigation of the effect of the catalyst thickness at constant catalyst residence time, the ratio between the amount of catalyst and the methane fed in each channel was kept constant. Higher catalyst thickness corresponds to larger amount of reactants in both channels. Consequently the heat flux generated and consumed increases due to a larger amount of the methane in the reactor. This results in increasing the radial temperature gradients along the channel, as can be seen in Figure 4.3.16a and 4.3.16b for reforming and combustion channel respectively.
Figure 4.3.14 Influence of catalyst thickness
a. Wall temperature along the reactor; b. Outlet conversions.
Figure 4.3.15 Influence of catalyst thickness on effectiveness factor in
a. reforming channel; b. combustion channel
Figure 4.3.16 Influence of catalyst thickness on radial temperature gradients in
a. reforming channel; b combustion channel
4.3.4. Comparison to conventional process

Because the overall reforming process is highly endothermic, in the conventional reformer the heat necessary to drive the endothermic reactions is provided by heating up the catalyst tubes in a fired furnace. A typical reformer may contain between 40 and 400 tubes. The internal diameter is in the range 70 -160 mm with a tube thickness 10 -20 mm. Large spaces are necessary between tubes to accommodate the burners and the radiation path of flames (Rostrup-Nielsen, 1989). For example, Lurgi steam reforming technology uses for an inlet flowrate of methane of 15 000 Nm$^3$/h ca. 19 m$^3$ catalyst. The tubes filled with catalyst are placed in a fire box with a volume of approximate 1600 m$^3$ achieving about 95% conversion.

Two indexes are defined in order to compare the performance of steam reforming in CPR with the conventional primary steam reformer. Reactor Volume Index ($RVI$) represents the ratio between the volume of the conventional reformer (including the space between the catalytic tubes) and the CPR volume to convert the same amount of methane. Catalyst Weight Index ($CWI$) represents the ratio between the amount of catalyst used in the conventional process and the one used in a CPR to convert the same amount of methane.

Calculations derived from CPR simulation results presented in section 4.3.3, indicate that conversion of a flowrate of 1kmol/h methane requires a CPR volume of 0.015 m$^3$ and a catalyst amount of 0.28 kg. Taking into consideration the equivalent values for Lurgi reformer, the approximate reactor volume and catalyst weight indexes are; $RVI$ =150 and $CWI$=85. These indicate a two order of magnitude reduction of reactor
volume and required amount of catalyst. For operation of the CPR at 29 bar the indexes values are \( RV = 120 \) and \( CWI = 65 \) respectively.

The volume reduction results mainly due to the replacement of homogeneous combustion by catalytic one therefore by eliminating the spaces allocated to accommodate the burners. This also reduces the temperature difference between wall and the process gas-phase from about 250 K in the industrial reformer (Xu and Froment 1989b) to a maximum of only 35 K in CPR design. The reduction of the amount of catalyst is a result of the minimisation of the mass transfer resistances. Indeed the effectiveness factor reported for an industrial steam reformer are in the range 0.02-0.03 (De Deken et al. 1982; Xu and Froment 1989b), which is an order of magnitude lower than the ones obtained for CPR design (see Figure 4.3.3a). In addition, operation at low pressure increases the reaction rates due to relaxation of the chemical equilibrium. The reaction rate of reforming, which is the main reaction in the system, reported by Xu and Froment (1989b) along a catalytic tube from a conventional reformer, has values in the range (0.8-1.5 kmol/kg cat/h), while within a CPR, see Figure 4.3.3b, the corresponding range is (2.9-12.2 kmol/kg cat/h). These ranges exclude the high values of the reaction rates near the reactor inlet due to low hydrogen concentration, for both conventional reactor and CPR. The water gas shift reaction rate occurs towards \( H_2 \) generation only along the CPR, while the results reported by Xu and Froment (1989b) indicate the water gas shift equilibrium is reversed in the second half of the reactor due to the high pressure the reactor operates at.
Overall, it can be seen from the theoretical point of view that steam reforming of methane in a CPR offers an important reduction of reactor volume and required amount of catalyst due to minimisation of heat and mass transfer resistances.

4.4. Conclusions

Steam reforming of methane coupled with methane catalytic combustion by means of indirect heat transfer in a Catalytic Plate Reactor (CPR) was studied. A two dimensional model was formulated to simulate CPR behaviour. Simplified kinetics for reforming process was used in order to obtain a base case that allowed autothermal coupling in almost isothermal conditions. For the base case investigated, a maximum difference between inlet and hot spot temperature of only 17 K occurs, while radial temperature gradients are negligible. It was shown that for a catalyst layer thickness of 20 μm the mass intraphase resistances are significant, therefore they cannot be neglected during reactor design. The thermal intraphase resistances are negligible, allowing to simplify the CPR model by considering the catalyst layer isothermal in radial direction. Influence of changes in catalyst layer thickness keeping constant the overall loading, and changes in catalyst layer thickness keeping constant the local loading on CPR performance and thermal behaviour was investigated. Changes in these parameters affect the ratio between heat generated and heat consumed along the reactor mainly due to different dependence of the reforming and combustion reaction rates on temperature.

Further the mathematical model was refined considering more complex kinetics for the reforming side. A base case characterising the operating conditions of the conventional steam reforming process was generated in order to study the situation when combustion is used simultaneously to provide heat for the endothermic side and to heat up both
reaction mixtures. This objective was realisable providing the necessary amount of fuel and the suitable pre-exponential factor for catalytic combustion, making possible to achieve high outlet conversions and 1058 K outlet temperature. The performance of CPR was compared to conventional steam reformer. A 2-order of magnitude reduction in the reformer volume and necessary amount of catalyst was achievable. The effectiveness factors for the chemical reactions of the reforming process are about one order of magnitude higher than in the conventional process, proving a significant reduction of intraphase resistances. The short distance between the heat source and heat sink increases the efficiency of heat transfer. Thus, for the base case presented the maximum radial temperature gradients in the reforming channel are only 35 K compared to 250 K for the conventional reformer.

The influence of channel gap and catalyst thickness on reactor behaviour was also addressed. At constant catalyst residence time, decreasing the channel gap minimises the heat and mass transfer resistances resulting to higher outlet conversions although the difference among the cases studied is not significant. At constant space-time, the increase of channel gap corresponds to higher amount of reactants per catalyst amount, in addition the external resistances becomes more important leading to significant lower outlet conversions and temperature. The intraphase resistances prove to be important even for catalyst thickness of micrometers for both reforming and combustion process. Increasing the catalyst thickness at constant catalyst residence time leads to lower outlet conversions, as a consequence of stronger intraphase resistances. Due to different influence on reforming and combustion side of the catalyst thickness, the axial temperature profile has characteristic features for each case studied.
Lastly, it can be concluded that steam reforming of methane in a CPR can be feasible from theoretical point of view providing that the flowrates, channel gap, catalyst loading and thickness are chosen with care.
5.1 Introduction

As already illustrated in section 2.7, Parametric Sensitivity Analysis (PSA) is an important and useful tool for studying the behaviour of chemical systems. In this chapter, PSA is utilised to study the performance of a Catalytic Plate Reactor where endothermic and exothermic reactions take place in alternate channels. The reaction of interest is the endothermic one, while the exothermic reaction is present to provide sufficient heat to drive the former. This poses constraints on the flowrates and the relative amounts of catalyst that can be utilised. Limited by these constraints this chapter investigates how much flexibility the designer has in altering various designs and operating parameters, while at the same time achieving an acceptable thermal behaviour. A short-cut model is formulated based on one-dimensional approach in order to show how PSA can be used for a quick check of the autothermal coupling suitability. Further, PSA developed based on a two-dimensional approach allows a more detailed and accurate investigation of CPR behaviour. The sensitivities of temperature and conversion related to several model parameters are evaluated.
5.2. One-Dimensional Approach

5.2.1 Reactor Model

For the model, a single plate of the CPR as represented in Figure 5.2.1 is considered. The following assumptions are employed: no radial gradients exist in the fluid and solid phases; reactions are considered to take place on the surface of the catalytic plates; kinetics for both reactions are first order; properties of the fluid and solid phases and velocities are constant.

![Diagram of single plate geometry in the catalytic plate reactor]

The differential mass and energy balances for a CPR with channels of the same height under overall adiabaticity are:

\[
\frac{dX_A}{dz} = \frac{k_A^0}{u_{zA} \cdot R} \cdot \exp \left( -\frac{E_A}{RT} \right) \cdot \left( 1 - X_A \right) \tag{5.2-1}
\]

\[
\frac{dX_B}{dz} = \frac{k_B^0}{u_{zB} \cdot R} \cdot \exp \left( -\frac{E_B}{RT} \right) \cdot \left( 1 - X_B \right) \tag{5.2-2}
\]

\[
\frac{dT}{dz} = \frac{(-\Delta H)_A k_A^0 \exp \left( -\frac{E_A}{R_g T} \right) c_{A0} (1 - X_A) + (-\Delta H)_B k_B^0 \exp \left( -\frac{E_B}{R_g T} \right) c_{B0} (1 - X_B)}{\left( \rho_A \cdot u_{zA} \cdot c_{pA} + \rho_B \cdot u_{zB} \cdot c_{pB} \right) \cdot R} \] \tag{5.2-3}
The initial conditions are:
\[ X_A = X_B = 0 \text{ and } T = T_0 \quad \text{at } z = 0 \]  
(5.2-4)

Further simplification can be obtained if \( z \) is eliminated dividing equations (5.2-1) and (5.2-3) by equation (5.2-2) and using the dimensionless temperature \( \theta = \frac{T}{T_0} \):

\[
\frac{dX_A}{dX_B} = \frac{k_A^0 \cdot \frac{u_{zB}}{u_{zA}} \cdot \exp \left( \frac{E_B - E_A}{R_g T_0 \cdot \theta} \right) \cdot (1 - X_A)}{k_B^0 \cdot \frac{u_{zA}}{u_{zB}} \cdot \exp \left( \frac{E_B - E_A}{R_g T_0 \cdot \theta} \right) \cdot (1 - X_B)} \]

(5.2-5)

\[
\frac{d\theta}{dX_B} = \frac{(-\Delta H)_B \cdot c_{Bo}}{\left( \rho_A c_{pA} \cdot \frac{u_{zA}}{u_{zB}} + \rho_B c_{pB} \right) T_0} + \frac{(-\Delta H)_A \cdot c_{Ao}}{\left( \rho_A c_{pA} \cdot \frac{u_{zA}}{u_{zB}} + \rho_B c_{pB} \right) T_0} \cdot \frac{k_A^0 \cdot \exp \left( \frac{E_B - E_A}{R_g T_0 \cdot \theta} \right) \cdot (1 - X_A)}{k_B^0 \cdot \exp \left( \frac{E_B - E_A}{R_g T_0 \cdot \theta} \right) \cdot (1 - X_B)} \]

(5.2-6)

The initial conditions become

\[ \theta = 1, \quad X_A = 0 \quad \text{at } X_B = 0 \]

(5.2-7)

Thus, the independent variable now is the conversion of the exothermic reaction \( x_B \), while the dependent variables are the conversion of the endothermic reaction \( x_A \), and the dimensionless temperature \( \theta \). Next, equations (5.2-5) and (5.2-6) are rendered dimensionless using the following dimensionless parameters:

- ratio of inlet velocities:
  \[ V = \frac{u_{zA}}{u_{zB}} \]
  (5.2-8)

- ratio of pre-exponential factors:
  \[ K = \frac{k_A^0}{k_B^0} \]
  (5.2-9)

- dimensionless difference of activation energies:
  \[ \gamma = \frac{E_B - E_A}{R_g T_0} \]
  (5.2-10)

- heat effect numbers:
  \[
  B_A = \frac{(-\Delta H)_A \cdot C_{Ao}}{\left( \rho_A c_{pA} V + \rho_B c_{pB} \right) T_0} \]
  (5.2-11)

  \[
  B_B = \frac{(-\Delta H)_B \cdot C_{Bo}}{\left( \rho_A c_{pA} V + \rho_B c_{pB} \right) T_0} \]
  (5.2-12)
The dimensionless balances are:

\[
\frac{dX_A}{dX_B} = \frac{K}{V} \exp\left(\frac{\gamma}{\theta}\right) \cdot \frac{1 - X_A}{1 - X_B} \quad (5.2-13)
\]

\[
\frac{d\theta}{dx_B} = B_B + B_A \cdot V \cdot \frac{dX_A}{dX_B} \quad (5.2-14)
\]

subject to initial conditions (5.2-7).

Equation (5.2-14) can be further integrated as follows

\[
\theta = 1 + B_A V \cdot X_A + B_B \cdot X_B \quad (5.2-15)
\]

Therefore the reactor model is given by one dimensionless differential equation:

\[
\frac{dx_A}{dx_B} = \frac{K}{V} \exp\left(\frac{\gamma}{1 + B_A \cdot V \cdot X_A + B_B \cdot X_B}\right) \cdot \frac{1 - X_A}{1 - X_B} \quad (5.2-16)
\]

where the dependent variable is the conversion of A, \(x_A\), and the independent variable is the conversion of B, \(x_B\); subject to the initial condition:

\[
x_A = 0 \quad \text{at} \quad x_B = 0, \quad (5.2-17)
\]

It must be noted that since the independent variable is \(x_B\), which varies from 0 to 1, the analysis that follows, corresponds to a sufficiently long reactor, where \(x_B = 1\) can be achieved. The model parameters used in the calculations are given in Table 5.2.1 and are chosen so that they approximate a steam reforming – methane combustion reaction system and inlet temperature 1000 K. It is conceivable that different catalyst combinations can lead to the same reactor thermal behaviour, but exhibit different sensitivity characteristics. This is explored by considering two base cases with different values for activation energy for the exothermic reaction. The pre-exponential factors were adjusted to obtain similar thermal behaviour. Further, the values of the dimensionless parameters given by the equations 5.2.8- 5.2.12 are determined and they are given in Table 5.2.2.
Table 5.2.1. Model Parameters used in the calculations (1D model).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Channel 1</th>
<th>Channel 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Phase</td>
<td></td>
<td>endothermic</td>
<td>exothermic</td>
</tr>
<tr>
<td>Density</td>
<td>kg/m³</td>
<td>0.23</td>
<td>0.36</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>J/kg K</td>
<td>2790</td>
<td>1320</td>
</tr>
<tr>
<td>Diffusion coefficient</td>
<td>m²/s</td>
<td>2.05E-4</td>
<td>1.75E-4</td>
</tr>
<tr>
<td>Heat of reaction</td>
<td>kJ/mol</td>
<td>205</td>
<td>-803</td>
</tr>
<tr>
<td>Inlet temperature</td>
<td>K</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Inlet concentration</td>
<td>mol/m³</td>
<td>3.3</td>
<td>1.2</td>
</tr>
<tr>
<td>Inlet velocity</td>
<td>m/s</td>
<td>4.9</td>
<td>3.5</td>
</tr>
<tr>
<td>Activation energy</td>
<td>kJ/mol</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td>Pre-exponential factor</td>
<td>m/s</td>
<td>2000</td>
<td>4700</td>
</tr>
<tr>
<td>Case I</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case II</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2.2. Values of the dimensionless parameters

<table>
<thead>
<tr>
<th>Model Parameters</th>
<th>Base case I</th>
<th>Base case II</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>0.444</td>
<td>0.0118</td>
</tr>
<tr>
<td>γ</td>
<td>1.20</td>
<td>4.81</td>
</tr>
<tr>
<td>V</td>
<td>1.411</td>
<td></td>
</tr>
<tr>
<td>$B_A$</td>
<td>-0.516</td>
<td></td>
</tr>
<tr>
<td>$B_B$</td>
<td>0.736</td>
<td></td>
</tr>
</tbody>
</table>

5.2.2. Sensitivity Equations

As mentioned above, the independent variable is the conversion of the exothermic reaction, $X_B$, and the dependent variables are the conversion of the endothermic reaction $X_A$, and dimensionless temperature $\theta$. The input parameters, $\Phi_j$, are: ratio of pre-exponential factors $K$, dimensionless difference of activation energies $\gamma$, ratio of inlet velocities $V$, heat effect numbers $B_A$, $B_B$, and inlet dimensionless temperature $\theta_0$. The equations of local sensitivities are obtained from eq. (5.2-15) and (5.2-16) as presented earlier and their general form is:

$$s(\theta, \Phi_j) = B_A V \cdot s(X_A, \Phi_j) + \frac{\partial \Pi}{\partial \Phi_j}$$

(5.2-18)
with the initial condition

\[ s(X_A;\Phi_j) = 0 \quad \text{at} \quad X_B = 0 \quad (5.2-20) \]

where

\[ \Pi = B_A V \cdot X_A + B_B \cdot X_B \quad (5.2-21) \]

\[ \Psi = \frac{K}{V} \quad (5.2-22) \]

\[ \Gamma = \frac{\gamma}{1 + B_A V \cdot X_A + B_B \cdot X_B} \quad (5.2-23) \]

\[ \Omega = \frac{\gamma B_A V}{(1 + B_A V \cdot X_A + B_B \cdot X_B)^2 + \frac{1}{1 - X_A}} \quad (5.2-24) \]

The derivatives of the expressions, \( \Psi, \Gamma, \Pi \), with respect to each input parameter considered, \( \Phi_j \), are given in Table 5.2.3. Solving simultaneously the equations of the mathematical model (5.2-15) – (5.2-16) and the sensitivities equations (5.2-18) – (5.2-19), all local sensitivities are obtained as a function of the independent variable \( x_B \). The variable of interest in analysing CPR thermal behaviour is the dimensionless temperature. Consequently the normalised sensitivities of temperature related to \( \Phi_j \) are calculated from

\[ S(\theta;\Phi_j) = \frac{\Phi_j}{\theta} \cdot s(\theta;\Phi_j) \quad (5.2-25) \]

The sensitivity analysis can be used to establish an acceptable deviation of input parameters in order to keep the reactor operation within desired limits. After the normalised sensitivity has been calculated as a function of the independent variable, its maximum absolute value, \( |S(\theta;\Phi_j)|_{\text{max}} \), can be easily determined. For an acceptable
relative variation of the dependent variable, $|\delta^{\text{rel}}_{y}|$, a corresponding acceptable relative deviation for the input parameter $\delta^{\text{rel}}_{\Phi_j}$ can be estimated from:

$$\delta^{\text{rel}}_{\Phi_j} \approx \frac{|\delta^{\text{rel}}_{y}|}{S(y; \Phi_j)_{\text{max}}} \quad (5.2-26)$$

Using eq. 5.2-26 the degree of flexibility for the various input parameters can be evaluated.

Table 5.2.3 Expressions and derivatives of the coefficients $\Pi, \Psi, \Gamma$, related to each input parameter $\Phi_j$

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>$\Pi$</th>
<th>$\Psi$</th>
<th>$\Gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expression</td>
<td>$B_A V \cdot X_A + B_B \cdot X_B$</td>
<td>$K$</td>
<td>$\frac{\gamma}{1 + B_A V \cdot X_A + B_B \cdot X_B}$</td>
</tr>
<tr>
<td>Corresponding Derivatives</td>
<td>$\frac{\partial \Pi}{\partial \Phi_j}$</td>
<td>$\frac{\partial \Psi}{\partial \Phi_j}$</td>
<td>$\frac{\partial \Gamma}{\partial \Phi_j}$</td>
</tr>
<tr>
<td>Input Parameter, $\Phi_j$</td>
<td>$K$</td>
<td>$0$</td>
<td>$\frac{1}{V}$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>$0$</td>
<td>$0$</td>
<td>$\frac{1}{1 + B_A V \cdot X_A + B_B \cdot X_B}$</td>
</tr>
<tr>
<td>$V$</td>
<td>$B_A \cdot X_A$</td>
<td>$-\frac{K}{V^2}$</td>
<td>$-\frac{\gamma B_A \cdot X_A}{(1 + B_A V \cdot X_A + B_B \cdot X_B)^2}$</td>
</tr>
<tr>
<td>$B_A$</td>
<td>$V \cdot X_A$</td>
<td>$0$</td>
<td>$-\frac{\gamma V \cdot X_A}{(1 + B_A V \cdot X_A + B_B \cdot X_B)^2}$</td>
</tr>
<tr>
<td>$B_B$</td>
<td>$X_B$</td>
<td>$0$</td>
<td>$-\frac{\gamma X_B}{(1 + B_A V \cdot X_A + B_B \cdot X_B)^2}$</td>
</tr>
<tr>
<td>$\theta_0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
</tbody>
</table>

A gPROMS code utilised to solve the reactor model together with the sensitivity equation is given in Appendix C1.
5.2.3. Results and Discussion

The relation between heat generation and heat consumption is important for the reactor thermal behaviour and performance. If the heat fluxes are unbalanced, then the thermal behaviour of the CPR swings between two extreme situations. When the rate of heat consumed is higher than the rate of heat generated, the system temperature drops and exhibits a "cold spot". The temperature drop constrains the reaction rates, which in turn lead to lower final conversions. In the reverse situation, if the rate of heat generation is higher than the rate of heat consumption, reaction temperature increases. High heat generation is directly linked to high exothermic reaction rate and thus depletion of the corresponding reactant. At a certain point though the rate of heat consumed becomes dominant due to the fact that relatively high amount of reactant is still present for the endothermic reaction. Thus, the temperature progressively drops and a "hot spot" is formed. This situation may not be desired since hot spots could damage the catalyst on both sides and affect reactor control and operability. Different catalysts can offer isothermal behaviour and similar performance, provided their loadings are suitably adjusted, and this indeed is observed for the two base cases considered (see Figure 5.2.2). However, a careful analysis is required to make the right reactor choice, so that small changes in operating or design parameters do not affect significantly its performance. Solving the sensitivity equations together with the equations of the reactor model, the normalised sensitivities can be calculated. The variable of interest is the dimensionless temperature, $\theta$, thus its normalised sensitivities related to all model parameters, $V, B_A, B_B, K, \gamma, \theta_0$, have been determined. They are plotted for each base case in Figure 5.2.3a and 5.2.3b respectively, as a function of the independent variable, which is the conversion of the exothermic reaction, $x_B$. 
Figure 5.2.2 Conversion of the endothermic reaction and dimensionless temperature as a function of the conversion of the exothermic reaction: a. base case I; b. base case II.

Comparing Figure 5.2.3a and 5.2.3b, it can be seen that for the same operating conditions two different catalysts exhibit large differences in reactor sensitivities. All normalised sensitivities of dimensionless temperature for base case I (BC I) have
absolute values lower than for base case II (BC II). Figures 5.2.4a and 5.2.4b show extreme values of sensitivities determined for BC I and BC II respectively.

Figure 5.2.3 Normalised sensitivities of dimensionless temperature as a function of conversion of exothermic reaction: a. base case I; b. base case II.
Figure 5.2.4 Extreme normalised sensitivities of dimensionless temperature for various design and operating parameters: a. base case I; b. base case II
5.2.3.1 Influence of $K$

5.2.3.1.1 *Comparison of sensitivity level for similar unperturbed reactor thermal behaviour*

Parameter $K$ represents the ratio of pre-exponential factors, as defined by equation (5.2-9) and provides a measure of the ratio of catalyst activities. An increase in $K$ can be obtained either by increasing the catalyst loading for endothermic reaction or by decreasing the catalyst loading for exothermic reaction. In the former case heat consumption increases, while in the latter heat production decreases. Both cases result to lower reactor temperature and give rise to a negative sign for $S(\theta, K)$. A change in $K$ can also be the consequence of deactivation for one of both catalysts. In order to quantitatively illustrate the changes in reactor behaviour for a small change in $K$, it is shown in Figure 5.2.5, the reactor temperature profiles for the two base cases with and without a -10% change in $K$ ($\delta_K = -10\%$). Note that before the change in $K$, both base cases show similar thermal behaviour, which is approximately isothermal. As shown in the Figure, the same relative change in catalyst activities results to an increase of the reactor temperature by up to 3.5% for BC I and up to 9.6% for BC II. It is worth noting that even though the temperature profiles for the new $K$ were calculated by solving the full reactor model, they can also be approximated by multiplying the sensitivity profiles $S(\theta; K)$ from Figure 5.2.3 by the corresponding relative change in $K$, i.e. $\theta_{new} = \theta_{base\_case} [1 + S(\theta; K) \cdot \delta_K]$, (see also equation 2.8-5).
Figure 5.2.5 Dimensionless temperature response to −10% change in ratio of pre-exponential factors, K: a. base case I; b. base case II.
5.2.3.1.2 Comparison of sensitivity level for different unperturbed reactor thermal behaviour

Starting from each base case (see Table 5.2.2), the ratio of pre-exponential factors, K, has been varied in order to obtain different unperturbed reactor thermal behaviour ranging from cold spot to hot spot. The extreme values for normalised sensitivities are shown as a function of K varied around its BC I and BC II values in Figure 6a and 6b respectively. As mentioned before, the BC I and BC II simulations corresponds to approximately isothermal behaviour. When K decreases a hot spot develops, while in the opposite a cold spot appears and these are indicated in the Figure. It is observed that the normalised sensitivity values are lower when the reactor operates with a hot spot and they increase when a cold spot is present. However, this increase is not significant for BC I, where γ is small. The extreme values of all normalised sensitivities are in the range (−12)–(+13) for BC II (i.e. large γ), while the range is (−1) – (+2) for BC I (i.e. small γ). Calculations performed with negative values of γ (not shown) demonstrated that the range of sensitivities becomes even smaller. The above results indicate that the most sensitive behaviour is obtained during cold spot and not hot spot operation. In this case, high reactant concentrations are available in the reactor, especially in the exothermic channel, and therefore there is a potential to achieve higher reaction rates as compared with isothermal or hot spot operation for specific changes of the input parameters.
Figure 5.2.6. Extreme normalised sensitivities of dimensionless temperature for different unperturbed reactor thermal behaviour: a. $B_A = -0.516; B_B = 0.736; V=1.411, \gamma=1.2$; b. $B_A = -0.516; B_B = 0.736; V=1.411, \gamma=4.81$;
5.2.3.2 Influence of $\gamma$.

Parameter $\gamma$, as defined by equation (5.2-10), represents the dimensionless difference of activation energies between exothermic and endothermic reactions. Changes in $\gamma$ affect reaction rates and hence heat generated and heat consumed. A higher $\gamma$ leads to a larger amount of heat consumed and to temperature decrease, as shown also by the negative sign of $S(0;\gamma)$. In Figure 5.2.7, temperature profiles are shown before and after a change in $\gamma$ by 0.1 units. Even though the temperature profiles are similar for the base cases, the profiles after introducing the change in $\gamma$ are considerable different.

For BC I maximum temperature drop is 3.5 % while for BC II it is 11 %. These are equivalent to 35K and 110K temperature decrease correspondingly. In Figure 5.2.8 sensitivities with respect to inlet temperature are shown as a function of the exothermic reaction conversion for various combinations of $\gamma$ and $K$ chosen in such a way that an almost isothermal operation is achieved for the unperturbed case. It can be seen that the weakest sensitivities are observed for the lowest $\gamma$, which can be obtained by either increasing the activation energy of the endothermic reaction or decreasing the activation energy of the exothermic one. The above result indicates that the highest sensitivities are observed for large differences in activation energies and when the exothermic reaction has higher activation energy than the endothermic.
Figure 5.2.7 Dimensionless temperature response to change in dimensionless difference of activation energies, $\gamma$ by 0.1 units: a. base case I; b. base case II.
Figure 5.2.8. Normalised sensitivities of dimensionless temperature, with respect to inlet dimensionless temperature $\theta_0$, for different kinetic parameters that provide an almost isothermal profile $B_A = -0.516; B_B = 0.736; V = 1.411$.

**5.2.3.3 Influence of Inlet Velocities Ratio.**

Parameter $V$ represents the ratio of inlet velocities in the endothermic and exothermic channels and it is also equal to the corresponding ratio of volumetric flowrates. Although the absolute values of $S(\theta, V)$ are somewhat higher for BC II (see Figure 5.2.4), the difference between the two cases is the smallest among all parameters considered. The negative sign of $S(\theta, V)$ indicates that an increase of $V$ induces a decrease in $\theta$. An increase in $V$ can be obtained either increasing the endothermic channel flowrate or decreasing the exothermic one. Both situations lead to more heat consumed than heat generated, consequently system temperature becomes lower. For
the extreme values of $S(\theta, V) : -0.72$ and $-0.87$, an increase of $V$ by 1% results to a maximum decrease of temperature by $7.2$ K for BC I and $8.7$ K for BC II.

5.2.3.4 Influence of Inlet Temperature.

Changes of inlet temperature have the most significant effect on reactor thermal behaviour for both cases (see Figure 5.2.4). In addition, the difference between them is the largest among all parameters considered. The positive sign of $S(\theta, \theta_0)$ indicates, as expected, that an increase in the inlet temperature increases the reactor temperature. For example, an increase by 1% in the inlet temperature (10 K) can lead to an increase of temperature in the reactor by up to $14$ K for BC I and $57$ K for BC II.

5.2.3.5 Influence of Heat Effect Numbers $B_A$, $B_B$.

The heat effect numbers as defined by equations (5.2.11)-(5.2.12) are directly proportional to inlet concentrations, thus the sensitivity related to them can be an indication of the sensitivity related to inlet composition. For both cases the profiles of sensitivities related to $B_A$, $B_B$ are mirror images of each other, i.e. $S(\theta; B_A) = -S(\theta; B_B)$ (see Figure 5.2.3). An increase of reactant concentration for exothermic channel results to larger heat generation and the temperature of reactor increases, while an increase of reactant concentration for endothermic channel results to larger heat consumption and the temperature in the reactor decreases. More specifically, 1 % increase in $c_{B_B}$ increases the temperature along the reactor by up to $7.7$ K for BC I and up to $16.5$ K for BC II. Similarly, an increase of 1 % in $c_{A_0}$ decreases the temperature along the reactor by up to $7.7$ K for BC I and $16.5$ K for BC II.
Parametric Sensitivity Analysis for CPRs

5.2.3.6 Acceptable Deviation of Input Parameters. The acceptable deviation of input parameters $\delta^\text{acc}_\theta$, are determined in this section so that the reactor temperature is maintained within ±50 K, ±100 K and ±150 K from the inlet temperature. This correspond to $\left|\delta^\text{acc}_\theta\right|$ of 5, 10, and 15 %. Their computation is straightforward using equation (5.2-26) and the extreme values of normalised sensitivity displayed in Figure 5.2.4. The results are shown in Figures 5.2.9a and 5.2.9b, for BC I and BC II respectively. It is clear that for BC I, which corresponds to small $\gamma$, there is significant flexibility in alteration of design parameters. For example, if it is desired to keep the reactor temperature within the range: 950 – 1050 K the ratio of catalyst loadings can vary by ±14 % for BC I, but by only ±5 % for BC II from its corresponding base case value. Evidently, if the acceptable range of reactor temperature variation is extended, the acceptable deviation of all input parameters also increases. The degree of flexibility is different for the various input parameters. For BC I, the highest acceptable deviation is exhibited by $K$ and the lowest by $\theta_0$, while for BC II by $V$ and $\theta_0$ respectively. Overall, Figures 5.2.9a and 5.2.9b show that there is more flexibility for alteration of the input parameters for BC I, where the difference of the activation energies of the two reactions is relatively small.
Figure 5.2.9 Acceptable deviation of input parameters for 5, 10, and 15 % temperature variation: a. base case I; b. base case II.
5.3 Two-dimensional Approach

Although, the one-dimensional approach gives important insights about CPR parametric sensitivity behaviour due to its simplicity, relevant parameters involved in transverse heat transfer such as: channel size, wall thickness and thermal conductivity do not appear in the model and consequently their contribution to the reactor sensitivity can not be investigated. At the same time, keeping the conversion of the exothermic reaction as the independent variable the previous parametric sensitivity study corresponds to a reactor with infinite length that can give invalid predictions, especially when 100 % outlet conversions are not achieved (Wu et al. 1998). A two-dimensional approach can overcome these limitations and provide additional information.

5.3.1 Reactor Model

In order to keep the mathematical formulation of the reactor model at a degree of complexity that allows reasonable computational effort to obtain the sensitivity equations by direct differential method, the reactor 2D model is based on the assumptions described below. It was considered that there are no significant variations with temperature and composition of the physical properties of the gas phase and gas velocities. A parabolic velocity profile, characteristic of fully developed laminar flow between two parallel plates, was considered along the channels. Both endothermic and exothermic reactions were considered to follow first order kinetics taking place only at the catalytic wall. Subject to these simplifications the 2D model for a CPR with "zero catalyst thickness" is presented in Table 5.3.1. Further, introducing the dimensionless variables and groups given in Table 5.3.2, the CPR model is presented in a dimensionless form in Table 5.3.3. Conversion as a function of axial dimensionless coordinate was determined by integrating the molar flow in the cross section:
Although the simplifications introduced are valid only if there are no significant variations of temperature and the number of moles in the reacting mixture, the sensitivity analysis is more detailed than the one based on a 1D model for an infinite reactor length. It offers the opportunity to study the reactor sensitivity related to the channel size, wall thickness and thermal conductivity which are directly linked to the heat transfer between the endothermic and exothermic channel.

