Experimental Investigation of Catalytic Biomass for Gas Turbine Applications

Jürgen Jacoby

Doctoral Thesis
2001

Department of Energy Technology
Division of Heat and Power Technology
Royal Institute of Technology
10044 Stockholm, Sweden
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Abstract

This thesis attempts to combine two technologies in the field of power generation that have experienced an increasing interest in research, namely catalytic combustion and biomass gasification. Catalytic combustion has been investigated by numerous research groups in both academic and commercial fields as it offers high efficiency combustion at low emission levels, a feature which has become essential to meet today’s stringent emission regulations. Single-digit emissions in ppm-levels of nitrogen oxides, carbon monoxides and hydrocarbons have already been demonstrated using natural gas as a fuel source. Gasified biomass offers the potential for reducing net emissions of carbon dioxide as a greenhouse gas. A reduction of nitrogen oxides as a combustion product is of interest as their oxidation in the earth atmosphere results in the formation of secondary pollutants which are potentially more harmful than the precursor itself. The purpose of the catalyst is to allow a stable reaction process of lean fuel-to-air mixtures. Biomass is an attractive fuel source due to its abundance. It has to be said though that this statement is only valid in certain geographical regions of the world. Through advanced gasification technologies, e.g. the circulating fluidized bed technology, biomass can be converted into a combustible gas which can in turn be used to fire a gas turbine for power generation. Gasified biomass has some distinct characteristics resulting in great demands on the combustor. Even though rich in hydrogen and carbon monoxide, its low heating value requires a technique to maintain a stable combustion, difficult to achieve via flame combustion. Furthermore it has a potentially high level of ammonia, which may generate emissions of nitrogen oxide.

All catalyst development has been performed at the Chair of Chemical Technology at the Royal Institute of Technology. This project presented here has been done in cooperation with this division.

The first part of this study gives the necessary background on this subject, as well as a state of the art in catalytic combustion. The approach to reach the above mentioned goal is pointed out. The fundamental principles of catalytic combustion and its advantages with respect to conventional techniques are explained.

A cold flow test facility has been set up and intensive experimental work has been carried out to optimize the flow field in the mixing zone and at the inlet of the catalyst. Satisfactory results could be achieved with respect to the velocity profile and the mixing quality of fuel and air in the mixing section. Numerical investigations were performed to get a deeper understanding of the flow field in the fuel injection head. The cold flow tests and the numerical studies led to the design of the combustion test facility. This facility offers flexibility for testing various compositions of the catalytic combustion and operating conditions. By means of temperature monitoring and gas analysis, catalyst performance can be evaluated. Catalyst characterization yields information on the lifetime.
Preface

The following papers and other publications have been presented as part of this work.

Jacoby J.; Fredriksson J.; Fransson, T., 1998

Jacoby, J.; Hofer, M; Fredriksson, J.; Fransson, T., 1998

*Catalytic Combustion of Gasified Biomass for Gas Turbine Application: Design of a Pressurised Pilot-scale Rig*, Book of Abstracts, September 1999, EUROPACAT-IV, Rimini, Italy


Jacoby, J.; Strasser, T.; Fransson, T.; Thevenin, P.; Järås, S., 2000


*Pressurised Pilot-Scale Catalytic Combustion of Gasified Biomass using Palladium Impregnated and Manganese Substituted Hexaaluminates*, 3rd International Congress on Environmental Catalysis, to be published in special issue of Applied Catalysis B: Environmental, December 2001, Tokyo, Japan
# TABLE OF CONTENTS

TABLE OF CONTENTS ........................................................................................................... I
LIST OF FIGURES ................................................................................................................ IV
LIST OF TABLES .................................................................................................................. VII
NOMENCLATURE ............................................................................................................... VIII
ABBREVIATIONS ............................................................................................................. IX