The model parameters used in the calculations are given in Table 5.3.4. Their values are similar to the ones used in the calculations presented for the 1D approach. The importance of the kinetic parameters on the sensitivity behaviour of the CPR has been already identified and discussed in the previous section. Similar PSA for exothermic reactions in CWRs (Priestley and Agnew 1975; Varma et al. 1999) revealed also a strong dependency of the parametric sensitivity behaviour on the activation energy. Therefore, three sets of kinetic parameters have been utilised, generating three case studies. The first two are similar to the ones used in the investigation based on 1D-Approach, corresponding to higher activation energy of the exothermic reaction than for the endothermic one, $E_{\text{exo}}>E_{\text{endo}}$. In addition, case III was selected so that the relation between the activation energies was reversed $E_{\text{exo}}<E_{\text{endo}}$. 

\[ x_j(\zeta) = 1.5\int_0^1 \left(1 - \zeta^2 \right) \left(1 - C_j(\zeta, \xi)\right) d\xi \] (5.3.1)
### GAS PHASE

<table>
<thead>
<tr>
<th>Mole balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1.5u_j^0\left[1 - \left(\frac{r_j}{R_j}\right)^2\right]c_j = D_j \frac{\partial^2 c_j}{\partial z^2} + \frac{\partial^2 c_j}{\partial z^2}]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Energy balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1.5u_j^0\left[1 - \left(\frac{r_j}{R_j}\right)^2\right] \rho_j c_j \frac{\partial T_j}{\partial z} = k_j \frac{\partial^2 T_j}{\partial z^2} + \frac{\partial^2 T_j}{\partial z^2}]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Boundary conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inlet:</strong> &amp; (z=0; \forall r_j), &amp; (c_j = c_j^0; T_j = T_j^0)</td>
</tr>
<tr>
<td><strong>Outlet:</strong> &amp; (z=L; \forall r_j), &amp; (\frac{\partial c_j}{\partial z} = \frac{\partial T_j}{\partial z} = 0)</td>
</tr>
<tr>
<td><strong>Symmetry:</strong> &amp; (\forall z; r_j=0), &amp; (\frac{\partial c_j}{\partial r_j} = \frac{\partial T_j}{\partial r_j} = 0)</td>
</tr>
<tr>
<td><strong>Reacting wall:</strong> &amp; (\forall z; r_j=R_j), &amp; (D_j \frac{\partial c_j}{\partial r_j} = -A_j^0 \exp\left(-\frac{E_j}{R_g T_j}\right)c_j)</td>
</tr>
<tr>
<td>&amp; &amp; (k_j \frac{\partial T_j}{\partial r_j} = (-\Delta H_j)A_j^0 \exp\left(-\frac{E_j}{R_g T_j}\right)c_j + (-1)^{j-1}k_s \frac{\partial T_s}{\partial r_s})</td>
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### SOLID PHASE

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<th>La Place’s equation</th>
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</thead>
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</table>

<table>
<thead>
<tr>
<th>Boundary conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inlet:</strong> &amp; (z=0; \forall r_s), &amp; (\frac{\partial T_s}{\partial z} = 0)</td>
</tr>
<tr>
<td><strong>Outlet:</strong> &amp; (z=L; \forall r_s), &amp; (\frac{\partial T_s}{\partial z} = 0)</td>
</tr>
<tr>
<td><strong>Reacting wall – channel 1</strong> &amp; (\forall z; r_s=0), &amp; (T_s = T_1)</td>
</tr>
<tr>
<td><strong>Reacting wall – channel 2</strong> &amp; (\forall z; r_s=1), &amp; (T_s = T_2)</td>
</tr>
</tbody>
</table>

\(j=1\) endothermic channel
\(j=2\) exothermic channel
Table 5.3.2 Dimensionless co-ordinates, variables and coefficients used in two-dimensional CPR model

<table>
<thead>
<tr>
<th>Dimensionless co-ordinates</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Axial: ( \zeta = \frac{z}{L} )</td>
<td></td>
</tr>
<tr>
<td>Radial for channel ( j ): ( \zeta_j = \frac{r_j}{R_j} )</td>
<td></td>
</tr>
<tr>
<td>Radial for solid wall: ( \zeta_s = \frac{r_s}{\delta} )</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dimensionless variables</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensionless concentration ( C_j = \frac{c_j}{c_j^0} )</td>
<td></td>
</tr>
<tr>
<td>Dimensionless temperature in gas phase ( \theta_j = \frac{T_j}{T_0} )</td>
<td></td>
</tr>
<tr>
<td>Dimensionless temperature in solid phase ( \theta_s = \frac{T_s}{T_0} )</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dimensionless coefficients:</th>
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</thead>
<tbody>
<tr>
<td>( \alpha_j = \frac{D_j}{u_{z_j}^0 L} )</td>
<td></td>
</tr>
<tr>
<td>( \sigma_j = \left( \frac{L}{R_j} \right)^2 )</td>
<td></td>
</tr>
<tr>
<td>( \beta_j = \frac{k_j}{\rho_j u_{z_j}^0 c_{p_j} L} )</td>
<td></td>
</tr>
<tr>
<td>( \varepsilon_j = \frac{R_j}{D_j} A_j^0 )</td>
<td></td>
</tr>
<tr>
<td>( \gamma_j = \frac{E_j}{R_g T_0} )</td>
<td></td>
</tr>
<tr>
<td>( \nu_j = \frac{D_j (\Delta H_j^0) c_j^0}{k_j T_0} )</td>
<td></td>
</tr>
<tr>
<td>( \lambda_j = \frac{k_s R_j}{k_j \delta} )</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.3.3 Two-dimensional CPR dimensionless model for first order exothermic-endothermic reaction

**GAS PHASE**

Molar balance

\[ 1.5 \left[ 1 - \xi_j^2 \right] \frac{\partial C_j}{\partial \xi_j} = a_j \left( \sigma_j \frac{\partial^2 C_j}{\partial \xi_j^2} + \frac{\partial^2 C_j}{\partial \zeta^2} \right) \]

Energy balance

\[ 1.5 \left[ 1 - \xi_j^2 \right] \frac{\partial \theta_j}{\partial \xi_j} = \beta_j \left( \sigma_j \frac{\partial^2 \theta_j}{\partial \xi_j^2} + \frac{\partial^2 \theta_j}{\partial \zeta^2} \right) \]

Boundary conditions

**Inlet:**  \( \zeta=0; \ \forall \xi_j \quad C_j = 1, \ \theta_j = 1 \)

**Outlet:**  \( \zeta=1; \ \forall \xi_j \quad \frac{\partial C_j}{\partial \zeta} = \frac{\partial \theta_j}{\partial \zeta} = 0 \)

**Symmetry:**  \( \forall \zeta; \ \xi_j=0 \quad \frac{\partial C_j}{\partial \xi_j} = \frac{\partial \theta_j}{\partial \xi_j} = 0 \)

**Reacting wall:**  \( \forall \zeta; \ \xi_j=1 \quad \frac{\partial C_j}{\partial \xi_j} = \varepsilon_j \exp \left( -\frac{y_j}{\theta_j} \right) C_j \)

\[ \frac{\partial \theta_j}{\partial \xi_j} = v_j \frac{\partial C_j}{\partial \xi_j} + (-1)^{j-1} \lambda_j \frac{\partial \theta_j}{\partial \xi_s} \]

**SOLID PHASE**

La Place’s equation

\[ \frac{\partial^2 \theta_s}{\partial \zeta^2} + \sigma_s \frac{\partial^2 \theta_s}{\partial \xi_s^2} = 0 \]

Boundary conditions:

**Inlet:**  \( \zeta=0; \ \forall \xi_s \quad \frac{\partial \theta_s}{\partial \zeta} = 0 \)

**Outlet:**  \( \zeta=1; \ \forall \xi_s \quad \frac{\partial \theta_s}{\partial \zeta} = 0 \)

**Reacting wall – channel 1**  \( \forall \zeta, \ \xi_s=0 \quad \theta_s=\theta_1 \)

**Reacting wall – channel 2**  \( \forall \zeta; \ \xi_s=1 \quad \theta_s=\theta_2 \)
Table 5.3.4. Model Parameters used in the calculations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Channel 1 endothermic</th>
<th>Channel 2 exothermic</th>
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<td>0.3</td>
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<tr>
<td>Channel height</td>
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<td>2</td>
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<tr>
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<td>J/kg K</td>
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<td>0.0735</td>
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<td>Inlet temperature</td>
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<td>1000</td>
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<td>Inlet concentration</td>
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<tr>
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<td>2021</td>
<td>1.73-10$^5$</td>
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<td>Case II</td>
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<td>8.27-10$^5$</td>
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<tr>
<td>Thickness</td>
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<tr>
<td><strong>Thermal conductivity</strong></td>
<td>W/m K</td>
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</table>
5.3.2 Sensitivity Equations

The sensitivity equations are derived from the reactor model equations using the direct differential method (Ungureanu et al. 1994, Varma et al. 1999, Kelkar and Ng. 2000). Their general mathematical formulation is given in Table 5.3.5 which gives the equations required to calculate the local sensitivity of the dependent variable $y$ with respect to the input parameter $\Phi_i$, $s^y_{\Phi_i}$. Note that $y$ can be the dimensionless temperature, $\theta$, or the dimensionless concentration of the reactant in each channel, $C_j$.

The sensitivity of the outlet conversion can be obtained from equation (5.3.1) as:

$$S^y_{\Phi_i} = -1.5 \int_0^1 \left(1 - \xi^2\right) s^C_{\Phi_i}(1, \xi) d\xi$$  \hspace{1cm} (5.3-2)

In the present study the input parameters investigated for their impact on reactor sensitivity are: pre-exponential factors, $A_1^0, A_2^0$; activation energies, $E_1, E_2$; inlet velocities, $u_1^0, u_2^0$; inlet concentrations, $c_1^0, c_2^0$; inlet temperature, $T_0$; channel height, $R$; wall thickness, $\delta$, and wall thermal conductivity, $k_s$. The derivatives of the dimensionless groups with respect to each input parameter appearing in the sensitivity equations are given in Table. 5.3.6. After the local sensitivities have been calculated the normalised sensitivity can be determined straightforward, based on its definition given in equation (2.7-4) as

$$S^y_{\Phi_i} = \frac{\Phi_i}{y} S^y_{\Phi_i}$$  \hspace{1cm} (5.3-3)

Sensitivity equations for each parameter were solved together with the reactor model. A gPROMs cod sample used to obtain the sensitivity equations with respect to the pre-exponential factor in the endothermic channel is given in Appendix C2. Similar cods were used for all the other parameters.
Table 5.3.5. Sensitivity equations for based on CPR two-dimensional model.

**GAS PHASE**

**Sensitivity of dimensionless concentrations:**

\[
1.5\left[1 - \xi_j^2\right] \frac{\partial s_j^{\phi_1}}{\partial \xi_j} = \frac{\partial \alpha_j}{\partial \Phi_1} \left( \sigma_j \frac{\partial^2 C_j}{\partial \xi_j^2} + \frac{\partial^2 C_j}{\partial \sigma_j^2}\right) + \alpha_j \left( \frac{\partial \sigma_j}{\partial \Phi_1} \frac{\partial^2 C_j}{\partial \xi_j^2} + \frac{\partial^2 C_j}{\partial \sigma_j^2} + \frac{\partial^2 C_j}{\partial \xi_j^2} + \frac{\partial^2 C_j}{\partial \sigma_j^2}\right)
\]

**Sensitivity of dimensionless temperature:**

\[
1.5\left[1 - \xi_j^2\right] \frac{\partial s_j^{\theta_1}}{\partial \xi_j} = \frac{\partial \beta_j}{\partial \Phi_1} \left( \sigma_j \frac{\partial^2 \theta_j}{\partial \xi_j^2} + \frac{\partial^2 \theta_j}{\partial \sigma_j^2}\right) + \beta_j \left( \frac{\partial \sigma_j}{\partial \Phi_1} \frac{\partial^2 \theta_j}{\partial \xi_j^2} + \frac{\partial^2 \theta_j}{\partial \sigma_j^2} + \frac{\partial^2 \theta_j}{\partial \xi_j^2} + \frac{\partial^2 \theta_j}{\partial \sigma_j^2}\right)
\]

**Boundary conditions**

**Inlet:** \(\xi = 0; \quad \forall \xi_j; \quad s_j^{\phi_1} = s_j^{\phi_1} = 0\)

**Outlet:** \(\xi = 1; \quad \forall \xi_j; \quad \frac{\partial s_j^{\phi_1}}{\partial \xi_j} = \frac{\partial s_j^{\phi_1}}{\partial \xi_j} = 0\)

**Symmetry:** \(\forall \xi; \quad \xi_j = 0; \quad \frac{\partial s_j^{\phi_1}}{\partial \xi_j} = \frac{\partial s_j^{\phi_1}}{\partial \xi_j} = 0\)

**Reacting wall:** \(\forall \xi; \quad \xi_j = 1\)

\[
\frac{\partial s_j^{\phi_1}}{\partial \xi_j} = \frac{\partial C_j}{\partial \xi_j} \left( s_j^{C_j} - \gamma_j \frac{\partial s_j^{\phi_1}}{\partial \xi_j} \right) + \frac{\partial}{\partial \Phi_1} \left[ \varepsilon_j \exp \left( - \frac{\gamma_j}{\theta_j} \right) C_j \right]
\]

\[
\frac{\partial s_j^{\theta_1}}{\partial \xi_j} = \frac{\partial \nu_j}{\partial \Phi_1} \frac{\partial C_j}{\partial \xi_j} + \nu_j \frac{\partial s_j^{C_j}}{\partial \xi_j} + (-1)^{j-1} \left[ \frac{\partial \lambda_j}{\partial \Phi_1} \frac{\partial \theta_j}{\partial \xi_j} + \lambda_j \frac{\partial s_j^{\theta_1}}{\partial \xi_j} \right]
\]

**SOLID PHASE**

**Sensitivity of dimensionless temperature**

\[
\frac{\partial^2 s_j^{\theta_1}}{\partial \sigma_j^2} + \sigma_j \frac{\partial^2 s_j^{\phi_1}}{\partial \sigma_j^2} + \frac{\partial \sigma_j}{\partial \Phi_1} \frac{\partial^2 s_j^{\phi_1}}{\partial \sigma_j^2} + \frac{\partial^2 s_j^{\phi_1}}{\partial \xi_j^2} = 0
\]

**Boundary conditions**

**Inlet:** \(\xi = 0; \quad \forall \xi_s; \quad \frac{\partial s_j^{\phi_1}}{\partial \xi_j} = 0\)

**Outlet:** \(\xi = 1; \quad \forall \xi_s; \quad \frac{\partial s_j^{\phi_1}}{\partial \xi_j} = 0\)

**Reacting wall – channel 1:** \(\forall \xi; \quad \xi_s = 0; \quad s_j^{\phi_1} = s_j^{\phi_1}; \)

**Reacting wall – channel 2:** \(\forall \xi; \quad \xi_s = 0; \quad s_j^{\phi_1} = s_j^{\phi_1}; \)

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Table 5.3.6. Mathematical expression of the term $\frac{\partial \Omega}{\partial \Phi_i}$ in sensitivity equations

<table>
<thead>
<tr>
<th>Parameter investigated $\Phi_i$</th>
<th>$\frac{\partial \Omega}{\partial \Phi_i}$ Expression</th>
<th>$\Omega$</th>
<th>$\sigma_j$</th>
<th>$\alpha_i$</th>
<th>$\beta_i$</th>
<th>$\epsilon_i$</th>
<th>$\gamma_i$</th>
<th>$\nu_i$</th>
<th>$\lambda_i$</th>
<th>$\omega_i$</th>
<th>$\epsilon_i \exp\left(\frac{\gamma_i}{\theta_1}\right) C_1$</th>
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<td>$T_0$</td>
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<td>$0$</td>
<td>$0$</td>
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<tr>
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<td>$0$</td>
<td>$0$</td>
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Table 5.3.6. Mathematical expression of the term $\frac{\partial \Omega}{\partial \Phi_i}$ in sensitivity equations (continued).

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<th>$\frac{\partial \Omega}{\partial \Phi_i}$</th>
<th>$\Omega$ Expression</th>
<th>$\sigma_i$</th>
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<th>$\beta_i$</th>
<th>$\varepsilon_i$</th>
<th>$\gamma_i$</th>
<th>$\nu_i$</th>
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<td>$\frac{1}{k_2 \delta}$</td>
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5.3.3. Acceptable Operation Criterion

The values of normalised sensitivities can show if reactor behaviour exceeds the operation limits for specific (%) deviations of the input parameters, $\delta_{\Phi_j}$. Following the definition of normalised sensitivity (eq. 2.7-4) a Normalised Sensitivity Threshold is expressed by

$$NS_T(y, \Phi_j) = \left| \frac{\delta^a_{\Phi_j}}{\delta_{\Phi_j}} \right|$$

(5.3-4)

where $\delta^a_{\Phi_j}$ is the acceptable relative variation of the dependant variable $y$. The "acceptable operation criterion" then states that for a specific deviation $\delta_{\Phi_j}$, the reactor must exhibit normalised sensitivities which meet the condition

$$\left| S^*_{\Phi_j} \right| \leq NS_T(y, \Phi_j)$$

(5.3-5)

5.3.4. Results and Discussion

Three case studies are considered corresponding to three sets of kinetic parameters. The pre-exponential factors are adjusted so that an almost isothermal profile is achieved along the reactor and ca. 90% conversion for both reactions. After solving the reactor model, the temperature and concentration, together with the corresponding sensitivity profiles have been obtained as a function of the axial and radial dimensionless coordinate. The dimensionless temperature profiles are displayed in Figure 5.3.1 showing that for cases I and II the reactor thermal behaviour is similar. Despite their similarities, different sensitivity behaviour has been obtained. Accordingly, a comparison between the first two cases for the normalised sensitivities of dimensionless temperature with respect to inlet temperature, $S^0_{\Theta_{in}}$, and inlet average velocity in the endothermic channel, $S^0_{\Theta_q}$, is illustrated in Figures 5.3.2a and 5.3.2b.
The positive sign of the normalised sensitivity of the dimensionless temperature with respect to the inlet temperature, $S^0_{T_i}$, (see Figure 5.3.2a) indicates that an increase in the inlet temperature leads to an increase of the dimensionless temperature along the reactor. It can be seen that for higher activation energy of the exothermic reaction, CPR exhibits higher sensitivities for the whole reactor length. The sensitivities do not vary significantly in the radial direction and their maximum is located around the axial dimensionless position 0.5.

The normalised sensitivity of the dimensionless temperature with respect to the inlet velocity in the endothermic channel, $S^0_{u_i}$, have negative sign along the reactor for both cases. Thus, an increase in the inlet velocity and consequently of the flowrate in the endothermic channel results in a decrease of the dimensionless temperature. Indeed, it is expected that by increasing the amount of the endothermic reactants more heat to be consumed leading to temperature decrease. In addition, for higher activation energy of the exothermic reaction, the normalised sensitivity absolute values are higher, meaning that for the same variation in the inlet velocity of the endothermic channel the change in temperature is more significant. Again, the sensitivities do not vary significantly in the radial direction and their maximum is located this time at the reactor outlet.

Comparing the Figures 5.3.2a and 5.3.2b it can be seen that $S^0_{T_i}$ exhibits larger difference between the case I and II, than $S^0_{u_i}$. This suggests that the influence of the each parameter is system dependent.
Figure 5.3.1 Dimensionless temperature profiles (a) case I; (b) case II.
Figure 5.3.2 Normalised sensitivities of dimensionless temperature with respect to (a) inlet temperature (b) inlet average velocity in the endothermic channel.
5.3.4.1 Sensitivities Hierarchy

Profiles for the normalised sensitivity of the dimensionless temperature and both exothermic and endothermic conversions are obtained for all model parameters. However, in order to provide a comparison among the parameters investigated, it was found easier to compare the magnitude of those sensitivities. Thus, the extreme value of normalised sensitivity of the dimensionless temperature related to each parameter $\Phi_i$ investigated, $S^\Phi_i$, and the sensitivities of the final conversions $S^X_{\Phi_i}$, $S^X_{\Phi_i}$ are hereby understood as maximum if they have a positive sign along the reactor, and as minimum if they have a negative sign along the reactor. Their values are displayed in Table 5.3.7 and are graphically represented in Figures 5.3.3, 5.3.4, and 5.3.5.

Table 5.3.7. Normalised sensitivity values for the cases considered.

<table>
<thead>
<tr>
<th>$\Phi_i$</th>
<th>Case I</th>
<th>Case II</th>
<th>Case III</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S^\Phi_{T_0}$</td>
<td>$S^X_{T_0}$</td>
<td>$S^X_{E_1}$</td>
<td>$S^\Phi_{E_1}$</td>
</tr>
<tr>
<td>$T_0$</td>
<td>0.52</td>
<td>3.9</td>
<td>4.2</td>
</tr>
<tr>
<td>$E_1$</td>
<td>3.5</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>$E_2$</td>
<td>-4</td>
<td>-9</td>
<td>-13</td>
</tr>
<tr>
<td>$A_1^0$</td>
<td>-0.52</td>
<td>-0.5</td>
<td>-0.82</td>
</tr>
<tr>
<td>$A_2^0$</td>
<td>0.47</td>
<td>0.75</td>
<td>0.55</td>
</tr>
<tr>
<td>$c_1^0$</td>
<td>-0.75</td>
<td>-1.55</td>
<td>-1.75</td>
</tr>
<tr>
<td>$c_2^0$</td>
<td>0.52</td>
<td>1.55</td>
<td>1.75</td>
</tr>
<tr>
<td>$u_1^0$</td>
<td>-0.33</td>
<td>-1</td>
<td>-0.85</td>
</tr>
<tr>
<td>$u_2^0$</td>
<td>0.34</td>
<td>0.75</td>
<td>1.1</td>
</tr>
<tr>
<td>$R$</td>
<td>0.006</td>
<td>-0.29</td>
<td>-0.29</td>
</tr>
<tr>
<td>$\delta$</td>
<td>0.002</td>
<td>0.004</td>
<td>0.003</td>
</tr>
<tr>
<td>$k_s$</td>
<td>-0.002</td>
<td>-0.004</td>
<td>-0.003</td>
</tr>
</tbody>
</table>

It can be seen that for all cases, the strongest sensitivities are those with respect to inlet temperature and activation energies; inlet velocities and concentrations, and pre-exponential factors show a moderate sensitivity, while channel height, wall thickness and wall thermal conductivity exhibit the lowest sensitivities. The low sensitivity related to $R$, $\delta$, $k_s$ demonstrates that for the channel and wall dimensions considered and for a thermal conductivity characteristic to metallic wall, the heat transfer between channels...
Parametric Sensitivity Analysis for CPRs

is very efficient and there are not significant variations in temperature profile for small changes in these parameters.

Variations in inlet compositions and velocities represent changes in the amount of reactants available in the system. These result in disturbances between the ratio of heat consumed and heat generated and therefore the temperature increases or decreases from its base case value depending on which parameter is altered. Kinetic parameters play an important role for reactor thermal behaviour, especially the activation energies. This suggests that in a CPR where the heat and mass transfer resistances have been minimised, chemical reactions remain the main source of disturbance in the system. A similar hierarchy is observed among the parameters investigated for their influence on conversion sensitivity. It is worth noticing that the sensitivity of conversions is more significant than the dimensionless temperature sensitivity. In addition, all parameters affect more the exothermic reaction than the endothermic one (see Figure 5.3.4 and 5.3.5). Although the sensitivity to channel height, R, is small, it is one order of magnitude higher than the sensitivity of dimensionless temperature related to the same parameter. This may suggest that for small changes in channel height, the influence of external mass transfer is noticeable. In order to provide a direct comparison between the cases considered the hierarchy of the normalised sensitivities $S_{\phi_i}^\theta$, $S_{\phi_i}^{X_{\text{exoth}}}$, $S_{\phi_i}^{X_{\text{end}}}$ is showed in a histogram representation in Figures 5.3.3, 5.3.4, 5.3.5 respectively.
Figure 5.3.3 Extreme values of normalised sensitivity of dimensionless temperature with respect to all parameters investigated

Figure 5.3.4 Extreme values of normalised sensitivity of exit endothermic reaction conversion with respect to all parameters investigated
Figure 5.3.5 Extreme values of normalised sensitivity of exit exothermic reaction conversion with respect to all parameters investigated

5.3.4.2 Influence of the relation between the activation energies

The results indicate that when $E_{exo}>E_{endo}$ (cases I and II), the higher the difference $\Delta E^{(+)}=E_{exo}-E_{endo}$ the stronger becomes the sensitivity with respect to the activation energies and the inlet temperature. For example, in case II corresponding to a $\Delta E^{(+)}=40$ kJ/mol, $S_{E_i}^{0'}=7.3$; $S_{E_i}^{0'}=15.5$; $S_{E_i}^{0'}=-23$, while for case I which has a $\Delta E^{(+)}=10$ kJ/mol, $S_{E_i}^{0'}=0.52$; $S_{E_i}^{0'}=3.5$; $S_{E_i}^{0'}=-4$.

When a higher activation energy for the endothermic reaction than for the exothermic one exists, $E_{endo}>E_{exo}$, even at high difference $\Delta E^{(-)}=E_{endo}-E_{exo}$, moderate sensitivities with respect to inlet temperature and activation energies are observed. For example, in case III, $\Delta E^{(-)}=50$ kJ/mol, and $S_{E_i}^{0'}=-0.55$; $S_{E_i}^{0'}=2.05$; $S_{E_i}^{0'}=-1.5$. The
negative sign of the normalised sensitivity related to the inlet temperature may suggest that case III has a self-regulating property of its thermal behaviour.

Application of Acceptable Operation Criterion (AOC). Below an example is discussed to illustrate the applicability of AOC. If for various reasons (catalyst deactivation; changes in reaction path, etc.) a variation of temperature along the reactor by only ±50K from its inlet value is allowed, then the acceptable relative variation of dimensionless temperature, $\delta^\text{acc}_t$, is ±5%. Further, let us assume for illustration purposes, that a 10% variation in the exothermic catalyst loading might occur, and we need to evaluate if this variation can bring the reactor temperature outside the acceptable operating range. A Normalised Sensitivity Threshold can be calculated according to equation (5.3-4),
Parametric Sensitivity Analysis for CPRs

NS\textsubscript{τ}(θ; A^0_2) = 0.5. The application of AOC is illustrated in Figure 5.3.6, where sensitivities of dimensionless temperature, θ, related to the pre-exponential factor of exothermic reaction, A^0_2, are plotted for both base cases together with the NS\textsubscript{τ} plane. As can be seen, the AOC given by equation (5.3-5) is fulfilled only by the base case I, while base case II (i.e. high activation energy of the exothermic reaction) exhibits a sensitivity higher than the threshold value. Consequently, a 10 % variation in catalyst loading for base case II can bring the reactor temperature outside the acceptable operation limits. Thus, a catalyst with lower activation energy is preferred.

5.4 Conclusions

Parametric Sensitivity Analysis (PSA) was applied to study CPR sensitivity behaviour based on one-dimensional and two-dimensional model. The first approach offers a short-cut model which can be easily used to check the suitability of autothermal coupling, while the second one introduce more complexity leading to a more accurate representation of the CPR sensitivity behaviour in terms of numbers of parameters investigated. Both approaches indicate that the activation energies and the inlet temperature are the most influential parameters. The results obtained based on the two-dimensional model showed that the least influential parameters are the geometrical parameters and wall thermal conductivity. This indicates that the heat transfer between channels is very efficient and there are not significant variations in CPR behaviour for small changes in these parameters.

Different catalysts can show similar thermal behaviour and final conversions, but exhibit different sensitivities to input parameters, making the reactor operation difficult to control and stabilise. It was found that the relation between the activation energies of the exothermic and endothermic reaction is an important issue. Combinations of
catalysts with high activation energy for the exothermic reaction and low activation energy for the endothermic one cause a strongly sensitive behaviour with respect to all parameters studied. While, in the reverse situation the system may have self-regulating property of its thermal behaviour.

PSA can be used to estimate design parameters window that allow keeping the CPR behaviour in the desired operating range, or to evaluate if small variations in these parameters can bring the reactor outside the operating range affecting its stability.
6.1. Introduction

The CPRs combine the function of heat exchanger and chemical reactor in the same piece of equipment. During pure heat exchange, flow arrangement has a direct impact on the temperature profile developed in the equipment (Welty et al. 1984). Therefore, it is expected that CPR behaviour and performance to be also influenced by the flow arrangement. In the previous chapters CPRs for co-current arrangement have been modelled and studied for some particular reaction systems. Another alternative to the flow arrangement is counter-current as shown in Figure 6.1.1. Catalyst layers are distributed towards the middle of the plate so that both plate ends are catalyst-free allowing only pure heat transfer between channels.

At the first sight this type of arrangement brings the advantage of integrating in the same piece of equipment the reaction zone and the preheating sections of the streams fed to reactor. Thus, the sensible heat stored in the effluent stream that leaves the reaction zone in one channel is utilised to preheat the stream fed in the other channel. This design eliminates the necessary piping between an additional external heat exchanger and the reaction zone. In addition, both ends of the plate are at low temperature, avoiding difficulties in sealing the reactor. These advantages make the counter-current operation more attractive than co-current one. However, an investigation of its behaviour is required in order to understand and compare the
advantages and the disadvantages of both designs. An efficient operation needs not only a high degree of heat integration, but also high reliability and controllability of the reactor.

Frauhammer et al. (1999) and later Kolios et al. (2001) addressed the counter-current coupling of methane stream reforming and methane combustion in adjacent channels using monoliths with square channels having both catalysts deposited at the monoliths wall. The authors used a one-dimensional dispersion model and studied the influence of different fuel gas flowrates, a varying axial distribution of the catalyst, and of homogeneous reactions on the heat exchange between the exothermic and the endothermic side. They identified several important aspects related to this reaction system. In certain conditions, the endothermic reaction can cool down both reaction mixtures, and poor conversions for both endothermic and exothermic reactions are achieved. A slight increase of the fuel gas flow leads to a sharp temperature maximum, which in turn ignite the homogeneous combustion and propagate it backward in the preheating zone. Although the conversion of the endothermic reaction can reach ca. 100
% around the position where the temperature peak is located, the cooling of the effluents in the preheating zone of the exothermic stream, favours the reverse reaction of steam reforming and its conversion drops below 100 %. The authors identified that the location of the catalyst zones in the channels related to each other may be used as a degree of flexibility to adjust the temperature profile, and prevent the detrimental reverse reaction in the endothermic side.

In the present chapter the modelling and simulation of the system steam reforming - methane combustion in a CPR in counter-current is addressed using a two dimensional model. The study is focused on the effects of flow arrangement on the overlapping of the endothermic and exothermic reaction zones without taking into consideration the preheating zones (see Figure 6.1.2).

![Figure 6.1.2 Counter-current flow arrangement for the overlapped reaction zones](image_url)

A comparison to the co-current arrangement is used to assess the impact of the flow arrangement on the reactor behaviour. Furthermore, a non-uniform catalyst distribution along the exothermic channel is explored in order to gain a better understanding about options for improving the thermal behaviour of CPRs.
Influence of Flow Arrangement

6.2. Reaction System and Mathematical Model

The reaction system refers to coupling of steam reforming of methane and methane combustion as presented in section 4.3. The mathematical model which describes the CPR given in Table 4.3.1 has been modified accordingly to simulate the counter-current flow arrangement. The modifications consist of swapping the inlet and outlet boundary conditions for the combustion channel, and changing the sign for the convection term in the equations for mass and energy balances. Thus, the flow in the combustion channel has the opposite direction to the one in the reforming channel. For completeness the equations for the gas phase in the combustion channel are given in Table 6.1. The equations for the catalyst layers, the gas phase for the endothermic channel, and solid wall, including the boundary conditions remain identical to the ones for the CPR in co-current arrangement, as given in Table 4.3.1.

The model was solved using gPROMS. The code is similar to the one used in Chapter 4 (see also Appendix B2) with the modifications discussed above. In addition, the solution method for the axial direction in combustion channel was selected as forward finite difference in order to have the opposite direction to the stream flow (Oh 1995).
Table 6.1. Equations of the mathematical model for combustion gas phase for counter-current flow.

**GAS PHASE**

**Material Balances:**

\[-\rho_2 u_{z_2} \frac{\partial \omega_{i,2}^g}{\partial z} = \frac{\partial}{\partial x_2} \left( \rho_2 D_{i,mix,2} \frac{\partial \omega_{i,2}^g}{\partial x_2} \right) + \frac{\partial}{\partial z} \left( \rho_2 D_{i,mix,2} \frac{\partial \omega_{i,2}^g}{\partial z} \right)\]

**Energy Balance:**

\[-\rho_2 u_{z_2} c_{p2} e^z = \frac{\partial}{\partial x_2} \left( k_2^s \frac{\partial T_{i}^g}{\partial x_2} \right) + \frac{\partial}{\partial z} \left( k_2^s \frac{\partial T_{i}^g}{\partial z} \right)\]

**Continuity Equation:**

\[\frac{\partial \rho_2 u_{z_2}}{\partial z} = 0\]

**Equation of State for Ideal Gas**

\[\rho_2 = \frac{P_2}{R_e T_{i}^g} \frac{1}{\sum \omega_{i,2}^m / M_{i,2}}\]

**Boundary Conditions**

1. Inlet conditions: \( z = L; \quad \forall x_2^g \)
   - inlet composition: \( \omega_{i,2}^g = \omega_{i,2}^0 \)
   - inlet temperature: \( T_{i}^g = T_0 \)
   - parabolic inlet velocity profile \( u_{z_2} = 1.5 \cdot u_0^{i,2} \left[ 1 - \left( \frac{x_2^g}{L} \right)^2 \right] \)

2. Outlet conditions: \( z = 0; \quad \forall x_2^g \)
   - zero flux \( \frac{\partial \omega_{i,2}^g}{\partial z} = \frac{\partial T_{i}^g}{\partial z} = \frac{\partial u_{z_2}}{\partial z} = 0 \)

3. Symmetry conditions at channel centre: \( \forall z; \quad x_2^g = 0 \)
   - \( \frac{\partial \omega_{i,2}^g}{\partial x_2^g} = \frac{\partial T_{i}^g}{\partial x_2^g} = \frac{\partial u_{z_2}}{\partial x_2^g} = 0 \)

4. Catalyst surface conditions: \( \forall z; \quad x_2^g = R_2 \)
   - \( \rho_2 D_{i,mix} \frac{\partial \omega_{i,2}^g}{\partial x_2^g} \bigg|_{x_2^g = R_2} = -\rho_2 D_{i,eff} \frac{\partial \omega_{i,2}^m}{\partial x_2^g} \bigg|_{x_2^g = R_2} \)
   - \( k_2^s \frac{\partial T_{i}^g}{\partial x_2^g} \bigg|_{x_2^g = R_2} = H_2 - \lambda_2^s \frac{\partial T_{i}^g}{\partial x_2^g} \bigg|_{x_2^g = R_2} \)

where \( H_2 \) is the total heat flux generated or consumed in the chemical reactions:

- no slip conditions
  \( u_{z_2} = 0 \)
6.3 Results and Discussion

6.3.1 Comparison between Co-current and Counter-Current Operation

The model parameters used in the calculations are identical with the ones in table 4.3.2, except the pre-exponential factor for catalytic combustion, which hereby is half the value given in Table 4.3.2. For steam reforming of methane the kinetics proposed by Xu and Froment (1989a) are used (see Table 2.5). While, for methane catalytic combustion a first order kinetic is adopted together with an activation energy of 90 kJ/mol and a pre-exponential factor of $2 \times 10^9$ s$^{-1}$. Coupling of steam reforming of methane with methane catalytic combustion in a CPR has been simulated for both co-current and counter current operation, using identical parameters of the mathematical model. Thus, a direct comparison between the reactor behaviour and performance under different flow arrangement conditions can be made.

First thing to compare is the reactor thermal behaviour in terms of axial temperature profile and radial temperature gradients. Figures 6.3.1a and 6.3.1b show the axial temperature profile for co-current operation in reforming and combustion channel respectively, while Figures 6.3.1c and 6.3.1d show the axial temperature profile for counter-current operation in reforming and combustion channel respectively. The radial temperature gradients defined as the difference between the temperature of the gas phase at the wall and at the channel centre, $\Delta T = T_{wall} - T_{centre}$, are shown in Figure 6.3.2a and 6.3.2b for co-current and counter-current operation respectively.
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Co-current

Counter-current

Figure 6.3.1 Temperature profiles along the reactor for
Co-current operation: a. reforming channel and b. combustion channel
Counter current operation: c. reforming channel and b. combustion channel

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Figure 6.3.2 Radial temperature gradients for
a. co-current operation; b. counter current operation
It can be seen that for co-current flow arrangement both reaction mixtures are slightly cooled down after they enter the reactor. The gas phase temperature drops from its inlet value 793 K (ζ=0) to a minimum of ca. 771 K located at the axial dimensionless position, ζ=0.15. Between the inlet, ζ =0, and ζ =0.15, the wall temperature is lower than the temperature of the gas phase at the centre of the channel. The lowest temperature gradient of ca. -24 K occurs at the inlet for both reforming and combustion channel (see also Figure 6.3.2a), then the temperature difference between wall and channel centre decreases towards the position ζ =0.15. Afterwards, the axial temperature keeps increasing along the reactor, and the wall temperature is slightly higher than the temperature of the gas phases. The maximum radial temperature gradient reaches the values of 12.6 K at ζ =0.85, for reforming channel; and 16.5 at ζ =0.9 for combustion channel. Eventually, the wall temperature at the reactor outlet, ζ=1, for co-current operation, reaches ca 914 K.

For the counter-current arrangement (see Figure 6.3.1c and 6.3.1d), the axial temperature profiles go through more pronounced extremes than in the co-current arrangement. Thus, in the reforming channel, Figure 6.3.1c, the reaction mixture temperature first drops from its inlet value of 793 K to ca. 732 K at ζ=0.2. Between the inlet and this location the wall temperature is lower than the gas phase temperature, the radial temperature gradient (see Figure 6.3.2b) has a value of -52 K at the channel inlet (ζ =0). Around the axial position ζ =0.25 a crossover of the axial temperature profiles occurs (see Figure 6.3.1c) and the wall temperature becomes higher than the gas phase temperature at the channel centre. Afterwards, the axial temperature keeps increasing reaching a maximum of ca. 1103 K at the outlet (ζ=1). The maximum radial temperature gradient, in reforming channel for counter-current arrangement occurs at
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the axial dimensionless position $\zeta = 0.9$, and has a value of 56 K (see Figure 6.3.2b). The temperature profiles in combustion channel (see Figure 6.3.1d) show different behaviour. At the channel inlet ($\zeta = 1$), the wall temperature has the highest temperature in the reactor, ca. 1103 K which represents ca. 310 K above the inlet temperature of the reaction mixture. The temperature at the channel centre increases very fast from its inlet value of 793 K, reaching a maximum of 1021 K at the position $\zeta = 0.85$. The wall temperature is higher than the gas phase temperature between the combustion channel inlet, $\zeta = 1$, and the axial dimensionless position of ca. $\zeta = 0.9$ where a crossover of the axial temperature profiles occurs. The axial temperature starts then to decrease till it reaches a minimum of ca 733, at $\zeta = 0.15$. The wall temperature is lower than the gas phase between $\zeta = 0.9$ and $\zeta = 0.15$, indicating that the heat flux consumed exceed the heat flux generated (see also Figure 6.3.3b), and the radial temperature gradient shows a minimum of ca. $-81$ K at $\zeta = 0.8$ (see Figure 6.3.2b). From the dimensionless axial position $\zeta = 0.15$ to the channel outlet $\zeta = 0$, the combustion mixture temperature slightly increases and reaches on outlet value of ca. 735 K.

The reactor thermal behaviour is a consequence of the relation between heat generation and heat consumption in exothermic and endothermic processes along the reactor. Generated and consumed heat fluxes are depicted in Figure 6.3.3a and 6.3.3b for co-current and counter-current operation respectively. It can be seen that both heat fluxes are more uniform distributed along the catalytic plate for co-current operation. For counter-current operation, the heat flux generation or consumption is more concentrated towards the inlet of the combustion channel, $\zeta = 1$. The ratio between the local heat generated and consumed at $\zeta = 0$, is 0.48 for co-current operation and 0.18 for counter-
current operation. This explains the more pronounced cooling of the reaction mixtures around the inlet of the reforming channel $\zeta=0$, for counter-current operation.

Figure 6.3.3 Generated and consumed heat fluxes along the reactor in a. co-current operation, b. counter-current operation
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The same ratio at $\zeta=1$ is 1.6 for co-current operation and 3.5 for counter-current operation, which results in a local overheating of both reaction mixtures. A comparison between the evolution of the heat fluxes and evolution of conversion in the reactor can be made (Figures 6.3.4a and 6.3.4b). Combustion conversion progresses steadily in co-current operation (Figure 6.3.4a), reaching an outlet value of 47.5%. For counter-current operation a higher conversion of fuel is reached 51%. However, 77% of the fuel converted reacts in only 20% of the reactor length, near the inlet of the combustion channel (between $\zeta=1$ and $\zeta=0.8$). Consequently, the generated heat flux is concentrated around the dimensionless axial position $\zeta=1$. The depletion of reactants in the reforming channel, towards the outlet, decreases the endothermic reaction rates and consequently the capability of the reaction mixture to consume the heat flux generated in the other channel. Thus, a high imbalance between the heat fluxes occurs and the excess heat generated overheats the gas phases, increasing the chances of igniting homogeneous combustion. The conversion for the reforming process is higher in co-current arrangement for the most of the reactor length. For example at $\zeta=0.85$, reforming conversion reached 43.1% for co-current operation and 40.1% for counter-current operation. However, the outlet reforming conversion is higher for the counter-current operation (62.8%) than for co-current operation (52%), due to more significant temperature increase near the combustion channel inlet, $\zeta=1$.

Overall, it can be seen that for identical inlet conditions and catalyst loadings, the CPR thermal behaviour is different for co-current and counter current flow arrangement. This influences also the reaction path in the endothermic channel. The molar ratio between CO and CO$_2$, at the catalyst surface for the endothermic channel, has been represented in Figure 6.3.5 for both co-current and counter-current flow.
Figure 6.3.4 Conversions in CPR for
a. co-current operation, b. counter-current operation
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![Graphs showing molar ratio and hydrogen mole fraction](image)

Figure 6.3.5 CPR performance in the endothermic channel for co-current and counter-current operation
a. CO/CO₂ molar ratio at channel centre; b. H₂ mole fraction at channel centre.

Table 6.2 summarises several characteristics of co-current and counter current flow arrangement, in terms of temperature and temperature gradients extremes recorded in the CPR, outlet conversions and ratio of overall and local generated and consumed heat fluxes in exothermic and endothermic processes.
Table 6.2 Comparison between co-current and counter-current flow for CPR.

<table>
<thead>
<tr>
<th></th>
<th>Co-current</th>
<th>Counter-current</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet temperature (both channels)</td>
<td>793 K</td>
<td>793 K</td>
</tr>
<tr>
<td>Minimum Temperature</td>
<td>771 K</td>
<td>732 K</td>
</tr>
<tr>
<td>Maximum Temperature</td>
<td>914 K</td>
<td>1103 K</td>
</tr>
<tr>
<td>Radial Temperature Gradients</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Minimum</td>
<td>-24 K</td>
<td>-81 K</td>
</tr>
<tr>
<td>Maximum</td>
<td>16.5 K</td>
<td>310 K</td>
</tr>
<tr>
<td>Reforming conversion</td>
<td>52 %</td>
<td>62.8 %</td>
</tr>
<tr>
<td>Combustion conversion</td>
<td>47 %</td>
<td>51 %</td>
</tr>
<tr>
<td>Ratio between overall generated and consumed heat fluxes</td>
<td>1.43</td>
<td>1.26</td>
</tr>
<tr>
<td>Ratio between local generated and consumed heat fluxes at $\zeta=0$</td>
<td>0.48</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>$\zeta=1$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>3.5</td>
</tr>
</tbody>
</table>

It can be concluded that the flow arrangement of a CPR affects the thermal behaviour of the reactor. Overall, the heat generation and consumption is balanced better for co-current operation than for counter-current operation. For the latter, higher conversions and a better utilisation of the overall heat generated in the exothermic process are achieved, on the expense of more pronounced temperature extremes in the reactor and higher radial temperature gradients. This increases the possibility for either extinction or run away of the CPR. For complex reaction networks, the impact of flow arrangement on the CPR thermal behaviour influences the reaction path and therefore the selectivity of the products.
6.3.2 Influence of Non-Uniform Catalyst Distribution on the Thermal Behaviour

Counter-current operation exhibits significant temperature extremes. Hot spots may destroy the catalyst layer on both sides, put more severe material constraints, or initiate the homogeneous combustion making the reactor to run away. Cold spots can lead to poor performances or reactor extinguishing. Therefore, significant temperature extremes are not desirable. A non-uniform catalyst distribution in the combustion channel is investigated as an option to moderate the sharp temperature rise near the combustion channel entrance. An increasing catalyst loading from the entrance towards the exist is used, in order to reduce the catalytic combustion reaction rate near the channel entrance and to enhance it towards the outlet, where due to fresh reforming reactants in the other channel the heat consumption cools down the reacting streams. The non-uniform catalyst distribution is represented in the mathematical model by means of a distribution factor, $f$, depending on the dimensionless axial co-ordinate, $\zeta$. The total amount of catalyst is kept constant, and hence:

$$\int_0^1 f(\zeta) d\zeta = 1 \quad (6.3-1)$$

The catalyst distribution factor $f(\zeta)$, multiplies the pre-exponential factor in the combustion channel, while the catalyst thickness is kept at its base case value. Two cases representing a linear and parabolic catalyst distribution are investigated and compared to the uniform catalyst distribution case. The corresponding distribution factors are given in Table 6.3 and are represented in Figure 6.3.6.

<table>
<thead>
<tr>
<th>Distribution Type</th>
<th>Distribution factor, $f(\zeta)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Uniform</td>
<td>1</td>
</tr>
<tr>
<td>2 Linear</td>
<td>$1.5-\zeta$</td>
</tr>
<tr>
<td>3 Parabolic</td>
<td>$0.5+1.128(\zeta-1.1)^2$</td>
</tr>
</tbody>
</table>
The axial dimensionless temperature in the solid wall for uniform and non-uniform catalyst distributions are shown in Figure 6.3.7. In addition, Table 6.4 summarises for each case the values of the extreme temperatures in the reactor and the outlet conversions.

![Catalyst distribution factor along the reactor](image1)

Figure 6.3.6 Catalyst distribution factor along the reactor 1-uniform; 2-linear; 3-parabolic.

![Wall dimensionless temperature profile](image2)

Figure 6.3.7 Wall dimensionless axial temperature profile for different catalyst distribution: 1-uniform; 2-linear; 3-parabolic.
Table 6.4 Comparison of the CPR performance for different combustion catalyst distribution

<table>
<thead>
<tr>
<th>Distribution Type</th>
<th>$T_{\text{min}}$ (K)</th>
<th>$T_{\text{max}}$ (K)</th>
<th>Reforming outlet conversion (%)</th>
<th>Combustion outlet conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uniform</td>
<td>732</td>
<td>1103</td>
<td>62.9</td>
<td>51.0</td>
</tr>
<tr>
<td>Linear</td>
<td>749</td>
<td>966</td>
<td>61.2</td>
<td>43.6</td>
</tr>
<tr>
<td>Parabolic</td>
<td>757</td>
<td>948</td>
<td>60.5</td>
<td>43.0</td>
</tr>
</tbody>
</table>

Figure 6.3.7 suggests that a non-uniform catalyst distributions (cases 2 and 3) moderate the temperature extremes in the reactor in comparison with the uniform catalyst distribution (case 1). Thus, the temperature rise near the combustion channel entrance ($\zeta=1$) is significantly lower, while towards the combustion channel exit ($\zeta=0$) the temperature becomes slightly higher than for a uniform catalyst distribution. The corresponding heat flux profiles for heat generation and consumption along the reactor, see Figure 6.3.8, also explains the moderation effect of non-uniform distribution.

Figure 6.3.8 Heat flux generated in the exothermic channel and heat flux consumed in the endothermic channel for different catalyst distribution: 1-uniform; 2-linear; 3-parabolic.
Towards the combustion inlet the heat generation was decreased significantly. However, despite a higher catalyst activity towards the channel outlet the combustion is still not able to sustain itself due to a strong cooling effect generated in the other channel by the reforming stream. The outlet conversions are slightly lower for reforming, but a noticeable decrease in the combustion conversions are observed (see Table 6.3). In addition, it can be seen that there are small differences between the linear (2) and parabolic (3) catalyst distribution. The parabolic one leads to a smoother temperature distribution along the reactor, although both conversions are slightly lower than the linear distribution.

These results indicate that the utilisation of a non-uniform catalyst distribution to equalise heat generation and consumption along the reactor to overcome the imbalance introduced by a different concentration distribution of the reactants in the two channels, in a counter-current flow, is a difficult task. Optimisation techniques may be necessary to achieve this goal.

6.4 Conclusion

The simulations for counter-current operation showed that there is a potential danger for combustion to run-away, issue was also identified by Kolios et al. (2001). The main reason that leads to this situation consists of the difficulty to match the heat flux consumed and generated mainly due to opposite reactant concentration depletion along axial co-ordinate. If the operating conditions which maintain the temperature profile in the desired range for co-current operation are applied for counter-current operation the CPR thermal behaviour may become unstable (run-away or extinguishing). Thus, the design of CPR for counter-current flow arrangement needs alternative solutions to balance the heat flux generated and consumed. An optimal design requires a search for a
suitable catalyst distribution in the reactor. This may include as also suggested by Kolios et al. (2001) to optimise the relative position of the catalyst layers for endothermic and exothermic side, catalyst distribution in the combustion channel, or fuel distribution along the reactor.
7.1 Introduction

The CPR design is influenced by a large number of factors, which need to be thoroughly understood. In a first stage, a preferred approach is to study experimentally the exothermic and endothermic reaction systems separately using reactors that are essentially single channels. The present work is part of a collaboration with the Department of Chemical Engineering of the University of Newcastle, where catalytic combustion was studied experimentally. Circular channels of 250 mm length and internal diameter of 2.29 mm, having a specific catalyst coated on their inner surface are part of the experimental set-up. Modelling is used to make quick checks and evaluate of catalytic combustion in small channels to aid the experimental study. More specifically it can help identifying what is the most suitable design for the heat sink necessary to keep the reacting channel in almost isothermal conditions during reaction. This is necessary when the catalytic channel is utilised for determination of the kinetic parameters or of the achievable generated heat flux. Two options are explored. The first one considers the reacting channel drilled in a solid metallic block with an external diameter of 50 mm, placed in a furnace. The second design uses as reacting channel a tube with wall thickness of ca 2 mm immersed in a fluidised bed in order to remove the heat generated by catalytic combustion. In order to evaluate the reacting wall temperature profile, a mathematical model is formulated using preliminary estimation for the methane catalytic combustion kinetics determined at the University of
Newcastle. Based on this model the reacting channel together with the heat sink is simulated comparing the performance and the thermal behaviour for the cases considered. Further the mathematical model is used to check the impact of velocity profile on the results of combustor simulations. CFD simulations are utilised to study the entrance effect in the reacting channel.

7.2 Design of the Heat Sink

An important aspect related to the study of catalytic combustion in small channels at isothermal conditions is related to the design of an efficient heat sink to absorb the heat generated during the reaction. Two options have been proposed for the practical implementations of such heat sink. The first design, named hereby “block reactor” embeds the reacting channel in a metallic block with an external diameter of about 50 mm, placed in a furnace. The metallic block is manufactured in halves so that a reacting channel with diameters between 2-4 mm can be easily drilled. After, the channel in each half is coated with catalyst, the two halves are welded together to reconstruct the circular channel. The external heat transfer from the metallic block surface occurs mainly by radiation. The disadvantage of such experimental arrangement is that for different sets of experiments a new “block reactor” needs to be manufactured which may be time and material consuming. Another alternative, named hereby “thin wall reactor”, uses tubes with wall thickness of ca. 2 mm immersed in a fluidised bed kept at constant temperature. Such tubes can be easily replaced during the experimental procedure. The main mechanism for the external heat transfer in this case occurs by convection.
7.3 Preliminary Kinetics for Methane Combustion

Preliminary estimation of the kinetic parameters for the catalyst used during the experimental work developed at the University of Newcastle pointed towards a power law expression as:

\[ r_{\text{CH}_4} = k_0 \exp \left( \frac{E}{R_s T} \right) \cdot [\text{CH}_4]^n \]  

(7.3-1)

Two sets of kinetic parameters in terms of activation energy, E, and reaction order, n, have been suggested for combustor modelling. The pre-exponential factors are adjusted so that for given inlet conditions to obtain a methane conversion closed to the one obtained experimentally. The values of activation energy and reaction order used in the calculations are given in Table 7.1.

<table>
<thead>
<tr>
<th>Data set</th>
<th>Activation Energy, E (kJ/mol)</th>
<th>Reaction order, n</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>II</td>
<td>139</td>
<td>0.71</td>
</tr>
</tbody>
</table>

These preliminary estimations of the kinetic parameters correspond to a Pd based catalyst, within different range of temperature. It is postulated that the change in the kinetic parameters may correspond to PdO ⇔ Pd transition.

7.4 Mathematical Model

The catalytic combustor consists of a small circular channel of stainless steel as represented in Figure 7.1, having a catalyst layer coated on its inner surface.
A two dimensional model is developed to model the methane catalytic combustion in small channels. The model refers to the geometry represented in Figure 7.1, where three different domains could be identified: the inner tube where catalytic combustion takes place, the solid wall, and the external environment. The assumptions the mathematical model is based on are similar with the ones described in chapter 2. They are as follows: steady state; a fully developed laminar flow characterises the hydrodynamics; ideal gas behaviour is assumed; catalytic combustion is considered to take place only on the catalytic wall, and is represented only by the methane total oxidation; intraphase resistances and pressure drop are neglected; the heat generated is transported through the metallic wall radially and axially. Modelling of the external heat transfer is embedded in the boundary condition of the external wall and is characteristic to each design for the heat sink (see section 7.2). For the “block reactor” the external heat transfer was assumed to occur only be radiation, while for the “thin wall reactor” only by convection. The equations of the mathematical model are given in Table 7.2. gPROMS code was utilised to solve the mathematical model (the code is given in Appendix D).
Table 7.2 Combustor Mathematical Model

**GAS PHASE**

**Material Balances:**
\[
\rho u_z \frac{\partial \omega_i}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \cdot \rho D_{i, \text{mix}} \frac{\partial \omega_i}{\partial r} \right) + \frac{\partial}{\partial z} \left( \rho D_{i, \text{mix}} \frac{\partial \omega_i}{\partial z} \right)
\]

**Energy Balances:**
\[
\rho u_z c_p \frac{\partial T_g}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \cdot k_g \frac{\partial T_g}{\partial r} \right) + \frac{\partial}{\partial z} \left( k_g \frac{\partial T_g}{\partial z} \right)
\]

**Continuity Equation:**
\[
\frac{\partial p}{\partial z} = 0
\]

**Equation of State for Ideal Gas**
\[
\rho = \frac{P}{R_g T_g \left( \sum_{i} \omega_i M_i \right)^{-1}}
\]

**Boundary Conditions**

1. Inlet conditions: \( z = 0 \); \( \forall r \)
   - inlet composition: \( \omega_i = \omega_i^0 \)
   - inlet temperature: \( T_g = T_g^0 \)
   - parabolic inlet velocity profile \( u_z = 2 \cdot u_z^0 \left[ 1 - \left( \frac{r}{R_{in}} \right)^2 \right] \)

2. Outlet conditions: \( z = L \); \( \forall r \)
   - zero flux \( \frac{\partial \omega_i}{\partial z} = \frac{\partial T_g}{\partial z} = \frac{\partial u_z}{\partial z} = 0 \)

3. Symmetry conditions at channel centre: \( \forall z \); \( r = 0 \)
   - zero flux \( \frac{\partial \omega_i}{\partial r} = \frac{\partial T_g}{\partial r} = \frac{\partial u_z}{\partial r} = 0 \)

4. Wall conditions: \( \forall z \); \( r = R_{in} \)
   - reacting wall
     \[
     \rho D_{i, \text{mix}} \frac{\partial \omega_i}{\partial r} = v_i \rho M_i
     \]
     \[
     k_g \frac{\partial T_g}{\partial r} \bigg|_{r=R_{in}} = r \left( -\Delta H \right) + \lambda_s \frac{\partial T_g}{\partial \chi_i} \bigg|_{r=R_{in}}
     \]
   - no slip conditions
     \( u_z = 0 \)

**Reaction Rate:**
\[
r = k^0 \exp \left( -\frac{E}{R_g T} \right) c_i^n c_{O_{2}}^m
\]
Table 7.2. Combustor mathematical model (cont.)

**SOLID WALL:**

\[
\frac{\partial^2 T_s}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T_s}{\partial r} \right) = 0
\]

**Boundary conditions:**

1. Inlet condition
   \[ z = 0; \quad \forall x_s; \quad \frac{\partial T_s}{\partial z} = 0 \]

2. Outlet condition
   \[ z = L; \quad \forall x_s; \quad \frac{\partial T_s}{\partial z} = 0 \]

3. Reacting wall
   \[ r = R_m; \quad \forall z; \quad T_s|_{r=R_m} = T|_{r=R_m} \]

4. External wall
   \[ r = R_{ex}; \quad \forall z; \quad \lambda_s \left. \frac{\partial T_s}{\partial x_s} \right|_{x_s=R_{ex}} = \sigma \cdot \varepsilon \cdot (T_r^4 - T_s^4) \text{ for external heat transfer by radiation} \]
   \[ \lambda_s \left. \frac{\partial T_s}{\partial x_s} \right|_{x_s=R_{ex}} = h \cdot (T_r - T_s) \text{ for external heat transfer by convection} \]

**i** – chemical species:

- i: CH₄, O₂, CO₂, H₂O;
- s – solid wall.

### 7.5 Results and Discussion

#### 7.5.1 Influence of the External Heat Transfer

First the combustor model was simulated using the kinetic set (I) as given in Table 7.1.

Typical conditions for catalytic combustion have been considered for the combustor simulations, and they are shown in Table 7.3. Inlet composition corresponds to a 5 % excess air. The inlet flowrate and consequently the inlet velocity was calculated to obtain an overall heat flux related to the combustor inner surface of about 10 kW/m², for 100 % conversion. Experiments at the University of Newcastle indicate that for these conditions, and an inlet temperature of about 1000 K the outlet conversion is about 90 %. Therefore, the pre-exponential factor was adjusted to obtain such conversion resulting in a value of 5000 m/s.
Table 7.3 Model parameters used in the calculations

<table>
<thead>
<tr>
<th><strong>Inlet conditions</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>1000 K</td>
</tr>
<tr>
<td>Pressure</td>
<td>atmospheric</td>
</tr>
<tr>
<td>Composition</td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>9.1 % (vol)</td>
</tr>
<tr>
<td>Air</td>
<td>90.9 % (vol)</td>
</tr>
<tr>
<td>Inlet velocity</td>
<td>4.9 m/s</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Geometry</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal diameter</td>
<td>2.29 mm</td>
</tr>
<tr>
<td>External diameter</td>
<td></td>
</tr>
<tr>
<td>&quot;Block Reactor&quot; –external heat transfer by radiation</td>
<td>50 mm</td>
</tr>
<tr>
<td>&quot;Thin Wall Reactor&quot; –external heat transfer by convection</td>
<td>6.35 mm</td>
</tr>
<tr>
<td>Length</td>
<td>250 mm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>External heat transfer</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Block Reactor&quot; –external heat transfer by radiation</td>
<td></td>
</tr>
<tr>
<td>Emissivity</td>
<td>0.9</td>
</tr>
<tr>
<td>&quot;Thin Wall Reactor&quot; –external heat transfer by convection</td>
<td></td>
</tr>
<tr>
<td>Heat transfer coefficient</td>
<td>529 W/m²</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Kinetics</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-exponential factor</td>
<td>5000 m/s</td>
</tr>
<tr>
<td>Activation energy</td>
<td>100 kJ/mol</td>
</tr>
<tr>
<td>Reaction order related to methane</td>
<td>1</td>
</tr>
</tbody>
</table>

Using different boundary conditions for the external heat transfer, the mathematical model considers both heat sink designs as discussed in section 7.2. After solving the mathematical model, temperature and concentration profiles are obtained along the radial and the axial co-ordinate. In both cases the furnace temperature and the fluidised bed temperature was considered constant and equal to the inlet temperature, 1000 K. The aim of these simulations was to identify which design gives the smallest temperature difference between the reacting wall and the inlet temperature. The combustor behaviour, in terms of the temperature and methane concentration profiles along the reactor, is given in Figure 7.2 and 7.3 for “block reactor” and “thin wall reactor” respectively. The highest temperature rise occurs near the reactor inlet, see Figure 7.2a and 7.3.a, where high concentration of methane determines high rate of heat
Modelling of a Catalytic Combustion in Small Circular Channels

generation. For a better comparison the difference between the wall temperature and the
gas temperature at the channel centre $\Delta T = T_{\text{wall}} - T_{\text{centre}}$ is given in Figure 7.4.

Figure 7.2 Combustor behaviour for external heat transfer by radiation ("block reactor") and kinetic parameter set (I)
a. temperature profiles; b. methane concentration profiles
Figure 7.3 Combustor behaviour for external heat transfer by convection ("thin wall reactor") and kinetic parameter set (I)

a. temperature profiles; b. methane concentration profiles
The temperature excursion is lower if the combustor is designed as a block reactor placed in a furnace than as a thin wall reactor placed in a fluidised bed. In the first case the maximum temperature rise above the inlet temperature is of 7.2 K, while in the second one it reaches 18 K (see Figure 7.4). Although small, this type of temperature differences can introduce noticeable difference in the values of the reaction rate. Thus, for activation energy of 100 kJ/mol, it can result in a reaction rate higher by 9.4 % and 23.7 % respectively.

For the heat sink design as a fluidised bed, the temperature rise near the reactor entrance can be reduced if the external heat transfer can be intensified. Thus, for an almost doubled heat transfer coefficient, compared to the one given in Table 7.2, a hot spot of about 10 K above the inlet temperature is obtained. A comparison is given in Figure 7.5 that shows the reacting wall temperature for the thin wall reactor placed in a fluidised bed for an external heat transfer coefficient of 529 and 1000 W/m² respectively.
Thus, provided that an external heat transfer coefficient in the fluidised bed of 1000 W/m$^2$ can be achieved, the performances of the two heat sink designs in terms of reacting wall temperature, are much closer to each other (see also Figure 7.2a). This may point to the fluidised bed arrangement as favourite due to an easier replacement and manufacture of the reacting channel.

The difference between the cases on the concentration profiles is not significant, similar outlet conversions are obtained for both situations. However, the difference between the methane concentration profiles at the reacting wall and the channel centre (see figures 7.2b and 7.3b) indicates the presence of the external mass transfer resistances.

It is worth noting that the above results have been obtained by considering as boundary conditions zero flux at the ends of the metallic wall. Different assumptions such as heat losses at the wall ends or constant inlet temperature for the wall may alter the temperature profiles discussed in this section. However, zero heat flux boundary conditions...
conditions is the most disadvantageous one in terms of the temperature rise and thus the rise in temperature obtained can be considered as an upper-bound.

7.5.2 Influence of Kinetics

The kinetics set (II) from table 7.1 was used together with the model parameters presented in Table 7.4 to simulate the combustor model. The sink design was considered as a fluidised bed that surrounds the catalytic channel. The pre-exponential factor was determined so that for an inlet temperature of 1023 K to achieve the conversion observed experimentally, namely 70%.

Table 7.4 Model parameters used in the calculations

<table>
<thead>
<tr>
<th>Inlet conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>1023 K</td>
</tr>
<tr>
<td>Pressure</td>
<td>atmospheric</td>
</tr>
<tr>
<td>Composition</td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>9.1 % (vol)</td>
</tr>
<tr>
<td>Air</td>
<td>90.9 % (vol)</td>
</tr>
<tr>
<td>Inlet velocity</td>
<td>5 m/s</td>
</tr>
<tr>
<td>Geometry</td>
<td></td>
</tr>
<tr>
<td>Internal diameter</td>
<td>2.29 mm</td>
</tr>
<tr>
<td>External diameter</td>
<td></td>
</tr>
<tr>
<td>&quot;Thin Wall Reactor&quot;-external heat transfer by convection</td>
<td>6.35 mm</td>
</tr>
<tr>
<td>Length</td>
<td>250 mm</td>
</tr>
<tr>
<td>External heat transfer</td>
<td></td>
</tr>
<tr>
<td>&quot;Thin Wall Reactor&quot;-external heat transfer by convection</td>
<td>1000 W/m²</td>
</tr>
<tr>
<td>Heat transfer coefficient</td>
<td></td>
</tr>
<tr>
<td>Kinetics</td>
<td></td>
</tr>
<tr>
<td>Pre-exponential factor</td>
<td>$1.47 \times 10^5 \text{ mol}^{0.29} \text{ m}^{0.13} /\text{s}$</td>
</tr>
<tr>
<td>Activation energy</td>
<td>139 kJ/mol</td>
</tr>
<tr>
<td>Reaction order related to methane</td>
<td>0.71</td>
</tr>
</tbody>
</table>

The combustor thermal behaviour is given in Figure 7.6a, while Figure 7.6b show the methane concentration profiles at channel centre and reacting wall. The maximum temperature rise does not exceed 4 degrees above the inlet temperature. This gives confidence that operating in this conversion range an almost isothermal temperature profile can be sustained along the reacting channel, subject to the condition that an
external heat transfer coefficient of 1000 W/m² K, can be achieved in the fluidised bed that surrounds the reacting channel.

Figure 7.6 Combustor behaviour for external heat transfer by convection ("thin wall reactor") and kinetic parameter set (II) a. temperature profiles; b. methane concentration profiles
7.5.3 Influence of Velocity Profile on the Model Accuracy

The calculations presented in the previous sections assumed a parabolic velocity profile for the whole channel length. In practice deviation from this profile may occur due to, for example, entrance effect or irregular shape of the walls. It is useful to determine how the assumptions for the velocity profile influence the combustor model accuracy. The impact of the velocity profile was determined by comparing the temperature and concentration profiles obtained simulating the combustor mathematical model for identical model parameters as given in Table 7.5, and for an inlet parabolic and flat velocity profiles.

Table 7.5 Model parameters to compare the influence of velocity profile

<table>
<thead>
<tr>
<th>Inlet conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>1000 K</td>
</tr>
<tr>
<td>Pressure</td>
<td>atmospheric</td>
</tr>
<tr>
<td>Composition</td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>9.1 % (vol)</td>
</tr>
<tr>
<td>Air</td>
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</tr>
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<td>Inlet velocity</td>
<td>4.9 m/s</td>
</tr>
<tr>
<td>Geometry</td>
<td></td>
</tr>
<tr>
<td>Internal diameter</td>
<td>2.29 mm</td>
</tr>
<tr>
<td>External diameter</td>
<td></td>
</tr>
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<td>&quot;Thin Wall Reactor&quot; – external heat transfer by convection</td>
<td>6.35 mm</td>
</tr>
<tr>
<td>Length</td>
<td>250 mm</td>
</tr>
<tr>
<td>External heat transfer</td>
<td></td>
</tr>
<tr>
<td>&quot;Thin Wall Reactor&quot; – external heat transfer by convection</td>
<td></td>
</tr>
<tr>
<td>Heat transfer coefficient</td>
<td>1000 W/m²</td>
</tr>
<tr>
<td>Kinetics</td>
<td></td>
</tr>
<tr>
<td>Pre-exponential factor</td>
<td>5000 m/s</td>
</tr>
<tr>
<td>Activation energy</td>
<td>100 kJ/mol</td>
</tr>
<tr>
<td>Reaction order related to methane</td>
<td>1</td>
</tr>
</tbody>
</table>

The results demonstrate that for a circular channel with the internal diameter of 2.29 mm the velocity profile do not influence significantly the temperature and concentration profiles. Figure 7.7 shows the temperature of the reacting wall for a flat and a parabolic profile. The difference between the profiles do not exceed 0.3 K. Also, for concentration
profiles the differences are minimal, as can be seen in Figure 7.8. It can be said that the influence of the velocity profile on the outlet conversion is negligible.