1. INTRODUCTION ........................................................................................................ 1
   1.1 General Introduction ...................................................................................... 1
   1.2 Background ..................................................................................................... 1
       1.2.1 The Role of Biomass in Power Generation ............................................ 1
       1.2.2 Biomass Preparation and Thermochemical Conversion for Use in Power Generation ...................................................... 4
       1.2.3 Typical Fuel Properties of Gasified Biomass ......................................... 8
   1.3 Combustion Emissions .................................................................................... 9

2. OVERVIEW OF CATALYTIC COMBUSTION ....................................................... 11
   2.1 Introduction................................................................................................... 11
   2.2 Some Fundamentals of High Temperature Catalysis for Gas Turbines ......................................................................................... 11
   2.3 Catalyst Deactivation .................................................................................... 15
   2.4 Catalysis in Gas Turbines for the Generation of Heat and Power – State of the Art .................................................................................. 15

3. OBJECTIVES ............................................................................................................ 19

4. APPROACH .............................................................................................................. 21

5. TEST FACILITIES AND IMPLEMENTATION .................................................... 23
   5.1 Introduction ................................................................................................... 23
   5.2 Weak Flammability as Design Criterion .................................................... 23
   5.3 Auto-Ignition Time and Flashback Risk as Design Criteria ......................... 24
   5.4 Cold Flow Test Facility ................................................................................ 25
       5.4.1 Fuel Injection System ........................................................................... 26
       5.4.2 Applied Measurement Techniques in the Cold Flow Test Facility .................................................................................. 27
   5.5 Combustion Test Facility ............................................................................. 30
       5.5.1 Temperature and Pressure Monitoring .................................................. 33
       5.5.2 Gas Analysis Equipment ..................................................................... 36
   5.6 Summary of the Experimental Test Facilities ............................................. 37
6. NUMERICAL INVESTIGATION OF THE FLOW FIELD IN THE MIXING SECTION ................................................................. 39

6.1 The Numerical Model ................................................................. 39
  6.1.1 Turbulence Model ................................................................. 40
  6.1.2 Boundary Conditions ............................................................ 41
  6.1.3 Discretization Schemes ......................................................... 41

6.2 Mixing Process of the Fuel / Air Mixture and Auto-Ignition of the Fuel ........................................................................ 41
  6.2.1 Modeling of the Geometry and Grid Generation ....................... 42
  6.2.2 Non-reacting Mixing Process in the Fuel Injection Head .......... 43
  6.2.3 Governing Equation and Chemistry Model for Investigation of the Reactive Flow ......................................................... 43

6.3 Flow Field in the Premixing Zone .............................................. 45

6.4 Convergence Strategy and Solution Algorithm ........................... 45

7. COLD FLOW RESULTS AND NUMERICAL INVESTIGATION OF THE NON-REACTING FLOW .............................. 47

7.1 Experimental Flow Field Optimization in the Cold Flow Test Facility ................................................................. 47
  7.1.1 Experimental Investigation of the Mixing Quality of Fuel and Air ................................................................. 49
  7.1.2 Pressure Drop Measurement .................................................... 51
  7.1.3 Summary of the Results obtained with the Cold Flow Test Facility ............................................................................ 52

7.2 Results from the Numerical Investigations .................................. 52
  7.2.1 Numerical Investigation of the Recirculation Zone Downstream of the Fuel Head ......................................................... 53
  7.2.2 Numerical Investigation of the Mixing Process Inside the Fuel Injection Head ......................................................... 54
  7.2.3 Ignition Modeling .................................................................... 56
  7.2.4 Summary of the Results obtained by Numerical Investigations ............................................................................ 57

8. CATALYST TESTING AND RESULTS .................................................. 59

8.1 Catalyst Preparation ..................................................................... 59

8.2 Catalyst Testing ........................................................................... 60

8.3 Catalyst Configuration I ............................................................... 61
  8.3.1 Comparison with Bench-Scale Experiments ......................... 66
  8.3.2 Conclusion of Catalyst Configuration I ................................. 68