Figure 7.7 The reacting wall temperature calculated using a parabolic and a flat velocity profile

Figure 7.8 Methane concentration along the radial dimensionless co-ordinate for different axial dimensionless position calculated using a parabolic and a flat velocity profile.
7.5.4 Design of the Channel Inlet

The hydrodynamic aspects related to the entrance effect in the reacting channel were investigated using CFD simulations (CFD-ACE+, developed by CFD Research Company 1998). Channel inlet is characterised by specific flow patterns caused by the entrance geometry, which depend on how the fuel-air mixture is fed in the channel. For the experiments made at the University of Newcastle, a capillary tube of 0.5 mm was used to feed the reacting mixture in the main channel. Thus, the gas stream suffers a sudden expansion from 0.5 mm to the reacting channel diameter, which is in the range of 2-4 mm. It is a well-known fact that during a sudden expansion, as represented in Figure 7.9 vortexes and recirculation patterns may develop in the corners (Bird et al. 1960).

\[
D_{kg} = \frac{D}{d} \quad \text{- expansion ratio}
\]

\[
k_{a} = \frac{L}{D} \quad \text{- aspect ratio}
\]

Figure 7.9 Sudden expansion geometrical characteristics

This type of flow behaviour also occurs at low Reynolds numbers (calculated based on smaller diameter). Experimental studies by Fearn et al. (1990), showed that even for a low Reynolds number as \( Re = 25 \), for a sudden expansion with an expansion ratio \( k_{e} = 3 \) and an aspect ratio \( k_{a} = 8 \), two symmetrical recirculation zones appear behind the expansion steps. Many authors (Shapira at al. 1990, Fearn et al. 1990, Durst et. al. 1993, Alleborn at al., 1997 ) argue that as the Reynolds number increases the recirculation zones increase and the flows become asymmetric (see Figure 7.10), one recirculation zone increases in length at the expense of the other recirculation zone. This phenomenon
is explained by observing that an increase of the velocity near one wall leads to a decrease in the pressure, which maintains the asymmetry of the flow pattern. Figure 7.10 shows results for simulation of the air flow through a sudden expansion from a diameter of 0.5 mm to 4 mm for a Reynolds number Re=30. It can be seen that asymmetric recirculation zones are formed.

![Figure 7.10 Asymmetric recirculation zones due to the sudden expansion (2D-CFD simulation results for air flow through a sudden expansion from 0.5 mm to 4 mm diameter, and Re=30).](image)

Alleborn et al (1997) showed that as Reynolds number, based on the smallest diameter, increases, Re = 625 according to their work, the fluid patterns became unstable and time periodic introducing large deviation from laminar flow. Modelling of such hydrodynamic behaviour coupled with chemical reaction for estimation of kinetic parameters is difficult and requires advanced CFD tools. Usually simpler models are preferred in order to couple them with optimisation programs in order to obtain an efficient evaluation of the kinetics from the experimental data. Thus, it is desired that such recirculation patterns to be avoided in order to increase the accuracy of the theoretical model that interpret the experimental data.
A first attempt to eliminate this type of flow behaviour around the inlet is to consider a gradual expansion, as represented in Figure 7.11, rather than a sharp expansion (see Figure 7.9). However, theoretical studies by Shapira et al. (1990) proved that only the asymmetric behaviour can be eliminated by a gradual smooth expansion, while the recirculation patterns are still present near the inlet.

![Figure 7.11 Gradual expansion](image)

In order to qualitatively observe the influence of the inlet geometry on the flow patterns near the inlet, 3D CFD simulations was utilised to study the air flow in three cases representing a simple channel without any inlet, a sharp expansion, and a gradual expansion as inlet. The geometrical characteristics corresponding to each case are given in Table 7.6

<table>
<thead>
<tr>
<th>Case</th>
<th>d (mm)</th>
<th>D (mm)</th>
<th>α (°)</th>
<th>Flowrate (l/h (NTP))</th>
<th>U (m/s)</th>
<th>Re</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Simple channel</td>
<td>-</td>
<td>2.5</td>
<td>-</td>
<td>15</td>
<td>2.5</td>
<td>74</td>
</tr>
<tr>
<td>(no inlet)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Sharp expansion</td>
<td>0.5</td>
<td>2.5</td>
<td>90</td>
<td>15</td>
<td>62</td>
<td>370</td>
</tr>
<tr>
<td>3 Gradual expansion</td>
<td>0.5</td>
<td>2.5</td>
<td>11.3</td>
<td>15</td>
<td>62</td>
<td>370</td>
</tr>
</tbody>
</table>
An inlet air flowrate of 15 l/h (NTP) together with an inlet air temperature of 800 K and an almost atmospheric pressure were considered for all cases. The corresponding inlet averaged velocities $U$, and the Reynolds number, $Re$, were calculated for the first case based on the diameter $D$, while for the other two cases based on the smaller diameter $d$ (see also Figures 7.9 and 7.11), and are also given in Table 7.6.

![Streamlines Comparison](image)

In order to give a comparison of the flow patterns around the inlet in the main channel, two streamlines are shown in Figure 7.12 for all the cases considered. It can be seen, that for the simple channel (Figure 7.12a) the stream lines are parallel to the wall channels as expected for a laminar flow. The presence of a sharp expansion (Figure 7.12b) introduces strong recirculation patterns that have 3D trajectories and are asymmetric. A gradual expansion (Figure 7.12c), eliminates the asymmetric behaviour, but maintains the recirculation patterns near the channel inlet. Thus, the design of the
inlet as a gradual smooth expansion is not sufficient to eliminate the recirculation patterns.

Theoretical and experimental studies by Christiansen et al. (1972) on flow through a sharp contraction, as represented in Figure 7.13 showed that the recirculation patterns are trapped in the corners before entering the channel with smaller diameter, $d_c$. At Reynolds number between 30 and 50 (calculated based on the small diameter, $d_c$), the velocity profile at the inlet of the smaller channel is almost flat. For larger values a concavity exists in the entrance-velocity profiles, which means that the axial velocity is lower in the centre of the tube and a little higher in the vicinity of the wall. The depth of concavity depends on the contraction ratio and the Re number. The authors present also the dependence of equivalent length (the distance downstream from the smaller channel entrance at which the centreline velocity achieved 99 % of its fully developed value) as a function of Reynolds number for different contraction ratio. For example, for the range of Re number between 100 - 200 and for a contraction ratio of $D_c/d_c = 1.2$ an equivalent length of 2 diameters is determined.

![Figure 7.13 Sharp contraction](image-url)
The opposite effects of a sharp expansion and of a sharp contraction pointed towards the idea to design the inlet of the catalytic channel as a succession of expansion-contraction geometrical profiles. Thus, the capillary tube of 0.5 mm needed to feed the reactants can be linked by the main reacting channel that have diameters of 2-4 mm, by means of a small chamber. This can trap the recirculation patterns. An example for such design is represented in Figure 7.14.

![Figure 7.14 Channel inlet design with expansion-contraction section.](image)

Air flowing through the 3D geometry as presented in Figure 7.14 was simulated along with the inlet conditions given in Table 7.7 using the commercial software package CFD-ACE+. The results obtained confirmed that the recirculation patterns are trapped in the cavity formed by the expansion-contraction geometry (see Figure 7.15).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet flowrate</td>
<td>25</td>
<td>l/h (NTP)</td>
</tr>
<tr>
<td>Inlet temperature</td>
<td>800</td>
<td>K</td>
</tr>
<tr>
<td>Inlet pressure</td>
<td>1</td>
<td>bar</td>
</tr>
<tr>
<td>Average velocity based on</td>
<td></td>
<td></td>
</tr>
<tr>
<td>inlet diameter d=0.5 mm</td>
<td>105</td>
<td>m/s</td>
</tr>
<tr>
<td>channel diameter D=2.38 mm</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>Reynolds number based on</td>
<td></td>
<td></td>
</tr>
<tr>
<td>inlet diameter d=0.5 mm</td>
<td>624</td>
<td></td>
</tr>
<tr>
<td>channel diameter D=2.38 mm</td>
<td>130</td>
<td></td>
</tr>
</tbody>
</table>
Figure 7.15 Stream lines and velocity vectors in the inlet expansion-contraction geometry

Figure 7.16 Velocity vectors around the reacting channel inlet
A close examination of the velocity vectors around the inlet in the reacting channel, see Figure 7.16, shows that the recirculation patterns are eliminated from the reacting channel and that. The deviations from the parabolic velocity profile are minimal. The previous section demonstrated that such deviations do not have a significant impact on the combustor performance. Thus, the inlet design proposed can eliminate the recirculation patterns near the channel entrance and gives confidence that the mathematical model discussed in section 7.4 has a reasonable degree of accuracy.

7.6. Conclusions

A mathematical model was formulated to investigate methane catalytic combustion in non-adiabatic small channels. The model was used to study the design of the heat sink necessary to absorb the heat generated by combustion, in order to maintain an almost isothermal profile along the reacting channel. Model simulations for first order kinetics with respect to methane and an activation energy of 100 kJ/mole, demonstrate that operating at high conversions, a block reactor placed in a furnace provides a hot spot of 7.2 K above the inlet temperature while in a thin wall tube reactor immersed in a fluidised bed the hot spot is 18 K. For kinetics with a fractional reaction order of 0.71 with respect to methane and an activation energy of 139 kJ/mol, operating with conversion of up to 70 %, the temperature excursion does not exceed 4 K above the gas inlet temperature. Simulations of the mathematical model for identical parameters but using a flat and a parabolic inlet velocity profile showed that the impact of the velocity profile on the temperature and concentration is negligible. In addition, an expansion-contraction geometry for the channel inlet eliminates recirculation patterns and gives confidence that a mathematical model using a parabolic velocity profile to represent the hydrodynamic has a reasonable degree of accuracy.
8.1 Conclusions

The present work is an introductory study of Catalytic Plate Reactors (CPRs). Mathematical models with different degree of complexity are formulated and simulated generating illustrative case studies. Overall it has been demonstrated that CPRs combine reaction with heat transfer in an intensified manner, representing a feasible alternative to the conventional reactors. The reduced dimensions of the reacting channels minimises the heat and mass resistances leading to significant volume and catalyst amount reduction in comparison to the conventional reactors. CPRs can operate reliable providing that the adequate amount of fuel and catalyst activity are utilised in order to maintain the overall and the local heat balance between the endothermic and the exothermic side. Undesirable behaviour such as formation of hot spots that can lead to the reactor run-away or cold spots that can lead to the reactor extinguishing can be avoided by selecting the design parameters based on sensitivity criteria. The most influential design parameters on CPRs behaviour and performance remain to the kinetic parameters, especially activation energy, and catalyst activity and thickness. Suitable combinations of catalysts for the endothermic and the exothermic side, selected based on a careful parametric sensitivity analysis of the reactor can provide a system with self regulating properties and guarantee a stable reactor operation.
The main conclusions that come out from this work are hereby outlined for the main chapters.

**Chapter 3** studied the autothermal coupling of the ethane dehydrogenation with methane combustion in a CPR, based on a two-dimensional model without intraphase resistances. It was found that the ratio of catalyst loading for the two reactions is a key variable and must be carefully adjusted in order to avoid severe hot or cold spots that can lead to either reactor run-away or extinguishing. A metallic wall with a thickness of 2 mm, due to its high thermal conductivity, makes possible an efficient heat transfer between the endothermic and exothermic channel for small temperature differences. The radial temperature profiles in the gas phases are also not significant. However, if a wall with low thermal conductivity (i.e. from ceramic material) is used not only significant radial temperature gradients appear but also poor heat transport along axial direction giving rise to hot spots.

**Chapter 4** addressed the study of steam reforming of methane coupled with methane catalytic combustion in a CPR. A two dimensional model was formulated to simulate CPR behaviour, taking into consideration the intraphase resistances. For thin catalyst layers (10 – 60 μm) the mass intraphase resistances are significant, therefore they cannot be neglected during reactor design, while the thermal intraphase resistances are negligible, allowing to simplify the CPR model by considering the catalyst layer isothermal in radial direction. The autothermal coupling can be made for isothermal operation as well as non-isothermal when combustion is used simultaneously to provide heat for the endothermic process and to heat-up both reaction mixtures. Using simplified kinetics, a base case was generated to study the isothermal operation, a maximum difference between inlet and hot spot temperature of only 17 K occurs, while
radial temperature gradients are negligible. Further the mathematical model was refined considering more complex kinetics for the reforming side. CPR behaviour was investigated for operating conditions similar to the industrial steam reforming process in order to make a comparison to a conventional reformer. It was found that a reduction in the reformer volume by 150 times and reduction for the necessary amount of catalyst by 85 times can be achieved. The effectiveness factors for the chemical reactions of the reforming process are about one order of magnitude higher than in the conventional process, proving a significant reduction of intraphase resistances. The short distance between the heat source and heat sink increases the efficiency of heat transfer. Thus, for the base case presented the maximum radial temperature gradients in the reforming channel are only 35 K compared to 250 K for the conventional reformer.

The influence of channel gap and catalyst thickness on reactor behaviour was also addressed. At constant catalyst residence time, defined as the ratio between the total amount of catalyst in the reactor and the inlet molar flowrate of methane, decreasing the channel gap minimises the heat and mass transfer resistances resulting to higher outlet conversions although the difference among the cases studied is not significant. At constant space-time, the increase of channel gap corresponds to higher amount of reactants per catalyst amount, in addition the external resistances becomes more important leading to significant lower outlet conversions and temperature. The study reveals that mass Fourier number can be used to identify adequate ranges for channel gap.

The intraphase resistances prove to be important even for catalyst thickness of micrometers for both reforming and combustion process. Increasing the catalyst thickness at constant catalyst residence time leads to lower outlet conversions, as a
Conclusions and Future Work

Consequence of stronger intraphase resistances. Due to different influence on reforming and combustion side of the catalyst thickness, the axial temperature profile has a specific behaviour for each case studied. Although it is aimed to minimise the catalyst thickness in order to have an efficient utilisation of the catalyst layer avoiding unnecessary intraphase resistances, sometimes when moderation of the reaction rates is required for better autothermal coupling they may have an advantageous role.

Chapter 5 uses Parametric Sensitivity Analysis to investigate the CPR sensitivity behaviour and to establish criteria to evaluate the reactor stability and reliability. Reactor sensitivity with respect to several design parameters such as channel gap, wall thickness, inlet velocities, inlet temperature and composition; pre-exponential factors, and activation energy has been calculated. For the system studied, which is loosely based on steam reforming of methane coupled with methane catalytic combustion, it was found that the main source of sensitive behaviour is the exothermic reaction. Combinations of catalysts with high activation energy for the exothermic reaction and low activation energy for the endothermic one cause a strong sensitivity with respect to all parameters investigated. Among the parameters studied the strongest influence comes from the activation energies followed by the inlet temperature. Sensitivity to inlet composition and velocities have moderate effect, while the lowest sensitivity was found with respect to geometrical parameters and wall thermal conductivity. This suggest that in a CPR where the heat and mass transfer resistances have been minimised, chemical reactions remain the main source of disturbance in the system. Applying suitable criteria, sensitivity values can be used to evaluate if expected perturbations in the design parameters maintain the reactor behaviour in an acceptable operating range.
Chapter 6 investigates the influence of the flow arrangement for the reaction system steam reforming of methane coupled with methane combustion. It was found that overall, the heat generation and consumption is balanced better for co-current operation than for counter-current one. Although, the counter-current flow arrangement may provide better thermal efficiency, the local heat balance proves difficult to achieve. The axial reactant concentration profiles in endothermic and exothermic channels have the opposite trend and this result in large differences between heat generation and consumption intensity. Thus, there is a potential danger for combustion to run-away, increasing the reactor instability. Successful counter-current operation needs to use a non-uniform catalyst distribution as a degree of flexibility in adjusting the rate of heat generated and consumed. Optimisation techniques are required to find such catalyst distribution.

Chapter 7 addressed modelling of methane catalytic combustion in small circular channels (inner diameter of 2.29 mm) corresponding to two experimental reactors for kinetic determination. First option consists of a small channel embedded in a solid metallic block placed in a furnace, while the second one is a small tube with the wall thickness of about 2 mm immersed in a fluidised bed. Thus, the investigation aimed to identify which option offers better conditions, in terms of achieving isothermal conditions. For first order kinetics with an activation energy of 100 kJ/mol, operating at high conversions (cca. 90 %), the maximum temperature excursion is about 7.5 K for the first option and 18 for the second one, above the inlet temperature. Combustor simulation with the kinetic expression \( r_{CH_4} = 1.47 \cdot 10^5 \exp \left( -\frac{139000}{R_T \cdot T} \right) \cdot (C_{CH_4})^{0.71} \), for the fluidised bed design, gives a temperature excursion of only 5K above the inlet temperature and an outlet methane conversion of cca. 70 %. Simulations of the
Conclusions and Future Work

A mathematical model for identical parameters but using a flat and a parabolic inlet velocity profile showed that impact of the velocity profile on the temperature and concentration is negligible. In addition, an expansion-contraction geometry for the channel inlet eliminates the recirculation patterns and minimises the experimental errors due to entrance effect.

8.2 Future Work

For the reaction system ethane dehydrogenation-methane combustion (Chapter 3), more complex kinetics, including the reactions for carbon deposition and catalyst deactivation may give a more realistic picture about the performance of such system. In the case of steam reforming of methane coupled with methane catalytic combustion in a CPR (Chapter 4 and 6), finding the optimal non-uniform catalyst distribution may lead to improved performance and thermal behaviour especially for counter-current operation. Parametric Sensitivity Analysis (PSA) for CPRs (Chapter 5) can be extended by increasing the complexity of the model to include the catalyst layer, and/or kinetics with different reaction orders so that sensitivities with respect to catalyst thickness and reaction order to be evaluated. Since simulations for counter-current operation indicate a potential danger for reactor instability, application of PSA in such a case may help to identify solutions to overcome this danger. For modelling of catalytic combustion in small channel, (Chapter 7) considering PdO transition is an interesting challenge which can help to find out if this phenomenon can be used for thermal regulation during the autothermal coupling of methane catalytic combustion with an endothermic process. Finally, the mathematical model of CPR for different reaction systems needs to be validated with adequate experimental data.
8.3 General Guidance for Catalytic Plate Reactors Design

A general design procedure having as objective the autothermal coupling of an exothermic-endothermic reaction system in a Catalytic Plate Reactor (CPR) may involve several steps such as preliminary, detailed, and optimal design as represented in the diagram in Figure 8.1. Such methodology is an interactive procedure, which applies to any type of equipment (Sinnott 1996), its adaptation for CPRs is based on the understandings obtained during the present work.

Once the design objective has been decided by specifying the reaction system, a preliminary design becomes necessary to gather process details and make preliminary estimations based on literature and experimental data. CPR design has a higher degree of complexity compared to conventional reactors since it involves not only good understanding of two different reaction systems separately but also the conditions that make possible their coupling. An evaluation of the autothermal coupling suitability using short-cut models and parametric sensitivity criteria identifies feasible design parameter ranges. Thus, preliminary evaluations are required in order to avoid unnecessary computational effort in the detailed design stage.

Further, at the level of detailed design, formulations and simulations of complex CPR models help to assess the reactor performance and behaviour. Accurate parametric studies based on such models can lead further to identify optimisation opportunities in the final stage of the CPR design, where selection of an optimal reactor can be made considering suitable criteria.
Conclusions and Future Work

Objective

Reaction System Specification

Data Collection & Preliminary Evaluation

Evaluation of Autothermal Coupling Suitability

Assessment of CPR Performance & Behaviour

Parametric Studies

Optimisation & Selection

Final Design

• literature data
• experimental data
• short-cut models
• PSA Criteria

• Modelling and simulation based on complex models

• Identify potential for optimisation
• Select the optimal design

Figure 8.1 Suggested CPR design procedure
Conclusions and Future Work

- Reaction System
  - operation conditions
  - kinetics
  - catalyst properties

- Plate
  - geometry
  - material properties

Preliminary Evaluation

Design Parameter Range for
- catalyst loading and activity
- catalyst thickness
- achievable heat fluxes
- flowrates
- channel gap

Autothermal Coupling Suitability

Short-cut models ↔ Parametric Sensitivity Analysis

Is this a viable system?

- NO
- YES
  → Detailed Design

Data Collection

Constrain Parameter Range

Reconsider the Reaction System

Figure 8.2 Preliminary design
8.3.1. Preliminary Design

The main issues that concern a preliminary approach for CPR design are highlighted in Figure 8.2. Within this frame, data collection concerning the exothermic and endothermic reaction system, geometry and material for reactor is essential in order to establish an appropriate design parameter range. Identifying the constraints that rises from the reaction systems autothermal coupling in a CPR can narrow the latter further.

8.3.1.1 Data Collection

For each individual reaction system, data about typical conditions such as temperature, pressure, composition that lead to high conversions and/or selectivity are necessary to establish the operating range. Further, catalyst properties such as porosity, loadings, thermal and mechanical strength, together with accurate kinetic data provide preliminary constraints for the operating range. The study developed in the present work revealed that the kinetic parameters and catalyst activity are key issues for CPR design, thus extra caution is required to determine accurately these parameters. It is also necessary to collect data regarding the plate used to support the catalysts such as material properties and thickness.

8.3.1.2 Preliminary Evaluation

Short-cut models or experimental data can be used in order to estimate catalyst residence time, the magnitude of intraphase resistances, and achievable heat fluxes independently for the exothermic and the endothermic reaction system.

Step 1. Catalyst Residence time

The catalyst residence time defined as the ratio between the amount of catalyst and inlet molar flowrate of the main reactant $\tau_c = W/F_j^0$ can be approximated for isothermal conditions maximising the conversion. This may involve solving simple models as the
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ones used to determine the kinetic parameters (Xu and Froment 1989a). For example for a simple reaction

\[ A \rightarrow \text{products} \]

this may involve solving a simple first order differential equation such as

\[ \frac{dx_A}{d\left(\frac{W}{F_A^0}\right)} = r_A, \text{ with the initial condition } \frac{W}{F_A^0} = 0, \quad x_A = 0 \quad (8.1) \]

**Step 2. Catalyst Thickness**

Selection of the catalyst thickness is subject to constraints established on one hand by the magnitude of the internal mass transfer resistances and on the other hand by the techniques available to stick a particular heterogeneous catalyst on metallic or other material type (Ismagilov et al. 2001). Conventional criteria (Mears 1971), or mathematical models of a catalyst slab with different thickness (Aris 1975; Froment and Bischoff 1990) can be employed to establish a correspondence between the catalyst thickness and the magnitude of the internal resistances. When establishing a range for the catalyst thickness, the designer need to keep in mind that it is desired to have an efficient utilisation of the catalyst, but at the same time to confer sufficient thermal and mechanical strength for the catalyst layer. If the internal resistance prove to be important, a re-estimation of the catalyst loading (see Step 1) needs to be done, by taking into consideration the effectiveness factor in equation 8.1

\[ \frac{dx_A}{d\left(\frac{W}{F_A^0}\right)} = \eta \cdot r_A, \quad (8.2) \]

**Step 3 Achievable Heat Fluxes**

The achievable heat fluxes per square meter of catalytic plate can be determined experimentally or approximated as

\[ H = \frac{\rho_{\text{cat}} \cdot \delta_{\text{cat}} \cdot x_{\text{max}} \cdot (-\Delta H)}{\tau_w} \quad (8.3) \]
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independently for the exothermic, $H_{exo}$, and the endothermic process, $H_{endo}$. One essential condition for the successful autothermal coupling of the endothermic and the exothermic process is to balance the overall heat flux on both sides. Therefore, the CPR duty needs to be based on as the minimum between the achievable exothermic and endothermic heat flux, $H_{min} = \min (H_{exo}, H_{endo})$.

Step 4. Flowrates and Channel Gap

Plate dimensions are usually subject to manufacture and layout constraints. However, in order to study the coupling of the exothermic and the endothermic process, geometry may be assumed as fixed within reasonable limits. The inlet molar flowrate of the main reactant can be then determined from the achievable heat flux determined in the previous step, as

$$ F^0 = \frac{H_{min} \cdot S}{(-\Delta H) \cdot x_{max}} $$

(8.4)

where $S$ is the plate surface.

Further, the total volumetric flowrate can be estimated based on the inlet composition, temperature and pressure, which usually are known condition for a given reaction system.

As shown in section 4.3.3, minimising the channel gap reduces the external mass resistances improving the CPR performance. A convenient criterion to set an upper boundary for the channel gap size proves to be the condition that the mass Fourier number, $F_{om}$ as defined by the equation 4.3-14, to be higher than unity.

$$ F_{om} = \frac{L}{u_0} \cdot \frac{D_A}{R^2} \geq 1 $$

(8.5)
which can help to estimate the magnitude of the half channel gap, $R$, based on reactor length, $L$, diffusion coefficient of the main reactant, $D_\Delta$, and the inlet average velocity as

$$R \leq \sqrt{\frac{L \cdot D_\Delta}{u_x^0}} \quad (8.6)$$

or in terms of the inlet total volumetric flowrate, $F_v^0$ as:

$$R \leq \frac{S \cdot D_\Delta}{F_v^0} \quad (8.7)$$

where $S$ is the plate surface.

Constraints based on the mass Fourier number establishes upper limit for the channel gap value. In addition, pressure drop constraints can also be important and determine its lower limit. For example, the pressure drop for laminar flow between two parallel plates can be determined as

$$\Delta P \approx \frac{3u_x^0 \mu L}{R^2} \quad (8.8)$$

The pressure drop limitation, $\Delta P_{\text{max}}$, are usually set by the process conditions that include the CPR. From the condition of a lower pressure drop in the reactor than the maximum accepted value

$$\Delta P \leq \Delta P_{\text{max}} \quad (8.9)$$

The lower boundary for half channel gap can be estimated as

$$R \geq \sqrt{\frac{3u_x^0 \mu L}{\Delta P_{\text{max}}}} \quad (8.10)$$
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Step 5. Autothermal Coupling Suitability

A successful autothermal coupling of an endothermic process and an exothermic one by means of indirect heat transfer needs to satisfy both overall and local heat balances. Thus, it is required to match the inlet flowrates (or average velocities) to satisfy the overall heat balance and the catalyst loading or activity to balance the local rate of heat generation and heat consumption. Short-cut models as the one described in section 5.2 are suitable for a quick estimation of the ratio of catalysts loadings.

In Chapter 5, it was shown that different combinations of catalysts for endothermic and exothermic process can give similar CPR behaviour and performance but exhibit different sensitivity to the design parameters. Parametric sensitivity analysis can be utilised to evaluate if reactor behaviour exceeds the operation limits for specific deviation of the input parameters (see section 5.3.3 equation 5.3-5) or to determine design parameter ranges which keep the reactor operation within desired limits (see section 5.2.2, equation 5.2-26).

Identification of the source of disturbance can help to reconsider the initial specification of the reaction system. For example, as shown in Chapter 5 the kinetic parameters, especially the relation between the activation energies of the exothermic and endothermic side can induce a highly sensitive CPR behaviour. Flexibility in choosing the kinetic parameters can be often limited, if there is not a suitable catalyst that can provide adequate kinetics, the only alternative remain to change the reaction system, for example the type of fuel used and re-start the procedure from step 1.
8.3.2. Detailed Design

Within the preliminary design stage parameter ranges have been identified. Complex models such as the one formulated in Chapter 3 and 4 (Table 3.1, Table 4.2.1 and Table 4.3.1) increase the prediction accuracy of CPR thermal behaviour and performance. Main objectives for simulations based on such models consist of identifying some key parameters (i.e. catalyst loadings, reactor length, necessary amount of fuel when the exothermic reaction is used simultaneously to provide the heat for the endothermic side and to heat up both reaction mixtures) and to develop parametric studies.

Parametric studies help to identify trends in reactor behaviour and potential for optimisation. Several examples of useful parametric studies are described below.

Influence of catalyst thickness, loading, and distribution:

The amount of catalyst and its distribution on the catalytic plate is directly correlated to the rate of heat generation/consumption in the CPR, bringing a degree of flexibility in achieving high CPR performance at the same time with a thermal behaviour that offers a safe and stable operation. Simulations based on complex models can help to identify the best way in balancing the local heat flux generated and consumed by adjusting the catalyst thickness and / or loading to either intensify or moderate the reaction rates. Non-uniform catalyst distribution can also be employed to increase the autothermal coupling compatibility of the endothermic and the exothermic process. Catalyst deactivation is an important factor to consider. Different deactivation rate can disturb the local heat balance and make the reactor unstable.
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Geometry: channel gap and wall thickness:

Parametric studies related to the channel gap are important because it affects the external resistances and has a direct impact on the reactor volume. The wall thickness becomes an important issue when the material used for the catalytic plate has low conductivity (i.e. ceramic materials). Thus, parametric studies related to wall thickness needs to be correlated to parametric studies related to its conductivity.

Inlet conditions

Typical inlet conditions for each individual reaction system can be previously established at the level of data collection, however autothermal coupling can require different operating conditions. Such an example can be the fuel concentration, which can be regarded as a possibility to offer more flexibility in the reactor operation.

8.3.3. Optimal Design

Optimisation of CPR has not been addressed in the present thesis, however the results obtained so far point towards specific problems that can be solved applying optimisation techniques and therefore are recommended as final stage for CPR design. Possible objectives for CPR optimal design may include maximisation of the outlet conversions, minimisation of the reactor volume etc. Since thermal behaviour seems to influence the reactor stability, recommended constraints during CPR optimisation refers to keeping the temperature profile within the operating range in order to avoid formation of hot or cold spots. The optimisation variable can be: catalyst distribution, and thickness, channel gap, reactor length, etc.
Catalyst Distribution. Finding the right catalyst distribution by trial and error procedure may be time consuming and cannot offer the guaranty for an optimal solution. Using optimisation techniques, an optimal non-uniform catalyst distribution in one or both channels can be identified so that to lead to a CPR thermal behaviour without hot or cold spots, and at the same time to achieve high conversions. This strategy proves to be necessary especially for counter-current flow. Due to opposite direction of reactants depletion along the reactor in the exothermic and endothermic side, the local heat generation and consumption becomes more difficult to balance using a uniform catalyst distribution. Optimisation can help to find relative locations of the catalytic zones in exothermic and endothermic channel, and/or the non-uniform distribution so that to avoid combustion run-away or the reactor extinguishing.

Catalyst thickness. Efficient catalyst utilisation requires minimisation of the internal resistances and therefore of its thickness. However, in certain conditions the internal resistance can be desired if moderation of the rate of heat generation/consumption is needed, then the catalyst layer can be used as a diffusion barrier. Thus, optimisation helps to find the catalyst thickness, which represent a trade-off between catalyst efficiency and a stable reactor thermal behaviour.