8.4 Catalyst Configuration II ............................................................... 68
  8.4.1 Conclusion of Catalyst Configuration II ................................. 70

8.5 Catalyst Configuration III ............................................................. 70
  8.5.1 Pressure Effects .................................................................... 76
  8.5.2 Nitrogen Oxides from Fuel-Bound Nitrogen ......................... 80
  8.5.3 Conclusion of Catalyst Configuration III .............................. 81

8.6 Catalyst Configuration IV ............................................................. 82
LIST OF FIGURES

Fig. 1-1: Total world primary energy and electricity consumption [Ecoal, 1999]. ................................................................. 3
Fig. 1-2: Sweden’s total power generation in 1999 [STEM, 2000]. ................................................................. 3
Fig. 1-3: Process diagram for conversion of biomass to energy [BIN, 1998]. ................................................................. 6
Fig. 1-4: Major path for fixed nitrogen formation and conversion [Prasad, 1984]. ................................................................. 9
Fig. 1-5: Schematic concentration of thermal NOx and CO in arbitrary units vs. combustion temperature [Zwinkels, 1996]. .......... 10
Fig. 2-1: Schematic of a monolithic catalyst [Jackson, 2001]. ................................................................. 12
Fig. 2-2: Different catalytic combustor design concepts [Johansson, 1998]. ................................................................. 17
Fig. 5-1: Schematic and photo of the cold flow test section. ................................................................. 26
Fig. 5-2: Second design of the fuel injection head and working principle. ................................................................. 27
Fig. 5-3: Schematic view of the combustion test facility. ................................................................. 30
Fig. 5-4: Schematic of the catalyst mounting, showing thickness of the catalyst segment and axial gap between two segments, catalyst height is not in true scale. ................................................................. 32
Fig. 5-5: Photo of a honeycomb monolith mounted in the mullite insulation ................................................................. 33
Fig. 5-6: Thermocouple and pressure tap location in catalytic combustion test facility shown for the case of three catalysts mounted ................................................................. 34
Fig. 5-7: Gas reactor temperature instrumentation and location of measurement planes and effect of air gaps on the overall conversion rate. ................................................................. 35
Fig. 5-8: Setup of gas analysis equipment for fuel gas and exhaust composition measurement. ................................................................. 36
Fig. 6-1: Structure of the commercial CFX 4 software package. ................................................................. 39
Fig. 6-2: Geometry and grid of one air passage of the fuel injection including all fuel injection locations. ................................................................. 42
Fig. 6-3: 2D geometry of the central plane of one air passage of the fuel injection. ................................................................. 42
Fig. 6-4: 3D mesh for numerical investigation of the mixing zone consisting of 310900 cells. ................................................................. 45
Fig. 7-1: Notation for flow field measurements. ................................................................. 48
Fig. 7-2: Measurement of a 360° flow field traversing of flap configuration showing the axial velocity profile, 15mm upstream of the inlet of the catalyst, mixing length 15 cm. ................................................................. 49
Fig. 7-3: Mixing quality profile 10 mm downstream of the catalyst using methane as a tracer gas. ................................................................. 50
Fig. 7-4: Mixing quality profile 10 mm downstream of the catalyst using helium as a tracer gas. ................................................................. 50
Fig. 7-5: Measured pressure drop over both designs of the fuel injection head and monolith vs. mass flow in the cold flow test facility. ................................................................. 52
Fig. 7-6: Comparison of numerical and experimental data of the axial velocity profile in the mixing section. ................................................................. 53
Fig. 7-7: Numerical and experimental data of the axial velocity profile of the basic configuration 15 mm upstream of the monolith inlet. ................................................................. 54
Fig. 7-8: Nomenclature of air and fuel inlets for 2D calculations of the mixing process inside the fuel injection head. .......................................................... 54
Fig. 7-9: Velocity profile in the centre plane of the fuel injection head for two different fuel injection velocities. ................................................. 55
Fig. 7-10: Concentration profile of methane in the centre plane of the fuel injection head for two different fuel injection velocities. ................. 55
Fig. 7-11: Concentration and velocity profile at 50 m/s inlet velocity for fuel and air ......................................................................................... 56
Fig. 7-12: Flow field and thermodynamic property profiles in the fuel injection head using a 7-step reaction scheme for hydrogen, 50 m/s inlet velocity for fuel and air. ......................................................... 57
Fig. 8-1: Typical temperature profile in the catalyst segment at different catalyst inlet temperatures during one experiment, $\lambda$ between 8.28 and 8.48. ....................................................................................................... 62
Fig. 8-2: Time resolved profile measured ignition of the catalyst. ............. 63
Fig. 8-3: Surface and gas phase temperature profiles along axial coordinate of the catalyst at different equivalence ratios at a fixed time (left-hand side) and at constant inlet flow velocity at different times and axial location, $A=60$ s, $B=300$ s, $C=600$ s; $D=900$ s, Zhu et al [2001]. ...................................................................................................... 64
Fig. 8-4: a)–Change of catalyst temperature as a function of the catalyst inlet temperature at $\lambda=11.1$, b)–Change of exhaust composition vs. average catalyst temperature at $\lambda=11.1$. ................................................................. 65
Fig. 8-5: Average catalyst temperature at three different operating conditions.......................................................................................................... 66
Fig. 8-6: Conversion of $H_2$, CO and CH$_4$ and outlet temperature profile over a Pd-LHA in a bench scale experiment on a catalyst, fuel composition 31.8% CO$_2$, 23.7% H$_2$, 10.6% CH$_4$, 33.9% CO, diluted in air by 1:99, lower fuel heating value of 9.28 MJ/kg. .......................... 67
Fig. 8-7: Temperature profile of two identical Pd / LHA catalysts vs. time, indication of homogeneous gas phase reaction occurring downstream of the catalysts. .................................................................................. 69
Fig. 8-8: Coefficient of determination $r^2$ shown for different data series. ............................................ 70
Fig. 8-9: Difference in ignition temperature of the two catalyst segments in Catalyst Configuration III. ........................................................................... 72
Fig. 8-10: Observed hysteresis behaviour in the ignition / extinguish temperature ........................................................................................................ 72
Fig. 8-11: Enlarged section of the extinction temperature as presented in the hysteresis curve shown in Fig. 8-9. .............................................................. 73
Fig. 8-12: Inlet and catalyst temperature and CO emission level at two very lean mixtures .................................................................................................. 73
Fig. 8-13: Catalyst temperature vs. inlet temperature for a)–3.7% CO – 7.8% H$_2$ and b)–13.1% CO – 19.1% H$_2$ fuel gas in Catalyst Configuration III. ............................................................................................... 74
Fig. 8-14: CO emissions at combustor outlet for various operating points, displayed are average temperature in both catalyst segments, respective data given in the table. ......................................................... 75
Fig. 8-15: a)–Catalyst temperature and b)–CO emission level at combustor outlet of Configuration III vs. the relative combustor inlet pressure. ............................... 78
Fig. 8-16: Effect of pressure on the outlet temperature of a catalytic combustor, Groppi et al. [1993].