Plate geometry. A catalytic plate with different combination of its lengths (L) and width (W) can have the same area, see Figure 8.3. Assuming for example that the channel gap is the same, in case a, where W>L, the inlet cross section is higher that in the case b where W<L. For identical flowrates (see also step 4 of the preliminary design), the plate designs showed in Figure 8.3a and 8.3.b results in different inlet velocities, which can affect the concentration and temperature profiles along the plate.
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Figure 8.3 Different configuration of the catalytic plate for the same area

An optimal combination of plate dimensions can be found in order to maximise conversion and to maintain a desired thermal behaviour.
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Appendix A

Ethane Dehydrogenation-Methane Combustion gPROMS code
Ethane Dehydrogenation-Methane Combustion Couplings: gPROMS Code

DECLARE
TYPE
Ethane_mass_fr = 0.6 ; 0 ; 1
Ethylene_mass_fr = 0.2 ; 0 ; 1
Hydrogen_mass_fr = 0.2 ; 0 ; 1
Nitrogen_mass_fr = 0.5 ; 0 ; 1
Ethane_mol_fr = 0.6 ; 0 ; 1
Ethylene_mol_fr = 0.2 ; 0 ; 1
Hydrogen_mol_fr = 0.2 ; 0 ; 1
Temperature = 700 ; 500 ; 1E20
Ethane_conc = 5.7 ; 0 ; 1E20
Ethylene_conc = 2.5 ; 0 ; 1E20
Hydrogen_conc = 2.5 ; 0 ; 1E20
Methane_mass_fr = 0.6 ; 0 ; 1
Oxygen_mass_fr = 0.2 ; 0 ; 1
Co2_mass_fr = 0.2 ; 0 ; 1
Water_mass_fr = 0.5 ; 0 ; 1
Nitrogen_mass_fr = 0.5 ; 0 ; 1
Methane_mol_fr = 0.6 ; 0 ; 1
Oxygen_mol_fr = 0.2 ; 0 ; 1
Co2_mol_fr = 0.2 ; 0 ; 1
Water_mol_fr = 0.2 ; 0 ; 1
Nitrogen2_mol_fr = 0.2 ; 0 ; 1
Methane_conc = 6.5 ; 0 ; 1E20
Oxygen_conc = 10 ; 0 ; 1E20
Co2_conc = 3.2 ; 0 ; 1E20
Water_conc = 3.2 ; 0 ; 1E20
D_temp2 = 1 ; 0.2 ; 1E4
D_temp1 = 1 ; 0.2 ; 1E4
Difusion_coefficient_a = 1.07E-4 ; 0 ; 1E20
Difusion_coefficient_c = 1.12E-4 ; 0 ; 1E20
Difusion_coefficient_d = 5.05E-4 ; 0 ; 1E20
Difusion_coefficient_b = 1.53E-4 ; 0 ; 1E20
Difusion_coefficient_m = 1.42E-4 ; 0 ; 1E20
Difusion_coefficient_n = 1.16E-4 ; 0 ; 1E20
Difusion_coefficient_o = 1.85E-4 ; 0 ; 1E20
Heat_cap = 1100 ; 0 ; 1E20
Heat_cap_c = 1100 ; 0 ; 1E20
Therm_cond = 0.07 ; 0 ; 1E20
Cond_solid = 18 ; 0 ; 1E20
Conversion = 0.3 ; -1E20 ; 1E20
Density = 0.35 ; 0 ; 1E20
Velocity = 8 ; 0 ; 1E20
Rate = 0 ; -1E20 ; 1E20
Heat_balance = 100000 ; -1E20 ; 1E20
Heat_flux = 4000 ; -1E20 ; 1E20
Constant_eq = 0.004 ; -1E20 ; 1E10
Mass_imbalance = 1E-5 ; -1E20 ; 1E20
END

A-1
MODEL Dehydrogenation

PARAMETER

# INLET MASS FRACTIONS, PRESSURE, TEMPERATURE, VELOCITY,
# ETHANE MOLE FRACTION

WAO, WCO, WDO, PI, TIO, U1O, YAO AS REAL

# MOLECULAR MASSES

MA, MC, MD, MI AS REAL

# DIFFUSION COEFFICIENTS

DAO, DCO, DDO AS REAL

# THERMAL CONDUCTIVITIES AT INITIAL TEMPERATURE

LA_AO, LA_CO, LA_DO, LA_IO AS REAL

# HEAT CAPACITY COEFFICIENTS

A_A, B_A, C_A, D_A AS REAL
A_C, B_C, C_C, D_C AS REAL
A_D, B_D, C_D, D_D AS REAL
A_I, B_I, C_I, D_I AS REAL

# CHANNEL DIMENSIONS: LENGTH AND HEIGHT

L, RI AS REAL

# KINETIC PARAMETERS, HEAT OF REACTION

KAO, KEO, KA, KE, DHA AS REAL

# UNIVERSAL GAS CONSTANT

Rg AS REAL

A-2
Ethane Dehydrogenation-Methane Combustion Coupling: gPROMS Code

DISTRIBUTION_DOMAIN
Axial AS (0 : 1)
Radial AS (0 : 1)

VARIABLES

# MASS FRACTIONS

WA AS DISTRIBUTION(Axial, Radial) OF Ethane_mass_fr
WC AS DISTRIBUTION(Axial, Radial) OF Ethylene_mass_fr
WD AS DISTRIBUTION(Axial, Radial) OF Hydrogen_mass_fr
WI AS DISTRIBUTION(Axial, Radial) OF Nitrogen_mass_fr

# MOLAR FRACTIONS

YA AS DISTRIBUTION(Axial, Radial) OF Ethane_mol_fr
YC AS DISTRIBUTION(Axial, Radial) OF Ethylene_mol_fr
YD AS DISTRIBUTION(Axial, Radial) OF Hydrogen_mol_fr
YI AS DISTRIBUTION(Axial, Radial) OF Hydrogen_mol_fr

# CONCENTRATIONS CALCULATED BASED ON MASS BALANCE

CMA AS DISTRIBUTION(Axial, Radial) OF Ethane_conc
CMC AS DISTRIBUTION(Axial, Radial) OF Ethylene_conc
CMD AS DISTRIBUTION(Axial, Radial) OF Hydrogen_conc

# TEMPERATURE AND DIMENSIONLESS TEMPERATURE

T1 AS DISTRIBUTION(Axial, Radial) OF Temperature
TETAl AS DISTRIBUTION(Axial, Radial) OF D_templ

# PHYSICAL PROPERTIES: DIFFUSION COEFFICIENTS, HEAT CAPACITY COEFFICIENTS, THERMAL CONDUCTIVITY

DA AS DISTRIBUTION(Axial, Radial) OF diffusion_coefficient_a
DC AS DISTRIBUTION(Axial, Radial) OF diffusion_coefficient_c
DD AS DISTRIBUTION(Axial, Radial) OF diffusion_coefficient_d
CF_A AS DISTRIBUTION(Axial, Radial) OF heat_cap
CF_C AS DISTRIBUTION(Axial, Radial) OF heat_cap
CF_D AS DISTRIBUTION(Axial, Radial) OF heat_cap
CP_I AS DISTRIBUTION(Axial, Radial) OF heat_cap
LA I AS DISTRIBUTION(Axial, Radial) OF therm_cond
LA_A AS DISTRIBUTION(Axial, Radial) OF therm_cond
LA_C AS DISTRIBUTION(Axial, Radial) OF therm_cond
LA_D AS DISTRIBUTION(Axial, Radial) OF therm_cond
LA_I AS DISTRIBUTION(Axial, Radial) OF therm_cond

A-3
# Ethane Dehydrogenation-Methane Combustion Coupling: gPROMS Code

### #DENSITY AND VELOCITY

**Rol** as DISTRIBUTION(Axial, Radial) OF Density

**U1** as DISTRIBUTION(Axial, Radial) OF Velocity

### #REACTION RATE

### #CONVERSIONS, EQUILIBRIUM CONSTANT, AVERAGE TEMPERATURE

**X1** as DISTRIBUTION(Axial) OF Conversion

**KE** as DISTRIBUTION(Axial) OF Constant_eq

**TAM** as DISTRIBUTION(Axial) OF Temperature

### #MASS IMBALANCE

**Mass imbalance** as Mass_imbalance

**Massl** as DISTRIBUTION(Axial) OF Mass_imbalance

### #CONSUMED HEAT FLUX ALONG THE REACTOR

**Heat_flux_consumed** as DISTRIBUTION(Axial) OF Heat_flux

### #HEAT IMBALANCE VARIABLES, HEAT IN, HEAT OUT, HEAT CONSUMED

**Q_{in, 1}** as Heat_balance

**Q_{out, 1}** as Heat_balance

**Q_{consumed}** as Heat_balance

**Heat_{imbalance}** as Heat_balance

### BOUNDARY

### # INLET CONDITIONS

### # AT z = 0 FOR ALL x

FOR x := 0 TO 1 DO

\[ \begin{align*}
W_{A}(0,x) &= W_{AO}; \\
W_{C}(0,x) &= W_{CO}; \\
W_{D}(0,x) &= W_{DO}; \\
T_{E_{A}}(0,x) &= 1; \\
U_{1}(0,x) &= 1.5*U_{10}*(1-x^2);
\end{align*} \]

END

### # OUTLET CONDITIONS

### # AT z = 1 FOR ALL x

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Ethane Dehydrogenation-Methane Combustion Coupling: gPROMS Code

FOR X := 0|+ TO 1|- DO
   PARTIAL(WA(1,X), Axial) = 0;
   PARTIAL(WC(1,X), Axial) = 0;
   PARTIAL(WD(1,X), Axial) = 0;
   PARTIAL(UL(1,X), Axial) = 0;
   PARTIAL(TETA(1,X), Axial) = 0;
END

# SYMMETRY CONDITIONS
# AT r = 0 FOR ALL z

FOR z := 0 TO 1 DO
   PARTIAL(WA(z,0), Radial) = 0;
   PARTIAL(WC(z,0), Radial) = 0;
   PARTIAL(WD(z,0), Radial) = 0;
   PARTIAL(UL(z,0), Radial) = 0;
   PARTIAL(TETA(z,0), Radial) = 0;
END

# REACTING WALL
# AT r = 1 FOR ALL z

FOR z := 0 TO 1 DO
   DA(z,1)*Rol(z,1)*PARTIAL(WA(z,1), Radial)/L*RI = -1E-3*MA*ReacRate(z);
   DC(z,1)*Rol(z,1)*PARTIAL(WC(z,1), Radial)/L*RI = 1E-3*MC*ReacRate(z);
   DD(z,1)*Rol(z,1)*PARTIAL(WD(z,1), Radial)/L*RI = Ul(z,1) = 0;
END

EQUATION

# MASS BALANCE

FOR z := 0|+ TO 1|- DO
   Rol(z,X)*Ul(z,X)*L*PARTIAL(WA(z,X), Axial)/(L*RI) =
   (PARTIAL(DA(z,X)*Rol(z,X)*PARTIAL(WA(z,X), Axial), Axial) +
   (1/RI^2)*(PARTIAL(DA(z,X)*Rol(z,X)*PARTIAL(WA(z,X),
   Radial), Radial)));
   Rol(z,X)*Ul(z,X)*L*PARTIAL(WC(z,X), Axial) =
   (PARTIAL(DC(z,X)*Rol(z,X)*PARTIAL(WC(z,X), Axial), Axial) +
   (1/RI^2)*(PARTIAL(DC(z,X)*Rol(z,X)*PARTIAL(WC(z,X),
   Radial), Radial));
Ethane Dehydrogenation—Methane Combustion Coupling: gPROMS Code

\[
\text{Rol}(s,x) \cdot \text{UL}(s,x) \cdot \text{PARTIAL}([\text{WD}(s,x), \text{Axial}]) = \\
(\text{PARTIAL}([\text{DD}(s,x) \cdot \text{Rol}(s,x) \cdot \text{PARTIAL}([\text{WD}(s,x), \text{Radial}]), \text{Radial}])) \\
(1/R1*2) \\
(\text{PARTIAL}(\text{DD}(s,x) \cdot \text{Rol}(s,x) \cdot \text{PARTIAL}([\text{WD}(s,x), \text{Radial}]), \text{Radial}))); \\
\]

END

# ENERGY BALANCE

FOR \( z: 0 > 1 \) DO
FOR \( x: 0 > 1 \) DO
\[
\text{Rol}(s,x) \cdot \text{CP1}(s,x) \cdot \text{UL}(s,x) \cdot \text{PARTIAL}([\text{TE01}(s,x), \text{Axial}]) = \\
(\text{PARTIAL}(\text{LA1}(s,x) \cdot \text{PARTIAL}([\text{TE01}(s,x), \text{Axial}]), \text{Axial})) = (1/R1*2) \\
(\text{PARTIAL}(\text{LA1}(s,x) \cdot \text{PARTIAL}([\text{TE01}(s,x), \text{Radial}]), \text{Radial}))); \\
\]
END
END

# CONTINUITY EQUATION

FOR \( z: 0 > 1 \) DO
FOR \( x: 0 > 1 \) DO
\[
\text{PARTIAL}([\text{Rol}(s,x) \cdot \text{UL}(s,x), \text{Axial}]) = 0 \\
\]
END
END

# AUXILIARY EQUATIONS

# NITROGEN MASS FRACTION

FOR \( z: 0 \) TO 1 DO
FOR \( x: 0 \) TO 1 DO
\[
\text{WI}(s,x) = (\text{WA}(s,x) + \text{WC}(s,x) + \text{WD}(s,x)) \\
\]
END
END

# DENSITY

FOR \( z: 0 \) TO 1 DO
FOR \( x: 0 \) TO 1 DO
\[
\text{Rol}(s,x) = 1E-3 \cdot 101325 \cdot \text{P1}/\text{GI}(s,x) \\
/ \text{WA}(s,x)/\text{WA}+\text{WC}(s,x)/\text{WC}+\text{WD}(s,x)/\text{WD}+\text{WI}(s,x)/\text{WI} \\
\]
END
END

# Molar fractions

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Ethane Dehydrogenation-Methane Combustion Coupling: gPROMS Code

 FOR z>0 TO 1 DO
 FOR x: 0 TO 1 DO
 YA(z,x)=WA(z,x)/WA(z,x)+WC(z,x)/MC+WD(z,x)/MD+WI(z,x)/MI;
 YC(z,x)=WC(z,x)/MC/(WA(z,x)/MA+WC(z,x)/MC+WD(z,x)/MD+WI(z,x)/MI);
 YD(z,x)=WD(z,x)/MD/(WA(z,x)/MA+WC(z,x)/MC+WD(z,x)/MD+WI(z,x)/MI);
 YI(z,x)=WI(z,x)/MI/(WA(z,x)/MA+WC(z,x)/MC+WD(z,x)/MD+WI(z,x)/MI);
 END
 END

 REACTION RATE

 FOR z: 0 TO 1 DO
 ReactRate(z)=KAO+EXP(-EA/Rg/T1(z,1))*PI*(YA(z,1)-YC(z,1)*YD(z,1)) / (KEO+EXP(-EE/Rg/T1(z,1))/PI));
 END

 CONCENTRATIONS

 FOR z: 0 TO 1 DO
 FOR x: 0 TO 1 DO
 CMA(z,x)=101325*Pl*YA(z,x)/Rg/Tl(z,x);
 CMC(z,x)=101325*Pl*YC(z,x)/Rg/Tl(z,x);
 CMD(z,x)=101325*Pl*YD(z,x)/Rg/Tl(z,x);
 END
 END

 TEMPERATURE

 FOR z: 0 TO 1 DO
 FOR x: 0 TO 1 DO
 Tl(z,x)=T10*TETA1(z,x);
 END
 END

 HEAT CAPACITY

 FOR z: 0 TO 1 DO
 FOR x: 0 TO 1 DO
 CP_A(z,x)=1E3*(A_A+B_A*(T1(z,x)/1000)+C_A*(T1(z,x)/1000)^2+D_A*(T1(z,x)/1000)^3)/MA;
 CP_C(z,x)=1E3*(A_C+B_C*(T1(z,x)/1000)+C_C*(T1(z,x)/1000)^2+D_C*(T1(z,x)/1000)^3)/MC;
 CP_D(z,x)=1E3*(A_D+B_D*(T1(z,x)/1000)+C_D*(T1(z,x)/1000)^2+D_D*(T1(z,x)/1000)^3)/MD;
 END
 END
Ethane Dehydrogenation-Methane Combustion Coupling: gPROMS Code

\[ \frac{\text{CP}_I(z,x)}{\text{C}_{P K z,x}} = 1 \times 10^3 \left( A_I + B_I \left( \frac{T_1(z,x)}{1000} \right)^2 + C_I \left( \frac{T_1(z,x)}{1000} \right) + D_I \frac{T_1(z,x)}{1000} \right) \]

\[ \frac{\text{CP}_K(z,x)}{\text{CP}_A(z,x)} = \frac{\text{CP}_D(z,x)}{\text{CP}_C(z,x)} = \frac{\text{CP}_I(z,x)}{\text{CP}_J(z,x)} \]

\[ \text{END} \]

# THERMAL CONDUCTIVITIES

\[ \text{FOR} \ z \ 0 \ \text{TO} \ 1 \ \text{DO} \]
\[ \text{FOR} \ x \ 0 \ \text{TO} \ 1 \ \text{DO} \]
\[ \text{LA}_A(z,x) = \text{LA}_0 A + TETA_1(z,x)^{0.75} \]
\[ \text{LA}_C(z,x) = \text{LA}_0 C + TETA_1(z,x)^{0.75} \]
\[ \text{LA}_D(z,x) = \text{LA}_0 D + TETA_1(z,x)^{0.75} \]
\[ \text{LA}_I(z,x) = \text{LA}_0 I + TETA_1(z,x)^{0.75} \]
\[ \text{LA}_J(z,x) = \text{LA}_0 J + TETA_1(z,x)^{0.75} \]
\[ \text{LA}_k(z,x) = \left[ \text{YA}(z,x) \text{LA}_A(z,x) + \text{YC}(z,x) \text{LA}_C(z,x) + \text{YD}(z,x) \text{LA}_D(z,x) + \text{YI}(z,x) \text{LA}_I(z,x) \right] \times \left[ \text{YA}(z,x) + \text{YC}(z,x) + \text{YD}(z,x) + \text{YI}(z,x) \right] \]
\[ \text{END} \]
\[ \text{END} \]

# DIFFUSION COEFFICIENTS

\[ \text{FOR} \ z \ 0 \ \text{TO} \ 1 \ \text{DO} \]
\[ \text{FOR} \ x \ 0 \ \text{TO} \ 1 \ \text{DO} \]
\[ \text{DA}(z,x) = \text{DA}_0 + TETA_1(z,x)^{1.75} \]
\[ \text{DC}(z,x) = \text{DC}_0 + TETA_1(z,x)^{1.75} \]
\[ \text{DD}(z,x) = \text{DD}_0 + TETA_1(z,x)^{1.75} \]
\[ \text{END} \]
\[ \text{END} \]

# HEAT FLUX CONSUMED

\[ \text{FOR} \ z \ 0 \ \text{TO} \ 1 \ \text{DO} \]
\[ \text{Heat_flux_consumed}(z) = \text{DHA} + \text{ReacRate}(z) \]
\[ \text{END} \]

# CONVERSION IN MASS BALANCE

\[ \text{FOR} \ z \ 0 \ \text{TO} \ 1 \ \text{DO} \]
\[ \text{XI}(z) = \text{INTEGRAL}(x=0:1; \text{Rol}(z,x) \text{UL}(z,x)) \]
\[ \text{INTEGRAL}(x=0:1; \text{Rol}(z,x) \text{UL}(z,x)) \]
\[ \text{INTEGRAL}(x=0:1; \text{Rol}(z,x) \text{UL}(z,x)) \]
\[ \text{Mass}(z) = \text{INTEGRAL}(x=0:1; \text{Rol}(z,x) \text{UL}(z,x)) \]
\[ \text{END} \]
Ethane Dehydrogenation-Methane Combustion Coupling: gPROMS Code

### AVERAGE TEMPERATURE IN THE CROSS SECTION
For z := 0 TO 1 DO
  \[ T_{\text{IN}} = \frac{\text{INTEGRAL}(x:0:1; R_0(z,x) \cdot U_1(z,x) \cdot T_1(z,x))}{\text{INTEGRAL}(x:0:1; R_0(z,x) \cdot U_1(z,x))}; \]
END

### EQUILIBRIUM CONSTANT AND EQUILIBRIUM CONVERSION
For z := 0 TO 1 DO
  \[ K_E(z) = K_{EO} \cdot \exp\left(-\frac{E_E}{R \cdot G \cdot T(z)}\right); \]
END

### HEAT IMBALANCE
Q_{\text{in,}1} = \text{INTEGRAL}(x:0:1; R_0(0,x) \cdot U_1(0,x) \cdot C_P(0,x) \cdot T_1(0,x)) ;
Q_{\text{out,}1} = \text{INTEGRAL}(x:0:1; R_0(1,x) \cdot U_1(1,x) \cdot C_P(1,x) \cdot T_1(1,x));
Q_{\text{consumed}} = \text{INTEGRAL}(x:0:1; R_0(0,x) \cdot U_1(0,x) \cdot \frac{W_{A(0,0)} \cdot X_1(1) \cdot (-D_{HA})}{M_A} / 10^3); \]

### MASS IMBALANCE
Mass_{\text{imbalance,}1} = \text{INTEGRAL}(x:0:1; R_0(0,x) \cdot U_1(0,x)) - \text{INTEGRAL}(x:0:1; R_0(1,x) \cdot U_1(1,x));

END # Model

MODEL Combustion

PARAMETER

### INLET MASS FRACTIONS, PRESSURE, TEMPERATURE, VELOCITY,
W_{BO}, W_{MO}, W_{NO}, W_{SO}, P_2, T_20, U_{20} AS REAL

### MOLECULAR MASSES
M_B, M_M, M_N, M_{SO}, M_{II2}, M_S AS REAL

### DIFFUSION COEFFICIENTS
D_{BO}, D_{MO}, D_{NO}, D_{SO} AS REAL
Ethane Dehydrogenation-Methane Combustion Coupling: gPROMS Code

#-----------------------------------------------
# THERMAL CONDUCTIVITIES AT INITIAL TEMPERATURE
# LA_BO, LA_MO, LA_NO, LA_SO, LA_I20 AS REAL
#-----------------------------------------------
# HEAT CAPACITY COEFFICIENTS
#-----------------------------------------------
# A_B, B_B, C_B, D_B AS REAL
# A_M, B_M, C_M, D_M AS REAL
# A_N, B_N, C_N, D_N AS REAL
# A_S, B_S, C_S, D_S AS REAL
# A_I2, B_I2, C_I2, D_I2 AS REAL
#-----------------------------------------------
# CHANNEL DIMENSIONS
#-----------------------------------------------
# L, R2 AS REAL
#-----------------------------------------------
# KINETIC PARAMETERS, HEAT OF REACTION
#-----------------------------------------------
# KBO, EB, DHB AS REAL
#-----------------------------------------------
# UNIVERSE GAS CONSTANT
#-----------------------------------------------
# Rg AS REAL
#-----------------------------------------------
# DISTRIBUTION_DOMAIN
# Axial AS (0:1)
# Radial AS (0:1)
#-----------------------------------------------
# VARIABLE
#-----------------------------------------------
# MASS FRACTIONS
#-----------------------------------------------
# WB AS DISTRIBUTION(Axial, Radial) OF Methane_mass_fr
# WM AS DISTRIBUTION(Axial, Radial) OF Oxygen_mass_fr
# WN AS DISTRIBUTION(Axial, Radial) OF CO2_mass_fr
# WS AS DISTRIBUTION(Axial, Radial) OF Water_mass_fr
# W12 AS DISTRIBUTION(Axial, Radial) OF Nitrogen2_mass_fr
#-----------------------------------------------
# MOLAR FRACTIONS
#-----------------------------------------------
# YB AS DISTRIBUTION(Axial, Radial) OF Methane_mol_fr
# YM AS DISTRIBUTION(Axial, Radial) OF Oxygen_mol_fr
# YN AS DISTRIBUTION(Axial, Radial) OF CO2_mol_fr
# YN AS DISTRIBUTION(Axial, Radial) OF CO2_mol_fr

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Ethane Dehydrogenation-Methane Combustion Coupling: gPROMS Code

**CONCENTRATIONS CALCULATED BASED ON MASS BALANCE**

- YS AS DISTRIBUTION(Axial, Radial) OF Water_mol_fr
- YI2 AS DISTRIBUTION(Axial, Radial) OF Nitrogen2_mol_fr

**TEMPERATURE AND DIMENSIONLESS TEMPERATURE**

- T2 AS DISTRIBUTION(Axial, Radial) OF Temperature
- TETA2 AS DISTRIBUTION(Axial, Radial) OF D_temp2

**PHYSICAL PROPERTIES: DIFFUSION COEFFICIENTS, HEAT CAPACITY, COEFFICIENTS, THERMAL CONDUCTIVITY**

- DB AS DISTRIBUTION(Axial, Radial) OF Diffusion_coefficient_b
- DM AS DISTRIBUTION(Axial, Radial) OF Diffusion_coefficient_m
- DW AS DISTRIBUTION(Axial, Radial) OF Diffusion_coefficient_w
- DS AS DISTRIBUTION(Axial, Radial) OF Diffusion_coefficient_s

- CP_B AS DISTRIBUTION(Axial, Radial) OF Heat_cap
- CP_M AS DISTRIBUTION(Axial, Radial) OF Heat_cap
- CP_N AS DISTRIBUTION(Axial, Radial) OF Heat_cap
- CP_S AS DISTRIBUTION(Axial, Radial) OF Heat_cap
- CP_I2 AS DISTRIBUTION(Axial, Radial) OF Heat_cap

- LA2 AS DISTRIBUTION(Axial, Radial) OF Therm_cond
- LA_B AS DISTRIBUTION(Axial, Radial) OF Therm_cond
- LA_M AS DISTRIBUTION(Axial, Radial) OF Therm_cond
- LA_N AS DISTRIBUTION(Axial, Radial) OF Therm_cond
- LA_S AS DISTRIBUTION(Axial, Radial) OF Therm_cond
- LA_I2 AS DISTRIBUTION(Axial, Radial) OF Therm_cond

**DENSITY AND VELOCITY**

- Ro2 AS DISTRIBUTION(Axial, Radial) OF Density
- U2 AS DISTRIBUTION(Axial, Radial) OF Velocity

**REACTION RATE**

- ReacRate2 AS DISTRIBUTION(Axial) OF Rate

**CONVERSION**

- X2 AS DISTRIBUTION(Axial) OF Conversion
Ethane Dehydrogenation-Methane Combustion Coupling: gPROMS Code

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### Mass Imbalance

\[ \text{Mass imbalance2} \quad \text{AS Mass imbalance} \]

\[ \text{Mass2} \quad \text{AS DISTRIBUTION(Axial) OF Mass imbalance} \]

### Consumed Heat Flux Along the Reactor

\[ \text{Heat_flux_generated} \quad \text{AS DISTRIBUTION(Axial) OF Heat_flux} \]

### Heat Imbalance Variables, Heat In, Heat Out, Heat Generated

\[ Q_{\text{in}_2} \quad \text{AS Heat balance} \]

\[ Q_{\text{out}_2} \quad \text{AS Heat balance} \]

\[ Q_{\text{generated}} \quad \text{AS Heat balance} \]

---

### Boundary Conditions

#### Inlet Conditions

\[ \text{At } z = 0 \quad \text{for all } x \]

FOR \( x := 0 \) TO \( 1 \) DO

- \( W_B(0, x) = W_B_0 \)
- \( W_M(0, x) = W_M_0 \)
- \( W_N(0, x) = W_N_0 \)
- \( W_S(0, x) = W_S_0 \)
- \( \Theta_2(0, x) = 0 \)
- \( U_2(0, x) = 1.5 + U_2_0 - (1 - x^2) \)

END

#### Outlet Conditions

\[ \text{At } z = 1 \quad \text{for all } x \]

FOR \( x := 0 \) TO \( 1 \) DO

- \( \text{PARTIAL}(W_B(1, x), \text{Axial}) = 0 \)
- \( \text{PARTIAL}(W_M(1, x), \text{Axial}) = 0 \)
- \( \text{PARTIAL}(W_N(1, x), \text{Axial}) = 0 \)
- \( \text{PARTIAL}(W_S(1, x), \text{Axial}) = 0 \)
- \( \text{PARTIAL}(\Theta_2(1, x), \text{Axial}) = 0 \)

END
Ethane Dehydrogenation-Methane Combustion Coupling: gPROMS Code

# SYMMETRY CONDITIONS
# AT x=0 FOR ALL z

FOR z := 0 TO 1 DO
    PARTIAL(WB(z,0), Radial) = 0;
    PARTIAL(WM(z,0), Radial) = 0;
    PARTIAL(WN(z,0), Radial) = 0;
    PARTIAL(WS(z,0), Radial) = 0;
    PARTIAL(U2(z,0), Radial) = 0;
    PARTIAL(TETA2(z,0), Radial) = 0;
END

# REACTING WALL
# AT x=1 FOR ALL z

FOR z := 0 TO 1 DO
    DB(z,1)*Ro2(z,1)*PARTIAL(WB(z,1), Radial)/(L*R2) =
    -1E-3*MB*ReacRate2(z);
    DM(z,1)*Ro2(z,1)*PARTIAL(WM(z,1), Radial)/(L*R2) =
    -2*1E-3*MM*ReacRate2(z);
    DN(z,1)*Ro2(z,1)*PARTIAL(WN(z,1), Radial)/(L*R2) =
    1E-3*MN*ReacRate2(z);
    DS(z,1)*Ro2(z,1)*PARTIAL(WS(z,1), Radial)/(L*R2) =
    2*1E-3*MS*ReacRate2(z);
    U2(z,1) = 0;
END

EQUATION

# MASS BALANCE
#----------------------------------------------

FOR z:= 0[+] TO 1[-] DO
    FOR x:= 0[+] TO 1[-] DO
        Ro2(s,x)*U2(s,x)*L*PARTIAL(WB(s,x), Axial) =
        (PARTIAL(DM(s,x)*Ro2(s,x)*PARTIAL(WB(s,x), Axial), Axial) +
        (1/R2^2)*)*(PARTIAL(DM(s,x)*Ro2(s,x)*PARTIAL(WB(s,x),
        Radial), Radial));
        Ro2(s,x)*U2(s,x)*L*PARTIAL(WM(s,x), Axial) =
        (PARTIAL(DN(s,x)*Ro2(s,x)*PARTIAL(WM(s,x), Axial), Axial) +
        (1/R2^2)*)*(PARTIAL(DN(s,x)*Ro2(s,x)*PARTIAL(WM(s,x),
        Radial), Radial));
        Ro2(s,x)*U2(s,x)*L*PARTIAL(WN(s,x), Axial) =
        (PARTIAL(DS(s,x)*Ro2(s,x)*PARTIAL(WN(s,x), Axial) +
        (1/R2^2)*)*(PARTIAL(DS(s,x)*Ro2(s,x)*PARTIAL(WN(s,x),
        Radial), Radial));
    END
END

A13
Ethane Dehydrogenation-Methane Combustion Coupling: gPROMS Code

R2(z, x)*U2(z, x)*PARTIAL(WS(z, x), Axial) =
(PARTIAL(DS(z, x) - R2(z, x)*PARTIAL(WS(z, x), Axial), Axial) -
(1/R2")2)*[PARTIAL(DS(z, x)*R2(z, x)*PARTIAL(WS(z, x),
Radial, Radial))];

END
END

# Energy Balance
#---------------------------------------------------------
#---------------------------------------------------------
FOR z := 0 TO 1 DO
FOR x := 0 TO 1 DO
R2(z, x)*CP2(z, x)*U2(z, x)*L*PARTIAL(TETA2(z, x), Axial) -
(PARTIAL(LA2(z, x)*PARTIAL(TETA2(z, x), Axial), Axial) +
(1/R2")2)*[PARTIAL(LA2(z, x)*PARTIAL(TETA2(z, x), Radial, Radial))];
END
END

# Continuity Equation
#---------------------------------------------------------
#---------------------------------------------------------
FOR z := 0 TO 1 DO
FOR x := 0 TO 1 DO
PARTIAL(R2(z, x)*U2(z, x), Axial) = 0 ;
END
END

# Auxiliary Equations
#---------------------------------------------------------
#---------------------------------------------------------
# Nitrogen Mass Fraction
#---------------------------------------------------------
#---------------------------------------------------------
FOR z := 0 TO 1 DO
FOR x := 0 TO 1 DO
W2(z, x) = 1 - (WB(z, x) + WM(z, x) + WN(z, x) + WS(z, x));
END
END

# Density
#---------------------------------------------------------
#---------------------------------------------------------
FOR z := 0 TO 1 DO
END

A14
FOR X := 0 TO 1 DO
Ro2(z,x)=E-3*(101325*P2/Rg/T2(z,x))/
(WB(z,x)/MB+WM(z,x)/MM+WN(z,x)/MN+WS(z,x)/MS+
WS(z,x)/MS+W12(z,x)/W12)
END
END

# molar fractions

FOR z := 0 TO 1 DO
FOR x := 0 TO 1 DO
YB(z,x)=WB(z,x)/MB/
(WB(z,x)/MB+WM(z,x)/MM+WN(z,x)/MN+WS(z,x)/MS+
W12(z,x)/W12)
YM(z,x)=WM(z,x)/MM/
(WB(z,x)/MB+WM(z,x)/MM+WN(z,x)/MN+WS(z,x)/MS+
W12(z,x)/W12)
YN(z,x)=WN(z,x)/MN/
(WB(z,x)/MB+WM(z,x)/MM+WN(z,x)/MN+WS(z,x)/MS+
W12(z,x)/W12)
YS(z,x)=WS(z,x)/MS/
(WB(z,x)/MB+WM(z,x)/MM+WN(z,x)/MN+WS(z,x)/MS+
W12(z,x)/W12)
YI2(z,x)=W12(z,x)/W12/
(WB(z,x)/MB+WM(z,x)/MM+WN(z,x)/MN+WS(z,x)/MS+
W12(z,x)/W12)
END
END

#Combustion reaction rate in mass balance

FOR z := 0 TO 1 DO
ReacRateZ(z)=KBO*EXP(-EB/Rg/T2(z,1))*CMB(z,1)
END

# CONCENTRATIONS

FOR z := 0 TO 1 DO
FOR x := 0 TO 1 DO
CMB(z,x)=101325*P2*YB(z,x)/Rg/T2(z,x)
CMM(z,x)=101325*P2*YM(z,x)/Rg/T2(z,x)
CMN(z,x)=101325*P2*YN(z,x)/Rg/T2(z,x)
CMS(z,x)=101325*P2*YS(z,x)/Rg/T2(z,x)
END
END

#TEMPERATURE

A15
ethane dehydrogenation-methane combustion coupling: gproms code

# heat capacity

for z:> 0 to 1 do
  for x:« 0 to 1 do
    t2(z,x)=t20*teta2(z,x)
  end
end

# heat capacity

for z: 0 to 1 do
  for x: 0 to 1 do
    cp_b(z,x)=1e3*(a_b+b_b*(t2(z,x)/1000)+c_b*(t2(z,x)/1000)^2+d_b*(t2(z,x)/1000)^3)/mb
    cp_m(z,x)=1e3*(a_m+b_m*(t2(z,x)/1000)^2+c_m*(t2(z,x)/1000)^2+d_m*(t2(z,x)/1000)^3)/mm
    cp_n(z,x)=1e3*(a_n+b_n*(t2(z,x)/1000)+c_n*(t2(z,x)/1000)^2+d_n*(t2(z,x)/1000)^3)/mn
    cp_s(z,x)=1e3*(a_s+b_s*(t2(z,x)/1000)+c_s*(t2(z,x)/1000)^2+d_s*(t2(z,x)/1000)^3)/ms
    cp_i2(z,x)=1e3*(a_i2+b_i2*(t2(z,x)/1000)+c_i2*(t2(z,x)/1000)^2+d_i2*(t2(z,x)/1000)^3)/mi2
    cp2(z,x)=wb(z,x)*cp_b(z,x)+wm(z,x)*cp_m(z,x)+wn(z,x)*cp_n(z,x)+wi2(z,x)*cp_i2(z,x)+ws(z,x)
  end
end