Fig. 8-17: a)–Catalyst temperature and b)–respective CO, NOx, and THC emissions for Catalyst Configuration III at $\lambda$=10.45 and $H_f$ = 3.94 MJ/kg, 500 ppm NH3 in the fuel feed.

Fig. 8-18: a)–Temperature and b)–corresponding emission profile of Catalyst Configuration IV (two Pd-LaAl11O18 and three LaMnAl11O19 segments).

Fig. 8-19: THC and CO emission levels at $\lambda$ = 7.08 and $\lambda$ = 6.95 and two corresponding lower heating values of the fuel.

Fig. 8-20: Catalyst temperature vs. content of hydrogen in the fuel at $\lambda$ = 6.95.

Fig. 8-21: Measured ignition temperature for Catalyst Configuration I and II vs. the H2 content in the fuel gas for a set of different experimental conditions.

Fig. 8-22: Illustration of a single temperature peak in the catalyst at $\lambda$=8.8 and $H_f$ = 8.01 MJ/kg with one catalyst mounted in the facility.

Fig. 8-23: Illustration of PdO-Pd transition at three different experiments marked by the circles.

Fig. 8-24: Fluctuations in the catalyst temperature measured with Catalyst Configuration III; a) exact cause not known, b) fluctuation caused by a pulsating raw C3H8 flow into the gas reactor at constant inlet temperature of $T_{inlet}$ = 420 K.

Fig. 8-25: Enlarged section of one period in catalyst oscillation and equivalent change in combustor outlet emission composition.

Fig. 8-26: a)–Temperature profile over a time period of 62 min under constant boundary conditions; b)–Measured temperature profiles reported by Jackson et al. [2001], case 1 showing a similar profile as in a), case 2 showing a stable outlet temperature.

Fig. B-1: Axial velocity profiles over the full flow diameter, fuel head design 1, 15 mm in front of the monolith and cross section of the fuel head geometry showing the angled inner air passages.

Fig. B-2: Measurement of a 360° flow field traversing of basic configuration showing the axial velocity profile, downstream of the fuel injection head and 15 mm upstream of the inlet of the monolith.

Fig. B-3: Measurement of axial velocity profile in the 0° plane using centre cone I.

Fig. B-4: Measurement of axial velocity profile in the 0° plane using centre cone II.

Fig. B-5: Measurement of a 360° flow field traversing using centre cone III showing the axial velocity profile, 15 mm upstream of the inlet of the monolith.

Fig. B-6: Measurement of the flow field in the mixing section using a honeycomb structure as a flow straightener.

Fig. B-7: Measurement of the flow field in the mixing section placing the honeycomb structure 60 mm downstream of the fuel injection head.

Fig. C-1: Rate dependency of the surface coverage for a bimolecular Langmuir-Hinshelwood reaction.
LIST OF TABLES

Table 1-1: Greenhouse gas (GHG) emissions of a several EU countries in 1990 and 1998. Kyoto emission targets in % of 1990, CO₂ equivalent, metric million tons [Grummer et al., 2000]. ..................................................... 2

Table 1-2: Three groups of thermochemical conversion processes [Warnecke, 2000]. ............................................................................................................. 5

Table 1-3: Pro and contra of different oxidizing agents. ............................................................................................................. 5

Table 1-4: Typical product gas composition from pressurized, fluidized bed gasification using wood, forest residue, paper mill residue and straw as a fuel, reference for the coal [Salo et al., 1998; McClosky, 1997]. ............................................................................................................. 8

Table 2-1: Overview of most commonly used support materials [Johansson, 1998]. ............................................................................................................. 12

Table 2-2: Operating conditions and design criteria for a combustion chamber of a conventional stationary gas turbine [Forzatti et al., 1999]. ............................................................................................................. 16

Table 5-1: Lower flammability limits of main fuel species and for two different compositions [Glassman, 1996]. ..................................................... 24

Table 5-2: Estimated auto-ignition delay time at design point. .......................................................... 25

Table 5-3: Design values of the combustion test facility. ....................................................................... 31

Table 5-4: Gas reactor pellet specification and photo of a pellet. ..................................................... 31

Table 5-5: Properties of the tested thermocouples and measured standard deviation at two reference temperatures. ........................................................................... 35

Table 5-6: On-line gas analysis system, all values taken from equipment manuals. .......................................................... 36

Table 5-7: Summary of measurement uncertainties of the gas analysis system for fuel composition measurements. ........................................................................... 37

Table 5-8: Summary of measurement uncertainties of the gas analysis system for emission composition measurements. ........................................................................... 37

Table 6-2: Calculated constant binary diffusion coefficient [White, 1974] and absolute mass fraction of the fuel components. ........................................................................... 43