# thermal conductivities

for z: 0 to 1 do
  for x: 0 to 1 do
    la_b(z,x)=la_b0*teta2(z,x)^0.75
    la_m(z,x)=la_m0*teta2(z,x)^0.75
    la_n(z,x)=la_n0*teta2(z,x)^0.75
    la_s(z,x)=la_s0*teta2(z,x)^0.75
    la_i2(z,x)=la_i20*teta2(z,x)^0.75
    la2(z,x)=(yb(z,x)*la_b(z,x)*mb*0.33+ym(z,x)*la_m(z,x)*mm^0.33+yn(z,x)*la_n(z,x)*mn*0.33+ys(z,x)*la_s(z,x)*ms*0.33+y_i2(z,x)*la_i2(z,x)*mi2^0.33)/(yb(z,x)*mb*0.33+ym(z,x)*mm^0.33+yn(z,x)*mn*0.33+ys(z,x)*ms*0.33+y_i2(z,x)*mi2^0.33)
  end
end

# diffusion coefficients

for z: 0 to 1 do
  for x: 0 to 1 do
    db(z,x)=db0*teta2(z,x)^1.75
    dm(z,x)=dm0*teta2(z,x)^1.75
    dn(z,x)=dn0*teta2(z,x)^1.75
    ds(z,x)=ds0*teta2(z,x)^1.75
  end
end

a16
Ethane Dehydrogenation-Methane Combustion Coupling: gPROMS Code

END
END

# HEAT FLUX GENERATED

For z :> 0 To 1 DO
Heat_flux_generated(z) = DHB * ReacRate2(z);
END

# CONVERSION

For z :> 0 To 1 DO
X2(z) = 1 - INTEGRAL(x:0:1; Ro2(z,x) * U2(z,x) * MB(z,x)) / INTEGRAL(x:0:1; Ro2(0,x) * U2(0,x) * WB(0,x));
Mass2(z) = INTEGRAL(x:0:1; Ro2(z,x) * U2(z,x));
END

# HEAT IMBALANCE

Q_in_2 = INTEGRAL(x:0:1; Ro2(0,x) * U2(0,x) * CP2(0,x) * T2(0,x));
Q_out_2 = INTEGRAL(x:0:1; Ro2(1,x) * U2(1,x) * CP2(1,x) * T2(1,x));
Q_generated = INTEGRAL(x:0:1; Ro2(0,x) * U2(0,x) * WB(0,0) * X2(1) * DHB / MB / 1E-3);

# MASS IMBALANCE

Mass_imbalance_2 = INTEGRAL(x:0:1; Ro2(0,x) * U2(0,x)) - INTEGRAL(x:0:1; Ro2(1,x) * U2(1,x));
END # Model

MODEL Solid

PARAMETER

# ASPECT RATIO, INLET TEMPERATURE

RW, TSO AS REAL

# WALL THERMAL CONDUCTIVITY AT INITIAL TEMPERATURE

LASS0 AS REAL

DISTRIBUTION_DOMAIN
Axial AS (0:1)
Radial AS (0:1)


**Ethane Dehydrogenation-Methane Combustion Coupling: gPROMS Code**

VARIABLES

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TETAS</td>
<td>Distribution (Axial, Radial) of D_temp</td>
</tr>
<tr>
<td>TS</td>
<td>Distribution (Axial, Radial) of Temperature</td>
</tr>
<tr>
<td>LAS</td>
<td>Distribution (Axial, Radial) of Cond_solid</td>
</tr>
</tbody>
</table>

BOUNDARY

`# Boundary conditions at the ends
# At z = 0 and z = 1 all x except 0 and 1`  

FOR x := 0 TO 1 DO  
  PARTIAL(TETAS(0, x), Axial) = 0;  
  PARTIAL(TETAS(1, x), Axial) = 0;  
END

EQUATION

`# Laplace equation
# FOR z := 0 TO 1 DO`  

FOR x := 0 TO 1 DO  
  PARTIAL(TETAS(z, x), Axial, Axial) + (1/2π^2) * PARTIAL(TETAS(z, x), Radial, Radial) = 0;  
END  
END

AUXILIARY EQUATIONS

TEMPERATURE

FOR z := 0 TO 1 DO  
  FOR x := 0 TO 1 DO  
    TS(z, x) = TSO * TETAS(z, x);  
  END  
END

SOLID THERMAL CONDUCTIVITY

FOR z := 0 TO 1 DO  
  FOR x := 0 TO 1 DO  
    LAS(z, x) = LAS0 * TETAS(z, x) * 0.75;  
  END  
END

END # model solid

MODEL Reactor

UNIT

<table>
<thead>
<tr>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA</td>
<td>Dehydrogenation</td>
</tr>
<tr>
<td>SB</td>
<td>Combustion</td>
</tr>
<tr>
<td>SS</td>
<td>Solid</td>
</tr>
</tbody>
</table>

SET

WITHIN SA DO

A18
Ethane Dehydrogenation-Methane Combustion Coupling: gPROMS Code

Axial := [BYDM, 2, 20];
Radial := [OCFEM, 3, 3];
END

WITHIN SB DO
Axial := [BYDM, 2, 20];
Radial := [OCFEM, 3, 3];
END

WITHIN SS DO
Axial := [BYDM, 2, 20];
Radial := [OCFEM, 3, 3];
END

EQUATION
$.enum$ (4.1)
FOR s := 0 TO 1 DO
SA.TLA(s,1)*PARTIAL(SA.TETA(s,1),SA.Radial)*
SA.ReacRate1(s)*SA.R1*SA.DHA/SA.T10+
PARTIAL(SA.TETA(s,0),SA.Radial)*SA.LAS(s,0)*SA.R1/
SA.RW;
SA.TLA(s,1) = SS.TEAS(s,0);
SB.TLA(s,1)*PARTIAL(SB.TETA(s,1),SB.Radial)*
SB.ReacRate1(s)*SB.R2*SB.DHB/SA.T20-
PARTIAL(SB.TETA(s,1),SB.Radial)*SB.LAS(s,1)*SB.R2/
SB.RW;
SS.TEAS(s,1) = SS.T2(s,1);
END

SA.Heat_balance = 100*(SA.Q_in_1 + SB.Q_in_2 - SA.Q_out_1-
SB.Q_out_2 + SB.Q_generated - SA.Q_consumed)/(SA.Q_in_1+
SB.Q_in_2 + SB.Q_generated);}

END # model reactor

BEGIN # model reactor
$enum$ (4.1)
PROCESS et2
UNIT sk AS Reactor
SET
WITHIN SK DO
WITHIN SA DO
YAO := 0.6; WAO := 0.5172; WCO := 0; WDO := 0; PI := 1; T10 := 923; U10 := 2.5; NA := 10; MC := 28; MD := 2; M1 := 28; DA0 := 1.067E-4; DC0 := 1.124E-4; DD0 := 0.038; LA_AO := 0.059; LA_CC := 0.0559; LA_D0 := 0.4305; LA_0 := 0.068; A_A := 0.889;

A19
System Dynamics Programme (gPROMS) Code

E = \text{Ethane Dehydrogenation-Methane Combustion Coupling}

\text{A} = -12.24

\text{C} = 43.95

\text{D} = -7.273

\text{B} = -3.38

\text{C} = 1.561

\text{D} = -17.64

\text{A} = 29.06

\text{B} = -1.913

\text{C} = 8.69

\text{D} = -0.869

\text{A} = 28.85

\text{B} = -1.569

\text{C} = 8.067

\text{D} = -2.868

\text{L} = 1

\text{R1} = 0.001

\text{R2} = 0.0526

\text{WHO} = -0.2209

\text{NNO} = 0

\text{NSO} = 0

\text{P2} = 1

\text{T20} = 923

\text{A} = 29.185

\text{B} = 16

\text{C} = 12

\text{D} = 44

\text{E} = 18

\text{F} = 20

\text{DNO} = 1.538E-4

\text{DMO} = 1.428E-4

\text{DNO} = 1.385E-4

\text{DSO} = 1.888E-4

\text{LA_20} = 0.1209

\text{LA_20} = 0.0561

\text{LA_20} = 0.0536

\text{LA_20} = 0.0591

\text{LA_20} = 0.0608

\text{A_B} = 1.986

\text{B_B} = 9.16

\text{C_B} = 12.67

\text{D_B} = -10.99

\text{A_P} = 25.44

\text{B_P} = 15.18

\text{C_P} = 7.344

\text{D_P} = 1.310

\text{A_P} = 32.22

\text{B_P} = 59.711

\text{C_P} = -34.95

\text{D_P} = 1.457

\text{A_S} = 32.19

\text{B_S} = 1.920

\text{C_S} = 10.54

\text{D_S} = -3.959

\text{A_I2} = 28.85

\text{B_I2} = 1.569

\text{C_I2} = 8.067

\text{D_I2} = 2.868

\text{L} = 1

\text{R2} = 0.001

A20
Ethane Dehydrogenation-Methane Combustion Coupling: gPROMS Code

KBO := 375 ;
KE := 88000 ;
DHB := 890000 ;
kg := 8.316 ;
END

WITHIN SS DO

RW := 0.002 ;
LASS := 25 ;
TSO := 923 ;
END

PRESET
RESET "az2"

SOLUTIONPARAMETERS
OutputLevel := 2 ;
gRMS := ON ;
gPLOT := ON ;
MaxNlterations := 1000 ;
BlockDecomposition := ON ;
SCHEDULE
SAVE "az3"
END
Appendix B1

Co-ordinate system for each domain of the CPR mathematical model used in chapter 4
Co-ordinate system for CPR model

Figure B1 Co-ordinate system for each domain of the CPR mathematical model
Appendix B2

Steam Reforming-Methane Combustion Coupling
(simplified kinetics): gPROMS code
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

# Mathematical model for STEAM REFORMING- METHANE COMBUSTION
# in a CATALYTIC PLATE REACTOR

DECLARE

TYPE

Methaner_mass_fr : 0.22 : 1
Waterr_mass_fr : 0.11 : 1
Hydrogen_mass_fr : 0.01 : 1
CO_mass_fr : 0.8 : 1
Methaner Mol_fr : 0.25 : 1
Water Mol_fr : 0.75 : 1
Hydrogen Mol_fr : 0.7 : 1
CO Mol_fr : 0.5 : 1
Temperature : 1000 : 1
Methaner conc : 3.3 : 1
Water conc : 10 : 1
Hydrogen conc : 0.03 : 1
CO conc : 0.01 : 1
Methaner Mol conc : 0.2 : 1
Water Mol conc : 0.1 : 1
Hydrogen Mol conc : 0.01 : 1

END
MODEL Reforming

PARAMETER

# INLET MASS FRACTIONS, PRESSURE, TEMPERATURE, VELOCITY,
# INLET MASS FRACTIONS, PRESSURE, TEMPERATURE, VELOCITY,
# INLET MASS FRACTIONS, PRESSURE, TEMPERATURE, VELOCITY,
# INLET MASS FRACTIONS, PRESSURE, TEMPERATURE, VELOCITY,
WA0, MC0, WDO, WEO, P1, T10, U10 AS REAL

# MOLECULAR MASSES

# DIFFUSION COEFFICIENTS

# Thermal conductivities at initial temperature

# Heat capacity coefficients

# CHANNEL DIMENSIONS: lengths and half channel gap

# GAS CONSTANT

DISTRIBUTION_DOMAIN

Axial AS (0:1)
Radial AS (0:1)

VARIABLE

# MASS FRACTIONS

WA AS DISTRIBUTION(Axial, Radial) OF Methane_mass_fr
WC AS DISTRIBUTION(Axial, Radial) OF Water_mass_fr
WD AS DISTRIBUTION(Axial, Radial) OF CO_mass_fr
WE AS DISTRIBUTION(Axial, Radial) OF Hydrogen_mass_fr

B2-2
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

# Molar fractions

YA AS DISTRIBUTION(Axial, Radial) OF Methane_mol_fr
YC AS DISTRIBUTION(Axial, Radial) OF Water_mol_fr
YD AS DISTRIBUTION(Axial, Radial) OF CO_mol_fr
YE AS DISTRIBUTION(Axial, Radial) OF Hydrogen_mass_fr

# Concentrations, mol/m^3

CMA AS DISTRIBUTION(Axial, Radial) OF Methane_conc
CMC AS DISTRIBUTION(Axial, Radial) OF Water_conc
CMD AS DISTRIBUTION(Axial, Radial) OF CO_conc
CME AS DISTRIBUTION(Axial, Radial) OF Hydrogen_conc

# Temperature and dimensionless temperature, K

T1 AS DISTRIBUTION(Axial, Radial) OF Temperature
TETAL AS DISTRIBUTION(Axial, Radial) OF D_temp

# Physical properties: diffusion coefficients, heat capacity, thermal conductivity

DA AS DISTRIBUTION(Axial, Radial) OF Diffusion_coefficient_a
DC AS DISTRIBUTION(Axial, Radial) OF Diffusion_coefficient_c
DD AS DISTRIBUTION(Axial, Radial) OF Diffusion_coefficient_d
DE AS DISTRIBUTION(Axial, Radial) OF Diffusion_coefficient_e
CP A AS DISTRIBUTION(Axial, Radial) OF Heat_capacity
CP_C AS DISTRIBUTION(Axial, Radial) OF Heat_capacity
CP_D AS DISTRIBUTION(Axial, Radial) OF Heat_capacity
CP_E AS DISTRIBUTION(Axial, Radial) OF Heat_capacity
LAI AS DISTRIBUTION(Axial, Radial) OF Therm_cond
LA_A AS DISTRIBUTION(Axial, Radial) OF Therm_cond
LA_C AS DISTRIBUTION(Axial, Radial) OF Therm_cond
LA_D AS DISTRIBUTION(Axial, Radial) OF Therm_cond
LA_E AS DISTRIBUTION(Axial, Radial) OF Therm_cond

# Density and velocity, kg/m^3; m/s

R0 AS DISTRIBUTION(Axial, Radial) OF Density
UL AS DISTRIBUTION(Axial, Radial) OF Velocity

# Conversions, averaged temperature

XI AS DISTRIBUTION(Axial) OF Conversion
TIM AS DISTRIBUTION(Axial) OF Temperature
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

BOUNDARY

# inlet conditions, x=0; z=0:1)

FOR x := 0 TO 1 DO
WA(0,x) - WAO;
WC(0,x) - WCO;
WD(0,x) - WDO;
WE(0,x) - WEO;
TETAl(0,x)-1;
UL(0,x) = 1.5*UL0*(1-x^2);
END

# OUTLET CONDITIONS
# AT z=1; x=0:1)

FOR x := 0 TO 1 DO
PARTIAL(WA(1,x), Axial) = 0;
PARTIAL(WC(1,x), Axial) = 0;
PARTIAL(WD(1,x), Axial) = 0;
PARTIAL(WE(1,x), Axial) = 0;
PARTIAL(UL(1,x), Axial) = 0;
PARTIAL(TETAl(1,x), Axial)=0;
END

# SYMMETRY CONDITIONS
# AT x=0 FOR ALL z=0:1)

FOR x := 0 TO 1 DO
PARTIAL(WA(s,0), Radial) = 0;
PARTIAL(WC(s,0), Radial) = 0;
PARTIAL(WD(s,0), Radial) = 0;
PARTIAL(WB(s,0), Radial) = 0;
PARTIAL(UL(s,0), Radial) = 0;
PARTIAL(TETAl(s,0), Radial) =0;
END

# REACTING WALL
# AT z=1 FOR ALL x
# equations for mass and energy balance are given in
reactor model

#------------------------------------------------------

B2-4
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

#--------------------------------------------------------
# non-slip condition at wall
#--------------------------------------------------------
FOR z := 0 TO 1 DO
  U1(s,1) = 0;
END

EQUATION

# MASS BALANCE

FOR z := 0 TO 1 DO
  FOR x := 0 TO 1 DO
    Ro1(z,x) = U1(z,x) \* \* PARTIAL(WA(z,x), Axial)
      + (L/R1) \^2 \* (PARTIAL(DA(z,x) \* Ro1(z,x) \* PARTIAL(WA(z,x), Radial), Radial));
    Ro1(z,x) = U1(z,x) \* \* (PARTIAL(WC(z,x), Axial)
      + (L/R1) \^2 \* (PARTIAL(DC(z,x) \* Ro1(z,x) \* PARTIAL(WC(z,x), Radial), Radial));
    Ro1(z,x) = U1(z,x) \* \^ PARTIAL(WD(z,x), Axial)
      + (L/R1) \^2 \* (PARTIAL(DD(z,x) \* Ro1(z,x) \* PARTIAL(WD(z,x), Radial), Radial));
    Ro1(z,x) = U1(z,x) \^ PARTIAL(WE(z,x), Axial)
      + (L/R1) \^2 \* (PARTIAL(DE(z,x) \* Ro1(z,x) \* PARTIAL(WE(z,x), Radial), Radial));
  
  \{WA(z,x) = WA0;
   WC(z,x) = WC0;
   WD(z,x) = WD0;
   WE(z,x) = WE0;\}
END

#--------------------------------------------------------
# Energy Balance
#--------------------------------------------------------
FOR z := 0 TO 1 DO
  FOR x := 0 TO 1 DO
    Ro1(z,x) = CP1(z,x) \* U1(z,x) \* \^ PARTIAL(TETAL(z,x), Axial)
      + (L/R1) \^2 \* (PARTIAL(TETAL(z,x), Radial), Radial));
  END
END

B2.5
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

$CONTINUITY EQUATION$

FOR z: 0 TO 1 DO
    FOR x: 0 TO 1 DO
        PARTIAL(Rol(z,x)*Ul(z,x), Axial) = 0
    END
END

$AUXILIARY EQUATIONS$

$Density variation with temperature and composition$

FOR z: 0 TO 1 DO
    FOR x: 0 TO 1 DO
        Rol(z,x) = 1E-3*(101325*Pl/Rg/Tl(z,x)) / (WA(z,x)/MA + WC(z,x)/MC + WD(z,x)/MD + WE(z,x)/ME)
    END
END

$molar fractions$

FOR z: 0 TO 1 DO
    FOR x: 0 TO 1 DO
        YA(z,x) = WA(z,x)/MA / (WA(z,x)/MA + WC(z,x)/MC + WD(z,x)/MD + WE(z,x)/ME)
        YC(z,x) = WC(z,x)/MC / (WA(z,x)/MA + WC(z,x)/MC + WD(z,x)/MD + WE(z,x)/ME)
        YD(z,x) = WD(z,x)/MD / (WA(z,x)/MA + WC(z,x)/MC + WD(z,x)/MD + WE(z,x)/ME)
        YE(z,x) = WE(z,x)/ME / (WA(z,x)/MA + WC(z,x)/MC + WD(z,x)/MD + WE(z,x)/ME)
    END
END

$concentrations$

FOR z: 0 TO 1 DO
    FOR x: 0 TO 1 DO
        CMA(z,x) = 101325*Pl*YA(z,x)/Rg/Tl(z,x)
        CMC(z,x) = 101325*Pl*YC(z,x)/Rg/Tl(z,x)
        CMD(z,x) = 101325*Pl*YD(z,x)/Rg/Tl(z,x)
        CME(z,x) = 101325*Pl*YE(z,x)/Rg/Tl(z,x)
    END
END
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

\[ \text{CME}(x_i) = 101325 + P_i \times T_A(x_i) / R_g / T_l(x_i) \]

END

#temperature

END

#heat capacity variation with temperature and composition

END

#thermal conductivities variation with temperature and composition

END

#DIFFUSION COEFFICIENTS variation with temperature

END

B2-7
# Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

```plaintext
# Model Combustion
PARAMETER

# Inlet mass fractions, pressure, temperature, velocity,
# --- molecular masses
# --- diffusion coefficients
# --- thermal conductivities at initial temperature
# --- heat capacity coefficients

MODEL Combustion
```

```plaintext
END # Model
```

```plaintext
# Conversion along the reactor axial coordinate
# Average temperature along reactor axial coordinate
```

```plaintext
END
```

```plaintext
FOR x:= 0 TO 1 DO
FOR x:= 0 TO 1 DO
DA(z,x)+DA+YETAI(z,x)*1.75 ;
DC(z,x)+DC+YETAI(z,x)*1.75 ;
DD(z,x)+DD+YETAI(z,x)*1.75 ;
DE(z,x)+DE+YETAI(z,x)*1.75 ;
END
END

# Average temperature along reactor axial coordinate
FOR z:= 0 TO 1 DO
XI(z)=1-INTEGRAL(x:0:1;Rol(z,x)*UI(z,x)*WA(z,x)) /
INTEGRAL(x:0:1;Rol(0,x)*UI(0,x)*WA(0,x)) ;
END
```
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

A_N, B_N, C_N, D_N AS REAL
A_S, B_S, C_S, D_S AS REAL
A_I2, B_I2, C_I2, D_I2 AS REAL

#CHANNEL DIMENSIONS
L, R2 AS REAL

#GAS CONSTANT
Rg AS REAL

DISTRIBUTION_DOMAIN
Axial AS (0 : 1)
Radial AS (0 : 1)

VARIABLE

#mass fractions
WB AS DISTRIBUTION(Axial, Radial) OF Methane_mass_fr
WM AS DISTRIBUTION(Axial, Radial) OF Oxygen_mass_fr
MN AS DISTRIBUTION(Axial, Radial) OF CO2_mass_fr
WS AS DISTRIBUTION(Axial, Radial) OF Water_mass_fr
W12 AS DISTRIBUTION(Axial, Radial) OF Nitrogen_mass_fr

#molar fractions
YB AS DISTRIBUTION(Axial, Radial) OF Methane_mol_fr
YM AS DISTRIBUTION(Axial, Radial) OF Oxygen_mol_fr
YN AS DISTRIBUTION(Axial, Radial) OF CO2_mol_fr
YS AS DISTRIBUTION(Axial, Radial) OF Water_mol_fr
YI2 AS DISTRIBUTION(Axial, Radial) OF Nitrogen_mol_fr

#concentrations calculated based on mass balance

CMB AS DISTRIBUTION(Axial, Radial) OF Methane_conc
CMN AS DISTRIBUTION(Axial, Radial) OF CO2_conc
CMS AS DISTRIBUTION(Axial, Radial) OF Water_conc

#Temperature and dimensionless temperature
T2 AS DISTRIBUTION(Axial, Radial) OF Temperature
TETA2 AS DISTRIBUTION(Axial, Radial) OF D_temp2

#Physical properties: diffusion coefficients, heat capacity, thermal conductivity

B2-9
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

DB AS DISTRIBUTION(Axial, Radial) OF
Diffusion_coefficient_b
DM AS DISTRIBUTION(Axial, Radial) OF
Diffusion_coefficient_m
DN AS DISTRIBUTION(Axial, Radial) OF
Diffusion_coefficient_n
DS AS DISTRIBUTION(Axial, Radial) OF
Diffusion_coefficient_s
CP B AS DISTRIBUTION(Axial, Radial) OF Heat_cap
CP M AS DISTRIBUTION(Axial, Radial) OF Heat_cap
CP_N AS DISTRIBUTION(Axial, Radial) OF Heat_cap
CP_S AS DISTRIBUTION(Axial, Radial) OF Heat_cap
CP_12 AS DISTRIBUTION(Axial, Radial) OF Heat_cap
CP2 AS DISTRIBUTION(Axial, Radial) OF Heat_cap
LA2 AS DISTRIBUTION(Axial, Radial) OF Therm_cond
LA_B AS DISTRIBUTION(Axial, Radial) OF Therm_cond
LA_M AS DISTRIBUTION(Axial, Radial) OF Therm_cond
LA_N AS DISTRIBUTION(Axial, Radial) OF Therm_cond
LA_S AS DISTRIBUTION(Axial, Radial) OF Therm_cond
LA_12 AS DISTRIBUTION(Axial, Radial) OF Therm_cond

# density and velocity
#--------------------------------------------------------
# Density and velocity
Ro2 AS DISTRIBUTION(Axial, Radial) OF Density
U2 AS DISTRIBUTION(Axial, Radial) OF Velocity
#--------------------------------------------------------
# Conversions
#--------------------------------------------------------
X2 AS DISTRIBUTION(Axial, Radial) OF Conversion

BOUNDARY

# INLET CONDITIONS
# AT x = 0, z = (0;1)
FOR x := 0 TO 1 DO
WB(0,x) = WBO;
WM(0,x) = WMO;
WB(0,x) = WBO;
WS(0,x) = WSO;
TETA2(0,x) = 1.5*U20*(1-x^2);
END

# OUTLET CONDITIONS
# AT x = 1 FOR z = (0;1)
FOR x := 0 TO 1 DO
PARTIAL(WB(1,x),Axial) = 0;
PARTIAL(WM(1,x), Axial) = 0;
B240
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

PARTIAL(WN(1,x), Axial) = 0;
PARTIAL(WS(1,x), Axial) = 0;
PARTIAL(U2(1,x), Axial) = 0;
PARTIAL(TETA2(1,x), Axial) = 0;
END

# SYMMETRY CONDITIONS
# AT r>0 FOR ALL z=[0;1]

FOR z := 0 TO 1 DO
  PARTIAL(WN(0,z), Radial) = 0;
  PARTIAL(WM(0,z), Radial) = 0;
  PARTIAL(U2(0,z), Radial) = 0;
  PARTIAL(TETA2(0,z), Radial) = 0;
END

# REACTING WALL
# AT r = 1 FOR z=[0;1]
# equations for mass and energy balance are given in reactor model

FOR z := 0 TO 1 DO
  U2(z,1) = 0;
END
EQUATION

$ MASS BALANCE$

FOR x := 0 TO 1 DO
  FOR x := 0 TO 1 DO
    Ro2(x,z)*U2(x,z)*L*PARTIAL(WB(x,z), Axial) =
    (PARTIAL(DB(x,z)*Ro2(x,z)*PARTIAL(WB(x,z), Axial), Axial) +
    ((L/R2)^2)*(PARTIAL(DB(x,z)*Ro2(x,z)*PARTIAL(WB(x,z), Radial), Radial)));
  END
END
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

\[ \text{Ro}_2(z,x) \times U_2(z,x) \times L \times \text{PARTIAL}(W_2(z,x), \text{Axial}) \]
\[ \text{PARTIAL}(D_2(z,x) \times \text{Ro}_2(z,x) \times \text{PARTIAL}(W_2(z,x), \text{Axial}), \text{Axial}) \]
\[ \text{PARTIAL}(D_2(z,x) \times \text{Ro}_2(z,x) \times \text{PARTIAL}(W_2(z,x), \text{Radial}), \text{Radial}) \]
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

FOR X :- 0 TO 1 DO
R o 2 (z,x) = 1E-3*(101325*P2/Rg/T2(z,x))/
(WB(z,x)/MB+WN(z,x)/MN+WS(z,x)/MN+ 
WS(z,x)/Mb+Wi2(z,x)/Mi2)
END
END

# molar fractions
FOR z :- 0 TO 1 DO
FOR x;« 0 TO 1 DO
YB(z,x) = WB(z,x)/MB/(WB(z,x)/MB+WM(z,x)/MM+WN(z,x)/MN+
WS(z,x)/MS+Wl2(z,x)/MI2)
YM(z,x) = WM(z,x)/MM/(WB(z,x)/MB+WM(z,x)/MM+WN(z,x)/MN+
WS(z,x)/MS+Wl2(z,x)/MI2)
YN(z,x) = WN(z,x)/MN/(WB(z,x)/MB+WM(z,x)/MM+WN(z,x)/MN+
WS(z,x)/MS+Wl2(z,x)/MI2)
YS(z,x) = WS(z,x)/MS/(WB(z,x)/MB+WM(z,x)/MM+WN(z,x)/MN+
WS(z,x)/MS+Wl2(z,x)/MI2)
YI2(z,x) = Wl2(z,x)/MI2/(WB(z,x)/MB+WM(z,x)/MM+WN(z,x)/MN+
WS(z,x)/MS+Wl2(z,x)/MI2)
END
END

# concentrations obtained from mass balance
FOR s :: 0 TO 1 DO
FOR x :: 0 TO 1 DO
CMB(z,x) = 101325*P2*YB(z,x)/Rg/T2(z,x)
CMW(z,x) = 101325*P2*YM(z,x)/Rg/T2(z,x)
CMN(z,x) = 101325*P2*YN(z,x)/Rg/T2(z,x)
CMS(z,x) = 101325*P2*YS(z,x)/Rg/T2(z,x)
END
END

# temperature
B243
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

FOR x:= 0 TO 1 DO
  T2(z,x)=T20*TA2(z,x) ;
END
END

#heat capacity variation with temperature and composition
FOR z:= 0 TO 1 DO
  FOR x:= 0 TO 1 DO
    CP_B(z,x)=1E3*(A_B+B_B*(T2(z,x)/1000)+
                      C_B*T2(z,x)/1000)+D_B*(T2(z,x)/1000)^3)/MB ;
    CP_M(z,x)=1E3*(A_M+B_M*(T2(z,x)/1000)+
                      C_M*T2(z,x)/1000)+D_M*(T2(z,x)/1000)^3)/MM ;
    CP_N(z,x)=1E3*(A_N+B_N*(T2(z,x)/1000)+
                      C_N*T2(z,x)/1000)+D_N*(T2(z,x)/1000)^3)/MN ;
    CP_S(z,x)=1E3*(A_S+B_S*(T2(z,x)/1000)+
                      C_S*T2(z,x)/1000)+D_S*(T2(z,x)/1000)^3)/MS ;
    CP_I2(z,x)=1E3*(A_I2+B_I2*(T2(z,x)/1000)+
                      C_I2*T2(z,x)/1000)+D_I2*(T2(z,x)/1000)^3)/MI2 ;
    CP2(z,x)=WB(z,x)*CP_B(z,x)+WM(z,x)*CP_M(z,x)+WN(z,x)*CP_N(z,x)+WI2(z,x)*CP_I2(z,x)+WS(z,x)*CP_S(z,x) ;
  END
END

#thermal conductivities variation with temperature and composition
FOR z:= 0 TO 1 DO
  FOR x:= 0 TO 1 DO
    LA_B(z,x)=LA_B0*TA2(z,x)^0.75 ;
    LA_M(z,x)=LA_M0*TA2(z,x)^0.75 ;
    LA_N(z,x)=LA_N0*TA2(z,x)^0.75 ;
    LA_S(z,x)=LA_S0*TA2(z,x)^0.75 ;
    LA_I2(z,x)=LA_I20*TA2(z,x)^0.75 ;
    LA2(z,x)=(WB(z,x)*LA_B(z,x)*MB*0.33+
               WM(z,x)*LA_M(z,x)*MM*0.33+
               WN(z,x)*LA_N(z,x)*MN*0.33+
               WS(z,x)*LA_S(z,x)*MS*0.33+
               WI2(z,x)*LA_I2(z,x)*MI2*0.33)/
               (WB(z,x)*MB*0.33+WM(z,x)*MM*0.33+
               WN(z,x)*MN*0.33+WS(z,x)*MS*0.33+
               WI2(z,x)*MI2*0.33) ;
  END
END

#DIFFUSION COEFFICIENTS variation with temperature
FOR x:= 0 TO 1 DO
END
END

END
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

```plaintext
$\\text{FOR } z := 0 \text{ TO } 1 \text{ DO}
  FOR x := 0 \text{ TO } 1 \text{ DO}
    \text{DB}(z,x) = DB0 \times \text{TETA}^2(z,x)^{1.75} \\
    \text{DM}(z,x) = DM0 \times \text{TETA}^2(z,x)^{1.75} \\
    \text{DS}(z,x) = DS0 \times \text{TETA}(z,x)^{1.75} \\
  END
END

$\\text{FOR } z := 0 \text{ TO } 1 \text{ DO}
  \text{TM2}(z) = \frac{\text{INTEGRAL}(x := 0 \text{ TO } 1; \text{Ro2}(z,x) \times \text{C2}(z,x) \times \text{U2}(z,x) \times \text{T2}(z,x))}{\text{INTEGRAL}(x := 0 \text{ TO } 1; \text{Ro2}(z,x) \times \text{U2}(z,x))} \\
  \text{X2}(z) = 1 - \frac{\text{INTEGRAL}(x := 0 \text{ TO } 1; \text{Ro2}(z,x) \times \text{U2}(z,x) \times \text{WB}(z,x))}{\text{INTEGRAL}(x := 0 \text{ TO } 1; \text{Ro2}(0,x) \times \text{U2}(0,x) \times \text{WB}(0,x))} \\
END
# Model

MODEL Comb_layer
# model of the catalyst layer in combustion channel

PARAMETER

$\\text{INLET MASS FRACTIONS, PRESSURE, TEMPERATURE, VELOCITY,}$

$\\text{Porosity, Tortuosity, Rp}$

$\\text{Thermal conductivity of the catalyst layer}$

$\\text{L, H_cat}$

$\\text{KINETIC PARAMETERS, HEAT OF REACTION}$

B245
```
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

KBO, EB, DNB AS REAL

#GAS CONSTANT

Rg AS REAL

DISTRIBUTION_DOMAIN
Axial AS (0:1)
Radial AS (0:1)

VARIABLE

#concentrations

CB AS DISTRIBUTION(Axial, Radial) OF Methane_conc
CM AS DISTRIBUTION(Axial, Radial) OF Oxygen_conc
CN AS DISTRIBUTION(Axial, Radial) OF CO2_conc
CS AS DISTRIBUTION(Axial, Radial) OF Water_conc

#Temperature

TL2 AS DISTRIBUTION(Axial, Radial) OF Temperature

#Physical properties: diffusion coefficients; effectiveness factor

DDB AS DISTRIBUTION(AXIAL) OF Diffusion_coefficient_b
DMM AS DISTRIBUTION(AXIAL) OF Diffusion_coefficient_m
DNN AS DISTRIBUTION(AXIAL) OF Diffusion_coefficient_n
DSS AS DISTRIBUTION(AXIAL) OF Diffusion_coefficient_s
Eff_factor_b AS DISTRIBUTION(AXIAL) OF Effect

#reaction rate

Reac_Rate2 AS DISTRIBUTION(Axial, Radial) OF Rate

DKB AS DISTRIBUTION(AXIAL) OF Knudsen_diff
DMH AS DISTRIBUTION(AXIAL) OF Knudsen_diff
DNH AS DISTRIBUTION(AXIAL) OF Knudsen_diff
DHS AS DISTRIBUTION(AXIAL) OF Knudsen_diff
FS AS DISTRIBUTION(AXIAL) OF Factor
FM AS DISTRIBUTION(AXIAL) OF Factor
FN AS DISTRIBUTION(AXIAL) OF Factor
FS AS DISTRIBUTION(AXIAL) OF Factor

TH_B AS DISTRIBUTION(AXIAL) OF Th

B246
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

\[ H_{fl\_gen} \text{ AS DISTRIBUTION(Axial) OF Heat\_flux} \]
\[ N_{reac\_2} \text{ AS DISTRIBUTION(Axial, Radial) OF N_{reac}} \]

BOUNDARY

# INLET CONDITIONS
# AT z = 0 FOR x=(0;1)

FOR x := 0 TO 1 DO
  PARTIAL(CB(0,x), Axial) = 0;
  PARTIAL(CM(0,x), Axial) = 0;
  PARTIAL(CN(0,x), Axial) = 0;
  PARTIAL(CS(0,x), Axial) = 0;
  PARTIAL(TL2(0,x), Axial) = 0;
END

# OUTLET CONDITIONS
# AT z = 1 FOR x=(0;1)

FOR x := 0 TO 1 DO
  PARTIAL(CB(1,x), Axial) = 0;
  PARTIAL(CM(1,x), Axial) = 0;
  PARTIAL(CN(1,x), Axial) = 0;
  PARTIAL(CS(1,x), Axial) = 0;
  PARTIAL(TL2(1,x), Axial) = 0;
END

# WALL CONDITIONS
# AT x=0 FOR z=(0;1)

# mass balance; no mass flux at wall

FOR s := 0 TO 1 DO
  PARTIAL(CB(s,0), Radial) = 0;
END
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

PARTIAL(CM(z,0), Radial) = 0;
PARTIAL(CN(z,0), Radial) = 0;
PARTIAL(CS(z,0), Radial) = 0;

# energy balance is given in reactor model

END

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
# Catalyst surface
# AT X = 1 FOR z = [0;1]
# are given in the reactor model
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

EQUATION

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
# MASS BALANCE and energy balance in the catalyst layer
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

FOR x: 0 TO 1 DO
FOR x: 0 TO 1 DO

Porosity*DBS(z)/Tortuosity*PARTIAL(CB(z,x), Radial, Radial) =
Reac_Rate2(z,x)*((H_cat/1000)^2);

Porosity*DMS(z)/Tortuosity*PARTIAL(CM(z,x), Radial, Radial) =
2*Reac_Rate2(z,x)*((H_cat/1000)^2);

Porosity*DSS(z)/Tortuosity*PARTIAL(CN(z,x), Radial, Radial) =
-2*Reac_Rate2(z,x)*((H_cat/1000)^2);

Porosity*DNS(z)/Tortuosity*PARTIAL(CS(z,x), Radial, Radial) =
-2*Reac_Rate2(z,x)*((H_cat/1000)^2);

-{ FB(z)*PARTIAL(CB(z,x), Radial, Radial) = Nreac_2(z,x) ;
  FM(z)*PARTIAL(CM(z,x), Radial, Radial) = Nreac_2(z,x) ;
  FN(z)*PARTIAL(CN(z,x), Radial, Radial) = Nreac_2(z,x) ;
  FS(z)*PARTIAL(CS(z,x), Radial, Radial) = Nreac_2(z,x) ;}

-LA_ef*PARTIAL(TL2(z,x), Radial, Radial) =
(H_cat/1000)^2*DH*Reac_Rate2(z,x);

END

END

#-----------------------------------------------------------------------------------
#Combustion reaction rate in mass balance
#-----------------------------------------------------------------------------------

FOR x: 0 TO 1 DO
FOR x: 0 TO 1 DO

Reac_Rate2(z,x) = KB0*EXP(-EB/Rg/TL2(z,x))*(CB(z,x)*1.E-4) ;
Nreac_2(z,x) = TH_B(z)*Reac_Rate2(z,x);

END

END

B248
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

FOR z=0 TO 1 DO
  Eff_factor_b(z)=Porosity*DBS(z)/Tortuosity*PARTIAL(CB(z,1), Radial)/ (Reac_rate2(z,1)* (H_cat/1000)^2)
  H_fl_gen(z) =Porosity*DBS(z)/Tortuosity*PARTIAL(CB(z,1), Radial)/ (H_cat/1000)*DHB
END

FOR z=0 TO 1 DO
  DBS(z)=97*Rp*(TL2(z,1)/16)^0.5
  DBM(z)=97*Rp*(TL2(z,1)/32)^0.5
  DBS(z)=97*Rp*(TL2(z,1)/44)^0.5
  DBS(z)=97*Rp*(TL2(z,1)/18)^0.5
END

FOR z=0 TO 1 DO
  FB(z)=1;
  FM(z)=DBS(z)/DBS(z);
  FN(z)=DBS(z)/DBS(z);
  FS(z)=DBS(z)/DBS(z);
  TH_B(z)=(Tortuosity/Porosity)*H_cat^2/1000/(1000*DBS(z));
END

END # Model

#---------------------------------------------------------------
MODEL Ref_layer
#model of catalyst layer in reforming channel
PARAMETER
# Catalyst properties,
# Porosity, Tortuosity, Rp, D AS REAL
#Thermal conductivity of the catalyst layer
#L_eff AS REAL
#Catalyst dimensions
#L, H_cat AS REAL
#KINETIC PARAMETERS, HEAT OF REACTION, equilibrium constant parameters
#KAO, E, D, H AS REAL
#KEO, EE AS REAL
#GAS CONSTANT
#R AS REAL

END
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

DISTRIBUTION_DOMAIN
Axial AS (0:1)
Radial AS (0:1)

VARIABLE

#concentrations calculated based on mass balance

CA AS DISTRIBUTION(Axial, Radial) OF Methane_conc
CC AS DISTRIBUTION(Axial, Radial) OF Water_conc
CD AS DISTRIBUTION(Axial, Radial) OF CO_conc
CE AS DISTRIBUTION(Axial, Radial) OF Hydrogen_conc
Rol AS DISTRIBUTION(Axial, Radial) OF Density

#Temperature and dimensionless temperature

TL1 AS DISTRIBUTION(Axial, Radial) OF Temperature

#Physical properties: diffusion coefficients, heat capacity, thermal conductivity

DAS AS DISTRIBUTION(AXIAL) OF Diffusion_coefficient_b
DCS AS DISTRIBUTION(AXIAL) OF Diffusion_coefficient_m
DDS AS DISTRIBUTION(AXIAL) OF Diffusion_coefficient_n
DES AS DISTRIBUTION(AXIAL) OF Diffusion_coefficient_s
Eff_factor_a AS DISTRIBUTION(AXIAL) OF Effect

#reaction rate

Reac_Ratel AS DISTRIBUTION(Axial, Radial) OF Rate
KE AS DISTRIBUTION(Axial, Radial) OF Rate

#Knudsen diffusivities

DKA AS DISTRIBUTION(Axial) OF Knudsen_diff
DKC AS DISTRIBUTION(Axial) OF Knudsen_diff
DKD AS DISTRIBUTION(Axial) OF Knudsen_diff
DKE AS DISTRIBUTION(Axial) OF Knudsen_diff
FA AS DISTRIBUTION(Axial) OF Factor
FC AS DISTRIBUTION(Axial) OF Factor
FD AS DISTRIBUTION(Axial) OF Factor
FE AS DISTRIBUTION(Axial) OF Factor
TH_A AS DISTRIBUTION(Axial) OF Th
N_cl_con AS DISTRIBUTION(Axial) OF Heat_flux

B220
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

**BOUNDARY**

`--- AS DISTRIBUTION(Axial, Radial) OF Nrec ---`  
Nrec I

**INLET CONDITIONS**  
# AT z =0 FOR x=(0;1)

FOR x := 0 TO 1  DO
  PARTIAL(CA(0,x),Axial) = 0;
  PARTIAL(CC(0,x),Axial) = 0;
  PARTIAL(CD(0,x),Axial) = 0;
  PARTIAL(CE(0,x),Axial) = 0;
  #TL1(0,x)=1000;
END

**OUTLET CONDITIONS**  
# AT z =1 FOR x=(0;1)

**mass balance**

FOR x := 0 TO 1  DO
  PARTIAL(CA(1,x),Axial) = 0;
  PARTIAL(CC(1,x),Axial) = 0;
  PARTIAL(CD(1,x),Axial) = 0;
  PARTIAL(CE(1,x),Axial) = 0;
END

**WALL CONDITIONS**  
# AT x=0 FOR ALL z

FOR z := 0 TO 1  DO
  PARTIAL(CA(z,0),Radial) = 0;
  PARTIAL(CC(z,0),Radial) = 0;
  PARTIAL(CD(z,0),Radial) = 0;
  PARTIAL(CE(z,0),Radial) = 0;
  # for energy balance in reactor model
END
Steam Reforming-Methane Combustion Coupling (simplified kinetics); gPROMS Code

#==============================================
# Catalyst surface
# AT x = 1 FOR ALL z
# are given in the reactor model
#===============================================

#==============================================
# MASS BALANCE and energy balance in the catalyst layer
#===============================================

FOR z:=0 TO 1 DO
FOR x:=0 TO 1 DO
Rol(z,x)=1e-3*(101325*P1/8.314/TL1(z,x))/
(CA(z,x)/16+CC(z,x)/16+CD(z,x)/28+CE(z,x)/2)
END
END

FOR z:=0 TO 1 DO
FOR x:=0 TO 1 DO
Porosity*DAS(z)/Tortuosity*PARTIAL(CA(z,x), Radial,Radial)=
Reac_Rate1(z,x)*((H_cat/1000)^2); 
Porosity*CH4(z)/Tortuosity*PARTIAL(CU(z,x), Radial,Radial)=
Reac_Rate1(z,x)*((H_cat/1000)^2); 
Porosity*DS(z)/Tortuosity*PARTIAL(CD(z,x), Radial,Radial)=
-Reac_Rate1(z,x)*((H_cat/1000)^2); 
Porosity*DE(z)/Tortuosity*PARTIAL(CE(z,x), Radial,Radial)=
-3*Reac_Rate1(z,x)*((H_cat/1000)^2); 
-LAef*PARTIAL(TL1(z,x), Radial,Radial)=((H_cat/1000)^2)*
DHA*Reac_Rate1(z,x);
END
END

FOR z:=0 TO 1 DO
FOR x:=0 TO 1 DO
Reac_Rate1(z,x)=KA0*8.314*TL1(z,x)*
EXP(-EA/Rg/TL1(z,x))*
(CA(z,x)-CD(z,x)*CE(z,x)/3/KE(z,x)/(CC(z,x)+1e-5));
KE(z,x)=exp(KEQ-EE/TL1(z,x))*(101325*P1/Rg/TL1(z,x))^2;
Nreac_1(z,x)=TH_A(z)*Reac_Rate1(z,x);
END
END

FOR z:=0 TO 1 DO
Eff_factor_a(z)=Porosity*DAS(z)/Tortuosity*PARTIAL(CA(z,1),
Radial)/
(Reac_Rate1(z,1)*((H_cat/1000)^2));
H_fl_cons(z)=Porosity*DAS(z)/Tortuosity*PARTIAL(CA(z,1),
Radial)/
((H_cat/1000)*DHA);
END

B22
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

FOR z: 0 TO 1 DO
  DK_A(z) = 97*Rp*(TL1(z,1)/16)^0.5 ;
  DK_C(z) = 97*Rp*(TL1(z,1)/16)^0.5 ;
  DK_D(z) = 97*Rp*(TL1(z,1)/28)^0.5 ;
  DK_E(z) = 97*Rp*(TL1(z,1)/2)^0.5 ;
END

FOR z: 0 TO 1 DO
  PA(z) = 1;
  FC(z) = DCs(z)/DAS(z);
  FD(z) = DES(z)/DAS(z);
  FE(z) = DES(z)/DAS(z);
  TH_A(z) = (Tortuosity/Porosity)*%cat.2/1000/
             ((1000*DAS(z)));
END

END # Model

MODEL Solid

PARAMETER

# Wall thickness over length, inlet temperature
RW, TSO, L AS REAL

# Wall thermal conductivity at initial cond.

LASS AS REAL
DISTRIBUTION_DOMAIN
Axial AS (0 : 1)
Radial AS (0 : 1)

VARIABLE

TETAS AS DISTRIBUTION (Axial, Radial) OF Dtempl
TS AS DISTRIBUTION (Axial, Radial) OF Temperature
LASS AS DISTRIBUTION (Axial, Radial) OF Cond_solid

BOUNDARY

# Boundary conditions at the ends
# At z = 0 and z = 1 all x except 0 and 1

FOR x: 0 TO 1 DO
  PARTIAL(TETAS(0, x), Axial) = 0 ;
  TETAS(0, x) = 1;
  PARTIAL(TETAS(1, x), Axial) = 0 ;
END

EQUATION

H223
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

# Heat equation LAPLACE

FOR z := 0+ TO 1- DO
  FOR x := 0+ TO 1- DO
    \[(1/L^2) \times \text{PARTIAL} (\Theta_z(z, x), \text{Axial, Axial}) \]
    \[+ (1/RW^2) \times \text{PARTIAL} (\Theta_z(z, x), \text{Radial, Radial}) = 0 ;\]
  END
END

# Auxiliary equations

# Temperature

FOR z := 0 TO 1 DO
  FOR x := 0 TO 1 DO
    T_S(z, x) = T_S0 + \Theta_z(z, x) ;
  END
END

# Solid thermal conductivity

FOR z := 0 TO 1 DO
  FOR x := 0 TO 1 DO
    L_A_s(z, x) = L_A_s0 + \Theta_z(z, x) \times 0.75 ;
  END
END

END # model solid

MODEL Reactor

UNIT

SA AS Reforming
SB AS Combustion
SS AS Solid
SL1 AS Ref_layer
SL2 AS Comb_layer

SET

WITHIN SA DO
  Axial := [RFIM, 2, 20] ;
  Radial := [OCFEM, 3, 3] ;
END

WITHIN SS DO
  Axial := [RFIM, 2, 20] ;
  Radial := [OCFEM, 3, 3] ;
END

WITHIN SS DO

END
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

Axial := [BFDM, 2, 20];
Radial := [OCFEM, 3, 3];
END

WITHIN SL1 DO
Axial := [BFDM, 2, 20];
Radial := [OCFEM, 3, 3];
END

WITHIN SL2 DO
Axial := [BFDM, 2, 20];
Radial := [OCFEM, 3, 3];
END

EQUATION
#-------------------------------------
FOR z := 0 TO 1- DO
#-------------------------------------
# energy balance at the surface of catalyst layer in
# reforming channel
#-------------------------------------
SA.LAl(z,1)\cdot PARTIAL(SA.Tl(z,1) , SA.Radial)*SL1.H_cat/SA.R1/1000-
-SL1.LA Ef*PARTIAL(SL1.TLl(z,1),SL1.Radial);
SA.Tl(z,1)\equiv SL1.TLl(z,1);
#-------------------------------------
# mass balance at the surface of catalyst layer in
# reforming channel
#-------------------------------------
SA.R01(z,1)*SA.DA(z,1) \cdot PARTIAL(SA.WA(z,1), SA.Radial)*SL1.H_cat/SA.R1/SA.MA-
-SL1.Porosity/SL1.Tortuosity*SL1.DAS(z) \cdot PARTIAL(SL1.CA(z,1), SL1.Radial);
1000*SA.R01(z,1)*SA.WA(z,1)/SA.MA=SL1.CA(z,1);
SA.R01(z,1)*SA.DC(z,1) \cdot PARTIAL(SA.WC(z,1), SA.Radial)*SL1.H_cat/SA.R1/SA.MC-
-SL1.Porosity/SL1.Tortuosity*SL1.DCS(z) \cdot PARTIAL(SL1.CC(z,1), SL1.Radial);
1000*SA.R01(z,1)*SA.WC(z,1)/SA.MC=SL1.CC(z,1);
SA.R01(z,1)*SA.DD(z,1) \cdot PARTIAL(SA.WD(z,1), SA.Radial)*SL1.H_cat/SA.R1/SA.MD-
-SL1.Porosity/SL1.Tortuosity*SL1.DDS(z) \cdot PARTIAL(SL1.CD(z,1), SL1.Radial);
1000*SA.R01(z,1)*SA.WD(z,1)/SA.MD=SL1.CD(z,1);
SA.R01(z,1)*SA.DE(z,1) \cdot PARTIAL(SA.WE(z,1), SA.Radial)*SL1.H_cat/SA.R1/SA.ME-
-SL1.Porosity/SL1.Tortuosity*SL1.DES(z) \cdot PARTIAL(SL1.CE(z,1), SL1.Radial);
1000*SA.R01(z,1)*SA.WE(z,1)/SA.ME=SL1.CE(z,1);
B225
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

# energy balance at the interface of catalyst layer in reforming channel and metallic wall

SL1.LA_ef*PARTIAL(SL1.TL1(z,0), SL1.Radial) =
- PARTIAL(SS.TS(z,0), SS.Radial)*SS.LAS(z,0)*SL1.N_cat/SS.RW/1000 ;

SS.TS(z,0) = SL1.TL1(z,0) ;

# energy balance at the surface of catalyst layer in combustion channel

SB.LA2(z,1)*PARTIAL(SB.T2(z,1), SB.Radial)*SL2.H_cat/ SB.R2/1000 -
SL2.LA_ef*PARTIAL(SL2.TL2(z,1), SL2.Radial);

SB.T2(z,1) = SL2.TL2(z,1) ;

# mass balance at the surface of catalyst layer in combustion channel

SB.DB(Z,1)*PARTIAL(SB.CMB(Z,1), SB.Radial)*SL2.H_cat/ SB.R2/1000 -
SL2.Porosity/SL2.Tortuosity*SL2.DBS(z)*PARTIAL(SL2.CM(z,1), SL2.Radial),

SB.CMB(Z,1) = SL2.CM(Z,1) ;

SB.DM(Z,1)*PARTIAL(SB.CMM(Z,1), SB.Radial)*SL2.H_cat/ SB.R2/1000 -

SB.CMM(Z,1) = SL2.CM(Z,1) ;

SB.DN(Z,1)*PARTIAL(SB.CMN(Z,1), SB.Radial)*SL2.H_cat/ SB.R2/1000 -

SB.CMN(Z,1) = SL2.CM(Z,1) ;

SB.DS(Z,1)*PARTIAL(SB.CMS(Z,1), SB.Radial)*SL2.H_cat/ SB.R2/1000 -

SB.CMS(Z,1) = SL2.CM(Z,1) ;

# energy balance at the interface of catalyst layer in combustion channel and metallic wall

SL2.LA_ef*PARTIAL(SL2.TL2(z,0), SL2.Radial) =
- PARTIAL(SS.TS(z,1), SS.Radial)*SS.LAS(z,1)*SL2.N_cat/SS.RW/1000 ;

SS.TS(z,1) = SL2.TL2(z,0) ;

END

FOR z := 0 TO 1 DO

SL1.DAS(z) = SA.DA(Z,1)*SL1.DKA(Z)/ (SA.DA(Z,1)+SL1.DKA(Z)) ;

SL1.DCS(z) = SA.DC(Z,1)*SL1.DKC(Z)/ (SA.DC(Z,1)+SL1.DKC(Z)) ;

SL1.DDS(z) = SA.DD(Z,1)*SL1.DKD(Z)/ (SA.DD(Z,1)+SL1.DKD(Z)) ;

SL1.DES(z) = SA.DE(Z,1)*SL1.DKE(Z)/ (SA.DE(Z,1)+SL1.DKE(Z)) ;

SL2.DBS(z) = SB.DB(Z,1)*SL2.DKB(Z)/ (SB.DB(Z,1)+SL2.DKB(Z)) ;

SL2.DMS(z) = SB.DM(Z,1)*SL2.DKM(Z)/ (SB.DM(Z,1)+SL2.DKM(Z)) ;

SL2.DNS(z) = SB.DN(Z,1)*SL2.DKN(Z)/ (SB.DN(Z,1)+SL2.DKN(Z)) ;

SL2.DSS(z) = SB.DS(Z,1)*SL2.DKS(Z)/ (SB.DS(Z,1)+SL2.DKS(Z)) ;

END

END # model reactor

B226
Steam Reforming-Methane Combustion Coupling (simplified kinetics); gPROMS Code

                        #*****************************************************************************

PROCESS cat_r05
UNIT
WITHIN SK DO
WITHIN SA DO

  WA0 :=0.229 ;
  WC0 :=0.771 ;
  WDO :=0 ;
  WEO :=0 ;
  P1 :=1.0656 ;
  T10 :=1.000 ;
  UD :=3.982 ;

  MA :=16 ;
  NC :=18 ;
  ND :=28 ;
  MEO :=2 ;

  DA0 :=2.05E-4 ;
  DCO :=2.51E-4 ;
  DDO :=1.98E-4 ;
  DB0 :=6.75E-4 ;

  LA_A0 :=0.139 ;
  LA_CO :=0.073 ;
  LA_DO :=0.0602 ;
  LA_E0 :=0.4205 ;

  A_A :=19.86 ;
  B_A :=50.16 ;
  C_A :=12.67 ;
  D_A :=-10.99 ;

  A_C :=32.19 ;
  B_C :=1.92 ;
  C_C :=10.54 ;
  D_C :=-3.589 ;

  A_D :=28.11 ;
  B_D :=1.672 ;
  C_D :=0.363 ;
  D_D :=-2.218 ;

  A_E :=29.06 ;
  B_E :=1.913 ;
  C_E :=0.60 ;
  D_E :=-0.869 ;

  L :=0.3 ;
  R1 :=0.001 ;

  Rg :=8.316 ;

END
WITHIN SB DO

WBG :=0.0526 ;
WBO :=0.2205 ;
WBO :=0 ;
WDO :=0 ;

R227
Steam Reforming-Methane Combustion Coupling (simplified kinetics): gPROMS Code

\[
P_2 = 1.0856; \\
T_{20} = 1000; \\
U_{20} = 2.695; \\
M = 1; \\
M_1 = 32; \\
M_2 = 44; \\
M_3 = 38; \\
M_4 = 28; \\
M_{BO} = 1.75 \times 10^{-4}; \\
M_{BO} = 1.36 \times 10^{-4}; \\
M_6 = 2.09 \times 10^{-4}; \\
LA_{BO} = 0.139; \\
LA_{NO} = 0.072; \\
LA_{NO} = 0.057; \\
LA_{NO} = 0.073; \\
LA_{NO} = 0.067; \\
A_B = 19.86; \\
B_B = 55.16; \\
C_B = 12.67; \\
D_B = -10.99; \\
A_M = 25.44; \\
B_M = 15.18; \\
C_M = -7.144; \\
D_M = 1.310; \\
A_N = 22.22; \\
B_N = 59.72; \\
C_N = 34.95; \\
D_N = 7.457; \\
A_S = 32.19; \\
B_S = 1.920; \\
C_S = 10.54; \\
D_S = -3.589; \\
A_{I2} = 28.85; \\
B_{I2} = 1.569; \\
C_{I2} = 8.067; \\
D_{I2} = 2.868; \\
L = 0.3; \\
R_2 = 0.001; \\
R_g = 8.316; \\
END
\]

WITHIN SS DO

\[
M = 0.0005; \\
L_{ASO} = 25; \\
T_{20} = 1000; \\
L = 0.3; \\
END
\]

WITHIN SL2 DO

\[
M_{cat} = 20 \times 10^{-3}; \\
Porosity = 0.4; \\
Tortuosity = 4; \\
R_p = 100 \times 10^{-9}; \\
B228
\]
Steam Reforming-Methane Combustion Coupling (simplified kinetics); gPROMS Code

\[ \begin{align*}
L &= 0.3; \\
K_{B0} &= 0.822E8; \quad \text{# in m/s} \\
\text{mol/(m}^3\text{cat)/s/(mol/m}^3\text{)=1/s} \\
E_B &= 90000; \\
DHB &= 80323; \\
Rg &= 8.316; \\
LA_{ef} &= 0.4; \\
\text{END}
\end{align*} \]

\[ \text{WITHIN SLL DO} \]

\[ \begin{align*}
P_{1} &= 1.085; \\
R_{\text{cat}} &= 203-3; \quad \text{# in mm, all the other} \\
\text{lengths are in m!!!!!} \\
\text{Porosity} &= 0.4; \\
\text{Tortuosity} &= 4; \\
\text{Ep} &= 100-9; \\
L &= 0.3; \\
\text{KAO} &= 2.22E2; \quad \text{# in mol/(m}^3\text{cat)/s/Pa} \\
\text{EA} &= 53326; \\
\text{DHA} &= 20533; \\
Rg &= 8.316; \\
LA_{ef} &= 0.4; \\
\text{KEO} &= 30.256; \\
\text{KE} &= 27010; \\
\text{END}
\end{align*} \]

\[ \text{PRESEN} \]

\[ \text{RESTORE "cat_45"} \]

\[ \text{SOLUTIONPARAMETERS} \]

\[ \begin{align*}
\text{OutputLevel} &= 2; \\
\text{gRMS} &= \text{ON}; \\
\text{gPLOT} &= \text{ON}; \\
\text{MaxInitIterations} &= 1000; \\
\text{BLOCKDECOMPOSITION} &= \text{ON}; \\
\text{SCHEDULE} \]

\[ \text{SAVE "cat_46"} \]

B29
Appendix C1

PSA One-dimensional Approach gPROMS Code
DECLARE

TYPE

Conversion = 0.8 ; 0 ; 1E20
Temperature = 0.8 ; -1E20 ; 1E20
Sensitivity = 0.0 ; -1E20 ; 1E20

END # Declare section

MODEL XSensitivity

PARAMETER

K, V, BA, BB, G, Ro AS REAL

DISTRIBUTION_DOMAIN

Axial AS (0 : 1)

VARIABLE

XA AS DISTRIBUTION(AXIAL) OF Conversion
TETA AS DISTRIBUTION(AXIAL) OF Temperature
SXG AS DISTRIBUTION(AXIAL) OF Sensitivity
STG AS DISTRIBUTION(AXIAL) OF Sensitivity
SXK AS DISTRIBUTION(AXIAL) OF Sensitivity
STK AS DISTRIBUTION(AXIAL) OF Sensitivity
STV AS DISTRIBUTION(AXIAL) OF Sensitivity
STV AS DISTRIBUTION(AXIAL) OF Sensitivity
STBA AS DISTRIBUTION(AXIAL) OF Sensitivity
STBA AS DISTRIBUTION(AXIAL) OF Sensitivity
STBB AS DISTRIBUTION(AXIAL) OF Sensitivity
STBB AS DISTRIBUTION(AXIAL) OF Sensitivity
STTO AS DISTRIBUTION(AXIAL) OF Sensitivity
STTO AS DISTRIBUTION(AXIAL) OF Sensitivity
NSTG AS DISTRIBUTION(AXIAL) OF Sensitivity
NSTK AS DISTRIBUTION(AXIAL) OF Sensitivity
NSTV AS DISTRIBUTION(AXIAL) OF Sensitivity
NSTV AS DISTRIBUTION(AXIAL) OF Sensitivity
NSTBA AS DISTRIBUTION(AXIAL) OF Sensitivity
NSTBA AS DISTRIBUTION(AXIAL) OF Sensitivity
NSTBB AS DISTRIBUTION(AXIAL) OF Sensitivity
NSTBB AS DISTRIBUTION(AXIAL) OF Sensitivity
NSTTO AS DISTRIBUTION(AXIAL) OF Sensitivity
NSTTO AS DISTRIBUTION(AXIAL) OF Sensitivity

BOUNDARY

# inlet conditions

XA(0) = 0 ;
TETA(0) = 1 ;
SXG(0) = 0 ;
STG(0) = 0 ;
SXK(0) = 0 ;
STK(0) = 0 ;
STV(0) = 0 ;
STV(0) = 0 ;
STBA(0) = 0 ;
STBA(0) = 0 ;
STBB(0) = 0 ;
STBB(0) = 0 ;
STTO(0) = 0 ;
STTO(0) = 0 ;
PARTIAL(XA(1),Axial) = 0 ;
PARTIAL(TETA(1),Axial) = 0 ;
PARTIAL(SXG(1),Axial) = 0 ;
PARTIAL(STG(1),Axial) = 0 ;
PARTIAL(SXK(1),Axial) = 0 ;
PARTIAL(STK(1),Axial) = 0 ;
PARTIAL(STV(1),Axial) = 0 ;
PARTIAL(STV(1),Axial) = 0 ;
PARTIAL(STTO(1),Axial) = 0 ;
EQUATION

FOR Z := 0 TO 1 DO

PARTIAL [XXA(Z), Axial] = 0;
PARTIAL [XXB(Z), Axial] = 0;
PARTIAL [XXS(Z), Axial] = 0;
PARTIAL [XXT(Z), Axial] = 0;
END # for section

FOR Z := 0 TO 1 DO

N S T G (Z) = N S T G (Z) * G / T E T A (Z);
N S T K (Z) = N S T K (Z) * K / T E T A (Z);
N S T V (Z) = N S T V (Z) * V / T E T A (Z);
N S T B (Z) = N S T B (Z) * B A / T E T A (Z);
N S T T (Z) = N S T T (Z) * T E T A (0) / T E T A (Z);
END # for

END # Model XSensitivity

PROCESS First2

UNIT XSensitivity WITHIN SK DO

Axial := [BFDM. 2. 500];
Ro := 1.5937;
K := 0.1189;
V := 1.411;
BA := -0.516;
BB := 0.7359;

END
G := 4.810

END # within section

PRESET
RESTORE "tamponl1"

SOLUTIONPARAMETERS

OutputLevel := 2
grSS := ON
gPLOT := ON
Maxinititerations := 2000

SCHEDULE

SAVE "tamponl3"

END # Process First
Appendix C2

PSA Two-dimensional Approach gPROMS Code
#This program calculates sensitivities related to
#the pre-exponential factor in the endothermic channel
#for a CPR using a 2-D model, using first kinetics
#for both endothermic and exothermic reactions

DECLARE

TYPE
Endo_con  = 0.1 : 0  : 1E5
Exo_con   = 0.1 : 0  : 1E5
Dim_temp  = 0.5 : 0  : 1E5
Conc_sens = 1  : -1E20 : 1E20
Temp_sens = 1  : -1E20 : 1E20
Conv      = 0.5  : 0  : 1E20

END

MODEL Endo

PARAMETER

Gas physico-chemical properties
#density, heat capacity, diffusivity, thermal conductivity

r1, cpl, D1, k1 AS REAL

Channel dimensions, inlet velocity
#length, channel height
L, R1, U10 AS REAL

Kinetics parameters, heat of reaction
#pre-exponential factor, activation energy
A1, E1, DH1 AS REAL

Inlet temperature and concentration
C10, T10 AS REAL

C2-1
PSA Two-dimensional Approach gPROMS Code

# Other constants
# Universal gas constant
#-----------------------------
Rg AS REAL

DISTRIBUTION_DOMAIN
Axial AS ( 0 : 1)
Radial AS ( 0 : 1)

VARIABLE
#------------------------------------------
# Dimensionless Concentration
#-----------------------------
Cl AS DISTRIBUTION(Axial, Radial) OF Endo_con

#------------------------------------------
# Dimensionless Temperature
#-----------------------------
TETA1 AS DISTRIBUTION(Axial, Radial) OF Dim_temp

#------------------------------------------
# Conversion of endothermic reaction
#------------------------------------------
XI AS DISTRIBUTION(Axial) OF Conv

#------------------------------------------
# Sensitivities
#------------------------------------------
SClAl AS DISTRIBUTION(Axial, Radial) OF Conc_sens
STIAl AS DISTRIBUTION(Axial, Radial) OF Conc_sens
NSTIAl AS DISTRIBUTION(Axial, Radial) OF Conc_sens
NXIAl AS DISTRIBUTION(Axial) OF Conc_sens

BOUNDARY
#------------------------------------------
# INLET Conditions
# $ at x=0 for all x
#------------------------------------------
FOR x :=0 TO 1 - DO
   Cl(0,x) = 1;
   TETA1(0,x) = 1;
   SClAl(0,x) = 0;

C1=1
PSA Two-dimensional Approach gPROMS Code

END

#===============================================
#Outlet Conditions
# at z=1 for all x
#===============================================

FOR X :=0|+ TO 1| - DO
    PARTIAL(CT1(X), Axial)=0;
    PARTIAL(TEMP1(X), Axial)=0;
    PARTIAL(SC1(X), Axial)=0;
    PARTIAL(ST1(X), Axial)=0;
END

#===============================================
#Symmetry conditions
# at x=0, all z
#===============================================

FOR Z :=0 TO 1 DO
    PARTIAL(CKZ, 0), Radial)=0;
    PARTIAL(TETAL(Z, 0), Radial)=0;
    PARTIAL(SC1(Z, 0), Radial)=0;
    PARTIAL(ST1(Z, 0), Radial)=0;
END

#===============================================
#reacting wall
# x=1, all z
#===============================================

# MASS BALANCE, sensitivity

FOR Z :=0 TO 1 DO
    PARTIAL(CT1(Z, 1), Radial)=E1*A1/CT1;
    EXP(-E1/Rg/TT1/TEMP1(Z, 1)))*CT1(Z, 1);
    PARTIAL(SC1(Z, 1), Radial)+PARTIAL(CT1(Z, 1), Radial)*
    (E1/Rg/TT1/TEMP1(Z, 1)))*ST1(Z, 1)+SC1(Z, 1)/CT1(Z, 1)+1/A1;
END