Table 7-1: Normalized standard deviation in % for various configurations of the fuel injection geometry. ........................................................................... 48

Table 8-1: Catalyst composition and abbreviation. ........................................................................... 59

Table 8-2: Summary of catalyst properties. .......................................................................................... 60

Table 8-3: Investigated catalyst configurations. .................................................................................. 60

Table 8-4: Calculated change of bulk flow velocity due to pressure increase. .................................. 77

Table 8-5: Data sheet for Fig. 8-15. .............................................................................................. 78

Table 8-6: Comparative overview of different configurations and operating conditions. ................. 88
NOMENCLATURE

**Latin Symbol**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>c</td>
<td>Concentration</td>
<td>[ppm] or [%]</td>
</tr>
<tr>
<td>$d_h$</td>
<td>Hydraulic diameter</td>
<td>[m]</td>
</tr>
<tr>
<td>f</td>
<td>Friction factor</td>
<td>[-]</td>
</tr>
<tr>
<td>i</td>
<td>Turbulence level</td>
<td>[%]</td>
</tr>
<tr>
<td>k</td>
<td>Reaction constant</td>
<td>[cm³/mol s]</td>
</tr>
<tr>
<td>k</td>
<td>Turbulent kinetic energy</td>
<td>[J/kg]</td>
</tr>
<tr>
<td>k</td>
<td>Constant</td>
<td>[varying]</td>
</tr>
<tr>
<td>l</td>
<td>Characteristic length</td>
<td>[m]</td>
</tr>
<tr>
<td>m</td>
<td>Sample number</td>
<td>[-]</td>
</tr>
<tr>
<td>n</td>
<td>Stoichiometric coefficient</td>
<td>[-]</td>
</tr>
<tr>
<td>n</td>
<td>Number of samples</td>
<td>[-]</td>
</tr>
<tr>
<td>p</td>
<td>Pressure</td>
<td>[kPa]</td>
</tr>
<tr>
<td>r</td>
<td>Radius</td>
<td>[mm]</td>
</tr>
<tr>
<td>s</td>
<td>Empirical standard deviation</td>
<td>[-]</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
<td>[s]</td>
</tr>
<tr>
<td>u</td>
<td>Velocity</td>
<td>[m/s]</td>
</tr>
<tr>
<td>$u_i$</td>
<td>Fluctuating velocity in tensor notation</td>
<td>[m/s]</td>
</tr>
<tr>
<td>x</td>
<td>Coordinate variable</td>
<td>[-]</td>
</tr>
<tr>
<td>x</td>
<td>Measurement value</td>
<td>[-]</td>
</tr>
<tr>
<td>A</td>
<td>Pre-exponential factor</td>
<td>[-]</td>
</tr>
<tr>
<td>D</td>
<td>Hydraulic diameter</td>
<td>[m]</td>
</tr>
<tr>
<td>D</td>
<td>Diffusivity</td>
<td>[m²/s]</td>
</tr>
<tr>
<td>E</td>
<td>Activation energy</td>
<td>[kJ/kg]</td>
</tr>
<tr>
<td>$F_{\text{lean}}$</td>
<td>Lean flammability limit</td>
<td>[%]</td>
</tr>
<tr>
<td>H_{lf}</td>
<td>Lower heating value of fuel</td>
<td>[MJ/kg]</td>
</tr>
<tr>
<td>L</td>
<td>Length</td>
<td>[m]</td>
</tr>
<tr>
<td>$N_i$</td>
<td>Species index, $i = 1, \ldots, N_s$</td>
<td>[-]</td>
</tr>
<tr>
<td>R</td>
<td>Reaction rate</td>
<td>[mol/s m³]</td>
</tr>
<tr>
<td>R</td>
<td>Gas constant</td>
<td>[J/kg K]</td>
</tr>
<tr>
<td>$R_{\text{rel}}$</td>
<td>True relative error</td>
<td>[%]</td>
</tr>
<tr>
<td>S</td>
<td>Source or sink term</td>
<td>[kg/s m³]</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>Y</td>
<td>Mass Fraction</td>
<td>[-]</td>
</tr>
<tr>
<td>W</td>
<td>Molecular weight</td>
<td>[kmol/kg]</td>
</tr>
<tr>
<td>$[X_i]$</td>
<td>Molar concentration of species $i$</td>
<td>[mol/m³]</td>
</tr>
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**Greek Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tbody>
<tr>
<td>$\Gamma$</td>
<td>Binary diffusion coefficient</td>
<td>[m²/s]</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>Scalar field variable</td>
<td>[-]</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Units</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Forward rate exponent</td>
<td>[-]</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Temperature exponent</td>
<td>[-]</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Thermal diffusivity</td>
<td>[m$^2$/s]</td>
</tr>
<tr>
<td>$\delta_{ij}$</td>
<td>Kronecker delta</td>
<td>[-]</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Turbulent eddy dissipation</td>
<td>[m$^2$/s$^3$]</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Equivalence ratio</td>
<td>[-]</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Viscosity</td>
<td>[kg/m s]</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
<td>[kg/m$^3$]</td>
</tr>
<tr>
<td>$\sigma_T$</td>
<td>Turbulent Prandtl number</td>
<td>[-]</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Backward rate exponent</td>
<td>[-]</td>
</tr>
</tbody>
</table>