EQUATION

C2-3
# Molar Balance

```g PROMS
FOR z := 0 TO 1 - DO
  FOR x := 0 TO 1 - DO
    1.5*(1-x^2)*PARTIAL(C1(z,x), Axial) + Dl/UlO/L*
      ((L/R1)^2*PARTIAL(C1(z,x), Radial, Radial) +
       PARTIAL(C1(z,x), Axial, Axial));
  END
END

FOR z := 0 TO 1 - DO
  FOR x := 0 TO 1 - DO
    1.5*(1-x^2)*PARTIAL(SC1A1(z,x), Axial) + Dl/UlO/L*
      ((L/R1)^2*PARTIAL(SC1A1(z,x), Radial, Radial) +
       PARTIAL(SC1A1(z,x), Axial, Axial));
  END
END
```

# Energy Balance

```g PROMS
FOR z := 0 TO 1 - DO
  FOR x := 0 TO 1 - DO
    1.5*(1-x^2)*PARTIAL(TETA1(z,x), Axial) + Kl/(rOl*U10*cpl)/L*
      ((L/R1)^2*PARTIAL(TETA1(z,x), Radial, Radial) +
       PARTIAL(TETA1(z,x), Axial, Axial));
  END
END

FOR z := 0 TO 1 - DO
  FOR x := 0 TO 1 - DO
    1.5*(1-x^2)*PARTIAL(STIA1(z,x), Axial) + Kl/(rOl*U10*cpl)/L*
      ((L/R1)^2*PARTIAL(STIA1(z,x), Radial, Radial) +
       PARTIAL(STIA1(z,x), Axial, Axial));
  END
END
```

# Conversion

```g PROMS
FOR z := 0 TO 1 DO
  XI(z) = INTEGRAL(x := 0; 1.5*(1-x^2)*(1-C1(z,x)));
  SX1Al(z) = 1.5*INTEGRAL(x := 0; 1-x^2)*SC1A1(z,x));

C2 - 4
```
PARAMETER
#Gas physico-chemical properties
#density, heat capacity, diffusivity, thermal conductivity
ro2, cp2, D2, k2 AS REAL

#channel dimensions, INLET VELOCITY
# length, channel height
L, R2, U20 AS REAL

#Kinetics parameters, HEAT OF REACTION
#pre-exponential factor, activation energy
A2, E2, DH2 AS REAL

#INLET TEMPERATURE AND CONCENTRATION
C20, T20 AS REAL

#other constants
#universal gas constant
Rg AS REAL

DISTRIBUTION_DOMAIN
Axial AS [ 0 : 1 ]
Radial AS [ 0 : 1 ]

VARIABLE
#DIMENSIONLESS CONCENTRATION

PSA Two-dimensional Approach gPROMS Code

C2 AS DISTRIBUTION(Axial, Radial) OF Endo_con

#***************************************************************
#DIMENSIONLESS temperature
#***************************************************************

TEMP AS DISTRIBUTION(Axial, Radial) OF Dim_temp

#***************************************************************
#conversion of endothermic reaction
#***************************************************************

X2 AS DISTRIBUTION(Axial) OF Conv

#***************************************************************
#sensitivities
#***************************************************************

SC1A1 AS DISTRIBUTION(Axial, Radial) OF Conc_sen8
ST1A1 AS DISTRIBUTION(Axial, Radial) OF Conc_sens
SX1A1 AS DISTRIBUTION(Axial) OF Conc_sens
NSX1A1 AS DISTRIBUTION(Axial) OF Conc_sens

BOUNDARY
#***************************************************************
#INLET Conditions
$ at x=0 for all x
#***************************************************************

FOR X :=0]+ TO 1]- DO
  C2(0,x)=1;
  TEMP(0,x)=1;
  SC1A1(0,x)=0;
  ST1A1(0,x)=0;
END

#***************************************************************
#Outlet Conditions
$ at x=1 for all x
#***************************************************************

FOR X :=0]+ TO 1]- DO
  PARTIAL(C2(1,x), Axial)=0;
  PARTIAL(TEMP(1,x), Axial)=0;
END
PSA Two-dimensional Approach gPROMS Code

PARTIAL(SC2A1(1,x), Axial)=0;
PARTIAL(ST2A1(1,x), Axial)=0;

END

# Symmetry conditions
# at x=0, all z
#------------------------------------------------------
FOR z := 0 TO 1 DO
    PARTIAL(C2(Z,0), Radial)=0;
    PARTIAL(TETA2(z,0), Radial)=0;
    PARTIAL(SC2A1(z,0), Radial)=0;
    PARTIAL(ST2A1(z,0), Radial)=0;
END

# Reacting wall
# x=1, all z
#------------------------------------------------------
# Mass Balance
FOR z := 0 TO 1 DO
    PARTIAL(C2(z,1), Radial)=R2*A2/D2*EXP(-E2/Rg/T20/TETA2(z,1))*C2(z,1);
    PARTIAL(SC2A1(Z,1), Radial)=PARTIAL(C2(z,1), Radial)*
        (E2/Rg/T20/TETA2(z,1)^2*ST2A1(z,1)+SC2A1(z,1)/C2(z,1));
END

EQUATION

# Molar Balance
#------------------------------------------------------
FOR z := 0 TO 1 DO
    FOR x := 0 TO 1 DO
        1.5*(1-x^2)*PARTIAL(C2(z,x), Axial)=D2/U20/L*
            ((L/R2)^2*PARTIAL(C2(z,x), Radial, Radial)+
            PARTIAL(C2(z,x), Axial, Axial));
    1.5*(1-x^2)*PARTIAL(SC2A1(z,x), Axial)=D2/U20/L*
        ((L/R2)^2*PARTIAL(SC2A1(z,x), Radial, Radial)+
        PARTIAL(SC2A1(z,x), Axial, Axial));

C2-7
ENERGY BALANCE

FOR z = 0 TO 1 DO
  FOR x = 0 TO 1 DO
    1.5*(1-x^2)*PARTIAL(TETA2(z,x), Axial) + \( \frac{k_2}{(r_0^2*U_0*cp)/L* ((L/R_2)^2*PARTIAL(TETA2(z,x), Axial, Axial)} + \)
    1.5*(1-x^2)*PARTIAL(ST2A1(z,x), Axial) + \( \frac{k_2}{(r_0^2*U_0*cp)/L* ((L/R_2)^2*PARTIAL(ST2A1(z,x), Axial, Axial)} + \)
  END
END

CONVERSION

FOR z = 0 TO 1 DO
  X2(z) = INTEGRAL(x:0:1; 1.5*(1-x^2)*[1-C2(z,x)])
  SX2A1(z) = 1.5*INTEGRAL(x:0:1; (1-x^2)*ST2A1(z,x))
END

MODEL Solid

PARAMETER

#Thickness, length, thermal conductivity

RW, L, ks AS REAL

DISTRIBUTION_DOMAIN

Axial AS (0:1)

C2-8
VAR ATABLE

TETAS AS DISTRIBUTION (Axial, Radial) OF DIM_TEMP
STSAL AS DISTRIBUTION (Axial, Radial) OF Conc_sens
NSTSAL AS DISTRIBUTION (Axial, Radial) OF Cone_sens

BOUNDARY

#BounDRy conditions AT the ends, zero heat flux

FOR x:0+ TO 1|- DO

PARTIAL(TETAS(0,x), Axial)=0;
PARTIAL(TETAS(1,x), Axial)=0;
PARTIAL(STSAL(0,x), Axial)=0;
PARTIAL(STSAL(1,x), Axial)=0;
END

EQUATION

#laplace equation

FOR z:0|+ TO l|- DO

FOR x :0+ TO 1|- DO

PARTIAL(TETAS(z,x), Axial, Axial)+(L/RW)^2=
PARTIAL(TETAS(z,x), Radial, Radial) =0 ;
PARTIAL(STSAL(z,x), Axial, Axial)+(L/RW)^2=
PARTIAL(STSAL(z,x), Radial, Radial) =0 ;
END
END
END

END

MODEL Reactor

UNIT

SA AS Endo
PSA Two-dimensional Approach gPROMS Code

SET

WITHIN SA DO
  Axial := [BTFM, 2, 20];
  Radial := [OCFEM, 3, 3];
END

WITHIN SB DO
  Axial := [BTFM, 2, 20];
  Radial := [OCFEM, 3, 3];
END

WITHIN SS DO
  Axial := [BTFM, 2, 20];
  Radial := [OCFEM, 3, 3];
END

EQUATION

#BOUNDARY CONDITIONS BETWEEN DOMAINS

#HEAT BALANCE

FOR z :-0 TO 1 DO
  PARTIAL(SA.TETAl(z,1), SA.RADIAL)-SA.R1*SA.A1*SA.DH1*SA.C10/
    SA.kl/SA.T10*SA.TETAl(z,1)*SA.C1(z,1)+SA.R1*SS.ks/SA.kl/SS.RW*
    PARTIAL(SS.TETAS(z,0), SS.Radial);

  SA.TETAl(z,1)-SS.TETAS(z,0);

  PARTIAL(SS.TETAS(z,0), SS.Radial)-
    SA.R1*SA.A1*SA.DH1*SA.C10/
    SA.kl/SA.T10*SA.TETAl(z,1)*SA.C1(z,1)+SA.R1*SS.ks/SA.kl/SS.RW*
    PARTIAL(SS.TETAS(z,0), SS.Radial);

  SS.TETAS(z,0)-SA.TETAl(z,1);
END

FOR z :-0 TO 1 DO
  PARTIAL(SA.STIA1(z,1), SA.RADIAL)-SA.D1*SA.DH1*SA.C10/SA.kl/SA.T10*
    PARTIAL(SA.C11(z,1), SA.RADIAL)+SA.R1*SA.k1/SA.kl/SA.RW*
    *PARTIAL(SS.STIA1(z,0), SS.Radial);

  SA.STIA1(z,1)-SS.STIA1(z,0);

  PARTIAL(SS.STIA1(z,0), SS.RADIAL)-
    SA.D1*SA.DH1*SA.C10/SA.k1/SA.RW*
    PARTIAL(SS.STIA1(z,0), SS.Radial);

  SA.STIA1(z,0)-SS.STIA1(z,0);
END

C2-10
PSA Two-dimensional Approach gPROMS Code

PARTIAL(2.5, 0.35, SB.Radial) - SB.R2*SS.xe/SS.x2/SS.xxx
PARTIAL(2.5, 0.35, SB.Radial);

SB.ST2A1(z, 1) = SS.STSA1(z, 1);

END

FOR z = 0 TO 1 DO
  FOR x = 0 TO 1 DO
    SA.NST1A1(z, x) = SA.ST1A1(z, x) * SA.AI / SA.TET1A1(z, x);
    SB.NST2A1(z, x) = SB.ST2A1(z, x) * SA.AI / SB.TET2A1(z, x);
    SS.NSTSA1(z, x) = SS.STSA1(z, x) * SA.AI / SS.TETSA1(z, x);
  END
END

FOR x = 0 TO 1 DO
  SA.NSX1A1(z) = SA.SX1A1(z) * SA.AI / SA.X1(z);
  SB.NSX2A1(z) = SB.SX2A1(z) * SA.AI / SB.X2(z);
END

SA.NSX1A1(0) = 0;
SB.NSX2A1(0) = 0;

END #Model reactor

#--------------------------

PROCESS sen_2d

UNIT
  SK AS Reactor

SET
  WITHIN SK DO
    WITHIN SA DO
      rol := 0.3315;
      cpl := 2785;
      DL := 2.05E-4;
      L1 := 0.0891;
      L := 0.3;
      K1 := 0.001;
      U10 := 4.851;
      A1 := 2021;
      EI := 900000;
      DNL := 2050000;
      C10 := 3.3423;
      T10 := 1900;
      Rg := 8.314;
    END
  END
END

C2-II
WITHIN SS DO
    ra0 := 0.366 ;
    cp0 := 1339 ;
    D0 := 1.7584 -
    k0 := 0.0735 ;
    L := 0.3 ;
    R2 := 0.001 ;
    U0 := 3.45 ;
    A3 := 17200*10.0585 ;
    E3 := 130950 ;
    DB3 := 603000 ;
    C30 := 1.2 ;
    T30 := 1000 ;
    Rg := 8.314 ;
END

WITHIN SS DO
    L := 0.3 ;
    NM := 0.0005 ;
    ks := 25 ;
END
END

PRESET
RESTORE "SENS2D.a2"

SOLUTION PARAMETERS
OutputLevel := 2;
gRMS := ON;
gPLOT := OFF;
MaxIterations := 1000;

SCHEDULE
SAVE "SENS2D.a3"
END
Appendix D

Combustor gPROMS Code
#2D mathematical model for catalytic combustion in small circular channels

DECLARE

TYPE

Methane_mass_fr 0.05 -1E20 1E20
Oxygen_mass_fr 0.222 -1E20 1E20
CO2_mass_fr 0 -1E20 1E20
Water_mass_fr 0 -1E20 1E20
Nitrogen2_mass_fr 0.78 -1E20 1E20

Methane_mol_fr 0.09 -1E20 1E20
Oxygen_mol_fr 0.2 -1E20 1E20
CO2_mol_fr 0 -1E20 1E20
Water_mol_fr 0 -1E20 1E20
Nitrogen2_mol_fr 0.7 -1E20 1E20

Methane_conc 1.2 -1E20 1E20
Oxygen_conc 10 -1E20 1E20
CO2_conc 0 -1E20 1E20
Water_conc 0 -1E20 1E20

D_temp2 1 0.2 1E4
D_temp3 1 0.2 1E4
Temperature 1000 -1E20 1E20

Diffusion_coefficient 1.07E-4 0 1E20

Heat_cap -1100 0 1E20
Thermal_cond 0.07 0 1E20
Cond_solid 25 0 1E20
Conversion 0.3 -1E20 1E20
Density 0.35 0 1E20
Velocity 5 -1E20 1E20
Rate 0 -1E20 1E20
Heat_balance 100000 -1E20 1E20
Heat_flux 4000 -1E20 1E20

Mass_imbalance 1E-5 -1E20 1E20

END

MODEL Combustor

PARAMETER

# INLET MASS FRACTIONS, PRESSURE, TEMPERATURE, VELOCITY,

WBO, WHO, WNO, P2, T20, U20 AS REAL
#MOLECULAR WEIGHT
#
#-----------------------------------------------
# MB, MM, MS, M12, MS
# AS REAL
#
#DIFFUSION COEFFICIENTS
#-----------------------------------------------
# DBO, DMO, DNO, DS0
# AS REAL
#
#Thermal conductivities at initial temperature
#-----------------------------------------------
# LA_BO, LA_MO, LA_NO, LA_SO, LA_I20
# AS REAL
#
#Heat capacity coefficients
#-----------------------------------------------
# A_B, B_B, C_B, D_B
# AS REAL
# A_M, B_M, C_M, D_M
# AS REAL
# A_N, B_N, C_N, D_N
# AS REAL
# A_S, B_S, C_S, D_S
# AS REAL
# A_I2, B_I2, C_I2, D_I2
# AS REAL
#
#CHANNEL DIMENSIONS
#-----------------------------------------------
# L, R2
# AS REAL
#
#KINETIC PARAMETERS, HEAT OF REACTION
#-----------------------------------------------
# KBO, EB, DHB
# AS REAL
#
#GAS CONSTANT
#-----------------------------------------------
# Rg
# AS REAL
#

DISTRIBUTION_DOMAIN
Axial
AS (0 : 1)
Combustor gPROMS Code

Radial AS (0 : 1)

VARIABLE

$==============================================$

#mass fractions

$==============================================$

Wb AS DISTRIBUTION(Axial, Radial) OF Methane_mass_fr
Wn AS DISTRIBUTION(Axial, Radial) OF Oxygen_mass_fr
Wn AS DISTRIBUTION(Axial, Radial) OF CO2_mass_fr
Ww AS DISTRIBUTION(Axial, Radial) OF Water_mass_fr
Ww AS DISTRIBUTION(Axial, Radial) OF Nitrogen_mass_fr

$==============================================$

#molar fractions

$==============================================$

Yb AS DISTRIBUTION(Axial, Radial) OF Methane_mol_fr
Yn AS DISTRIBUTION(Axial, Radial) OF Oxygen_mol_fr
Yn AS DISTRIBUTION(Axial, Radial) OF CO2_mol_fr
Yw AS DISTRIBUTION(Axial, Radial) OF Water_mol_fr
Yw AS DISTRIBUTION(Axial, Radial) OF Nitrogen_mol_fr

$==============================================$

#concentrations

$==============================================$

CMB AS DISTRIBUTION(Axial, Radial) OF Methane_conc
CMO AS DISTRIBUTION(Axial, Radial) OF Oxygen_conc
CMO AS DISTRIBUTION(Axial, Radial) OF CO2_conc
CMW AS DISTRIBUTION(Axial, Radial) OF Water_conc

$==============================================$

#Temperature and dimensionless temperature

$==============================================$

T2 AS DISTRIBUTION(Axial, Radial) OF Temperature
TETA2 AS DISTRIBUTION(Axial, Radial) OF D_temp2

$==============================================$

#Physical properties: diffusion coefficients, heat
#capacity, thermal conductivity

$==============================================$

DB AS DISTRIBUTION(Axial, Radial) OF Diffusion_coefficient
DM AS DISTRIBUTION(Axial, Radial) OF Diffusion_coefficient
DN AS DISTRIBUTION(Axial, Radial) OF Diffusion_coefficient
DS AS DISTRIBUTION(Axial, Radial) OF Diffusion_coefficient

CP_B AS DISTRIBUTION(Axial, Radial) OF Heat_cap
CP_M AS DISTRIBUTION(Axial, Radial) OF Heat_cap
Combustor gPROMS Code

CP_N AS DISTRIBUTION(Axial, Radial) OF Heat_cap
CP_S AS DISTRIBUTION(Axial, Radial) OF Heat_cap
CP_I2 AS DISTRIBUTION(Axial, Radial) OF Heat_cap
CP2 AS DISTRIBUTION(Axial, Radial) OF Heat_cap
LA2 AS DISTRIBUTION(Axial, Radial) OF Therm_cond
LA_B AS DISTRIBUTION(Axial, Radial) OF Therm_cond
LA_N AS DISTRIBUTION(Axial, Radial) OF Therm_cond
LA_M AS DISTRIBUTION(Axial, Radial) OF Therm_cond
LA_S AS DISTRIBUTION(Axial, Radial) OF Therm_cond
LA_I2 AS DISTRIBUTION(Axial, Radial) OF Therm_cond

#density and velocity

Ro2 AS DISTRIBUTION(Axial, Radial) OF Density
U2 AS DISTRIBUTION(Axial, Radial) OF Velocity

#reaction rate

ReacRate2 AS DISTRIBUTION(Axial) OF Rate

#Conversions

X2 AS DISTRIBUTION(Axial) OF Conversion

#Mass imbalance

Mass_imbalance2 AS Mass_imbalance
Mass2 AS DISTRIBUTION(Axial) OF Mass_imbalance

#Consumed heat flux along the reactor

Heat_flux_generated AS DISTRIBUTION(Axial) OF Heat_flux
H_total AS Heat_flux
H_gen AS Heat_flux
Combustor gPROMS Code

# Heat balance variables, heat in, heat out, heat generated

Q_in_2
Q_out_2

AS Heat_balance
AS Heat_balance

BOUNDARY

# INLET CONDITIONS
# AT Z = 0 FOR ALL r

# mass balance

FOR X := 0[+ TO 1]- DO
  WB(0,x) = WBO;
  WN(0,x) = WNO;
  WS(0,x) = WSO;
  TETA2(0,x)=1;
  U2(0,x) = 2*U20*(1-x^2);
END

# OUTLET CONDITIONS
# AT Z = 1 FOR ALL r

# mass balance

FOR X := 0[+ TO 1]- DO
  PARTIAL(WB(1,x), Axial) = 0;
  PARTIAL(WM(1,x), Axial) = 0;
  PARTIAL(WN(1,x), Axial) = 0;
  PARTIAL(WS(1,x), Axial) = 0;
  PARTIAL(U2(1,x), Axial) = 0;
  PARTIAL(TETA2(1,x), Axial)=0;
END

D-3
# SYMMETRY CONDITIONS
# AT r=0 FOR ALL z

# mass balance

FOR z := 0 TO 1 DO
    PARTIAL(WB(z,0), Radial) = 0;
    PARTIAL(WM(z,0), Radial) = 0;
    PARTIAL(WN(z,0), Radial) = 0;
    PARTIAL(WS(z,0), Radial) = 0;
    PARTIAL(U2(z,0), Radial) = 0;
    PARTIAL(TETA2(z,0), Radial) = 0;
END

# REACTING WALL
# AT r = 1 FOR ALL z

# mass balance

FOR z := 0 TO 1 DO
    DB(z,1)*Ro2(z,1)*PARTIAL(WB(z,1), Radial)/(R2) = -1E-3*MB*ReacRate2(z);  
    DM(z,1)*Ro2(z,1)*PARTIAL(WM(z,1), Radial)/(R2) = -2*1E-3*MM*ReacRate2(z);  
    DN(z,1)*Ro2(z,1)*PARTIAL(WN(z,1), Radial)/(R2) = 1E-3*MN*ReacRate2(z);  
    DS(z,1)*Ro2(z,1)*PARTIAL(WS(z,1), Radial)/(R2) = 2*1E-3*MS*ReacRate2(z);  
    U2(z,1) = 0;
END

EQUATION
# MASS BALANCE

FOR Z :- 0|+ TO l|- DO
    FOR X :- 0|+ TO l|- DO
        Ro2(z,x)*U2(z,x)*L*PARTIAL(WB(z,x),Axial) - (PARTIAL(DB(z,x)*Ro2(z,x)*PARTIAL(WB(z,x),Radial),Radial)) + ((L/R2)^2)/x*PARTIAL(x*DB(z,x)*Ro2(z,x)*PARTIAL(WB(z,x),Radial),Radial));
    END
END

# ENERGY BALANCE

FOR Z :- 0|+ TO l|- DO
    FOR X :- 0|+ TO l|- DO
        Ro2(z,x)*U2(z,x)*L*PARTIAL(TETA2(z,x),Axial) - (PARTIAL(LA2(z,x)*Ro2(z,x)*PARTIAL(TETA2(z,x),Axial),Axial) + ((L/R2)^2)/x*PARTIAL(x*LA2(z,x)*Ro2(z,x)*PARTIAL(TETA2(z,x),Radial),Radial)));
    END
END

# CONTINUITY EQUATION

FOR Z :- 0|+ TO l|- DO
    FOR X :- 0|+ TO l|- DO
        PARTIAL(Ro2(z,x)*U2(z,x), Axial) = 0 ;
    END
END
Combustor gPROMS Code

#=================================#
# AUXILIARY EQUATIONS #
#=================================#

# Nitrogen Mass fraction
#=================================#

FOR z: 0 TO 1 DO
FOR x: 0 TO 1 DO
W12(z,x) = 1 - (WB(z,x) + WH(z,x) + WO(z,x) + WS(z,x))
END
END

# Density
#=================================#

FOR z: 0 TO 1 DO
FOR x: 0 TO 1 DO
Ro2(z,x) = 1E-3 * (101325 * P2 / Rg / T2(z,x)) / (WB(z,x) / MB + WM(z,x) / MM + WN(z,x) / MN +
WS(z,x) / MS + W12(z,x) / MI2)
END
END

# molar fractions
#=================================#

FOR z: 0 TO 1 DO
FOR x: 0 TO 1 DO
YB(z,x) = WB(z,x) / MB / (WB(z,x) / MB + WH(z,x) / MH + WN(z,x) / MN +
WS(z,x) / MS + W12(z,x) / MI2)
YM(z,x) = WM(z,x) / MM / (WB(z,x) / MB + WH(z,x) / MH + WN(z,x) / MN +
WS(z,x) / MS + W12(z,x) / MI2)
YN(z,x) = WN(z,x) / MN / (WB(z,x) / MB + WH(z,x) / MH + WN(z,x) / MN +
WS(z,x) / MS + W12(z,x) / MI2)
YS(z,x) = WS(z,x) / MS / (WB(z,x) / MB + WH(z,x) / MH + WN(z,x) / MN +
WS(z,x) / MS + W12(z,x) / MI2)
Y12(z,x) = WX2(z,x) / MI2 / (WB(z,x) / MB + WH(z,x) / MH + WN(z,x) / MN +
WS(z,x) / MS + W12(z,x) / MI2)
END
END

D-8
# Combustion reaction rate in mass balance

FOR z := 0 TO 1 DO
    \text{ReacRate2}(z) = \text{KBO} \times \exp\left(-\frac{\text{EB}}{\text{Rg} \times \text{T2}(z, 1)}\right) \times \text{CHB}(z, 1)
END

# Concentrations obtained from mass balance

FOR z := 0 TO 1 DO
    FOR x := 0 TO 1 DO
        \text{CMB}(z, x) = 101325 \times \text{P2} \times \text{YB}(z, x) / \text{Rg} / \text{T2}(z, x)
        \text{CMM}(z, x) = 101325 \times \text{P2} \times \text{YM}(z, x) / \text{Rg} / \text{T2}(z, x)
        \text{CMN}(z, x) = 101325 \times \text{P2} \times \text{YN}(z, x) / \text{Rg} / \text{T2}(z, x)
        \text{CMS}(z, x) = 101325 \times \text{P2} \times \text{YS}(z, x) / \text{Rg} / \text{T2}(z, x)
    END
END

# Temperature

FOR z := 0 TO 1 DO
    FOR x := 0 TO 1 DO
        \text{T2}(z, x) = \text{T20} \times \text{TETA2}(z, x)
    END
END

# Heat capacity

FOR z := 0 TO 1 DO
    FOR x := 0 TO 1 DO
        \text{CP_B}(z, x) = 1E3 \times \left(\frac{A_B + B_B \times \text{T2}(z, x) / 1000}{\text{MB}}\right) \times \left(2 + D_B \times \text{T2}(z, x) / 1000^3\right) / \text{MB}
        \text{CP_M}(z, x) = 1E3 \times \left(\frac{A_M + B_M \times \text{T2}(z, x) / 1000}{\text{MM}}\right) \times \left(2 + D_M \times \text{T2}(z, x) / 1000^3\right) / \text{MM}
        \text{CP_N}(z, x) = 1E3 \times \left(\frac{A_N + B_N \times \text{T2}(z, x) / 1000}{\text{MN}}\right) \times \left(2 + D_N \times \text{T2}(z, x) / 1000^3\right) / \text{MN}
        \text{CP_S}(z, x) = 1E3 \times \left(\frac{A_S + B_S \times \text{T2}(z, x) / 1000}{\text{MS}}\right) \times \left(2 + D_S \times \text{T2}(z, x) / 1000^3\right) / \text{MS}
        \text{CP_I2}(z, x) = 1E3 \times \left(\frac{A_{I2} + B_{I2} \times \text{T2}(z, x) / 1000}{\text{MI2}}\right) \times \left(2 + D_{I2} \times \text{T2}(z, x) / 1000^3\right) / \text{MI2}
    END
END

D-9
Combustor gPROMS Code

CP2(z,x)=WB(z,x)*CP_B(z,x)+WM(z,x)*CP_M(z,x)
+WN(z,x)*CP_N(z,x)+WI2(z,x)*CP_I2(z,x)+WS(z,x)
*CP_S(z,x)
END
END

#thermal conductivities

FOR z: 0 TO 1 DO
FOR x: 0 TO 1 DO
LA_B(z,x)=LA_B0*TETA2(z,x)*0.75
LA_M(z,x)=LA_M0*TETA2(z,x)*0.75
LA_N(z,x)=LA_N0*TETA2(z,x)*0.75
LA_I2(z,x)=LA_I20*TETA2(z,x)*0.75
LA2(z,x)=(YT(z,x)*LA_B(z,x)*MB*0.33 +
YM(z,x)*LA_M(z,x)*MM*0.33 +
YN(z,x)*LA_N(z,x)*MN*0.33 +
YS(z,x)*LA_S(z,x)*MS*0.33 +
YI2(z,x)*LA_I2(z,x)*MI2*0.33)/
(YB(z,x)*MB*0.33+YM(z,x)*MM*0.33 +
YN(z,x)*MN*0.33+YS(z,x)*MS*0.33 +
YI2(z,x)*MI2*0.33)
END
END

#diffusion coefficients

FOR z: 0 TO 1 DO
FOR x: 0 TO 1 DO
DB(z,x)=DB0*TETA2(z,x)*1.75
DM(z,x)=DM0*TETA2(z,x)*1.75
DS(z,x)=DS0*TETA2(z,x)*1.75
END
END

#heat flux generated

For z: 0 TO 1 DO
Heat_flux_generated(z)=DHB*ReacRate2(z)
END
H_total=INTEGRAL(z:0:1;Heat_flux_generated(z))
END
Combustor gPROMS Code

# Conversion in mass balance
FOR Z := 0 TO 1 DO
X(2)(z)+1*INTEGRAL(x:=0:1;X*Ro2(z,x)*U2(z,x)*WB(z,x)) /
INTEGRAL(x:=0:1;X*Ro2(0,x)*U2(0,x)*WB(0,x));
Mass2(z)=INTEGRAL(x:=0:1;X*Ro2(z,x)*U2(z,x));
END

# Calculus for heat imbalance
Q_in_2=2*3.14*R2^2*INTEGRAL(x:=0:1;X*Ro2(0,x)*U2(0,x)*CP2(0,x)*T2(0,x))
Q_out_2=2*3.14*R2^2*INTEGRAL(x:=0:1;X*Ro2(1,x)*U2(1,x)*CP2(1,x)*T2(1,x))
H_gen=2*3.14*R2*L*H_total

# Mass imbalance
Mass_imbalance2=INTEGRAL(x:=0:1;Ro2(0,x)*U2(0,x)) -
INTEGRAL(x:=0:1;Ro2(1,x)*U2(1,x));

END # Model

MODEL Solid

PARAMETER

# Wall thickness over length, Inlet temperature
RM, TSO, TF, R2, L AS REAL

# Wall thermal conductivity at initial cond.
LAS0, h_coff AS REAL
DISTRIBUTION_DOMAIN
Axial AS (0 : 1)
Radial AS (0 : 1)

VARIABLE

TETAS AS DISTRIBUTION (Axial,Radial) OF D_temp
TETAF AS D_temp
TS AS DISTRIBUTION (Axial,Radial) OF Temperature
LAS AS DISTRIBUTION (Axial,Radial) OF Cond_solid
Heat_flux_transf AS DISTRIBUTION (Axial) OF Heat_flux
H_total_trans AS Heat_flux
H_transfer AS Heat_flux
H_imbalance AS Heat_flux

BOUNDARY

# Boundary conditions at the ends
# At x = 0 and x = 1 all x except 0 and 1

FOR x := 0 TO 1- DO
    PARTIAL(TETAS(0, x), Axial) = 0 ;
    PARTIAL(TETAS(1, x), Axial) = 0 ;
END

# Boundary condition at the external side of the wall
# external heat transfer
# all x except the end and x=1

FOR z := 0 TO 1 DO
    #PARTIAL(TETAS(z,1),Radial) = 
    #Sig*Emis+RW/LAS(z,1)*(TETAP*4-TETAS(z,1)*4 ) ;
    PARTIAL(TETAS(z,1),Radial) =
    h_Coff*RW/LAS(z,1)*(TETAF-TETAS(z,1)) ;
END
EQUATION

#Heat equation LAPLACE

FOR Z :- 0 TO 1 DO
  FOR X :- 0 TO 1 DO
    PARTIAL(LAS(z,x)*PARTIAL(TETAS(z,x), Axial), Axial) + (L/RW)^2 * (1/(R2+RW*x))* PARTIAL(LAS(z,x)*TETAS(z,x), Radial), Radial) = 0 ;
  END
END

#AUXILIARY EQUATIONS

#temperature

FOR Z :- 0 TO 1 DO
  FOR X :- 0 TO 1 DO
    TS(z,x) - TSO*TBTAS(z,x)
  END
END

#Solid thermal conductivity

FOR Z :- 0 TO 1 DO
  FOR X :- 0 TO 1 DO
    LAS(z,x) = LAS*0.75
  END
END

TETAF = TF/TSO;

For Z :- 0 TO 1 DO
  #Heat_flux_transf(z) = 1000*Sig*Emis*(-TF/1000)^4 + H(TS(z,1))/1000^4)
  #Heat_flux_transf(z) = h_coff*(-TF+TS(z,1))
  Heat_flux_transf(z) = h_coff*(-TF+TS(z,1))
END

H_total_trans = INTEGRAL(z:-0:1;Heat_flux_transf(z))
H_transf = 2*3.14*L*(R2+RW)*H_total_trans

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Combustor gPROMS Code

END #model solid

$------------------------------------------------------------$
MODEL Reactor

UNIT
SB AS Combustor
SS AS Solid

SET
WITHIN SS DO
Axial := [BFDM, 2, 50];
Radial := [OCFEM, 1, 3];
END
WITHIN SS DO
Axial := [BFDM, 2, 50];
Radial := [OCFEM, 1, 3];
END

EQUATION
$------------------------------------------------------------$
FOR z := 0 TO 1 DO
SB.LA2(z,1)/SB.R2*PARTIAL(SB.TETA2(z,1), SB.Radial).
SB.ReacRate2(z)*SB.DHB/ SB.T20 +
PARTIAL(SS.TETAS(z,0), SS.Radial)*SS.LAS(z,0)/
SS.RW
SS.TETAS(z,0) . SB.TETA2(z,1)
SS.H_imbalance=SB.Q_in_2+SB.Hjgen-(SB.Q_out_2+SS.H_transf); 
END

END # model reactor
$------------------------------------------------------------$
PROCESS combustor
UNIT
CO AS Reactor

WITHIN CO DO

MB0 :=0.0526 ;
MM0 :=0.2209 ;
MG0 :=0 ;
MM0 :=0 ;
P2 :=1 ;
T20 :=1000 ;
U20 :=4.9 ;
M0 :=16 ;
MM :=32 ;
MM :=44 ;
M12 :=18 ;
DB0 :=1.538-4 ;

D44
Combustor gPROMS Code

WITHIN SS DO
END

WITHIN SS DO
END

SAVE "comb2"

SCHEDULE
SAVE "comb2"