**Superscripts**

- $n$ Time step
- $-$ Average

**Subscripts**

- $b$ Backward reaction
- $f$ Forward reaction
- $i, j, k$ Coordinate index
- $i$ Sample index
- $i$ Species index
- $j$ Reaction index
- $th$ Thermal
- $w$ Face value on west side of control volume
- $T$ Turbulent
- $W$ Cell centre value of control volume west side
- $WW$ Cell centre value of control volume two cells upwind

**ABBREVIATIONS**

- ADC Analog to digital converter
- ATBD Analog time burst detector
- BET Brunauer, Emmett, Teller (in connection with surface area measurements)
- CFB Circulating fluidized bed
- CFD Computational fluid dynamics
- CPU Central processing unit
- DFT Discrete Fourier transformation
- FID Flame ionization detector
- FDBD Fourier domain burst detector
- GHSV Gas hourly space velocity
- GT Gas turbine
- (T)HC (Total) Hydrocarbon
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
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<tbody>
<tr>
<td>KTH</td>
<td>Kungl. Tekniska Högskolan</td>
</tr>
<tr>
<td>LDA</td>
<td>Laser-Doppler anemometry</td>
</tr>
<tr>
<td>LNG</td>
<td>Liquefied natural gas</td>
</tr>
<tr>
<td>NDIR</td>
<td>Non-dispersive infrared</td>
</tr>
<tr>
<td>PCU</td>
<td>Pressure calibration unit</td>
</tr>
<tr>
<td>PPU</td>
<td>Parallel processing unit</td>
</tr>
<tr>
<td>RMS</td>
<td>Root mean square</td>
</tr>
<tr>
<td>RSA</td>
<td>Real time signal analyser</td>
</tr>
<tr>
<td>SCR</td>
<td>Selective catalytic reduction</td>
</tr>
<tr>
<td>SCNR</td>
<td>Selective non-catalytic reduction</td>
</tr>
<tr>
<td>SNR</td>
<td>Signal to noise ratio</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal conductivity detector</td>
</tr>
<tr>
<td>ULEV</td>
<td>Ultra-low emission vehicle</td>
</tr>
</tbody>
</table>

Catalysis: Heterogeneous catalysis, unless stated otherwise in the text
a.u.: Arbitrary units
1. INTRODUCTION

1.1 General Introduction

The rapid growth of the world-wide consumption of fossil fuels during the 20th century, mainly in industrialized countries, implies that these fuel sources will eventually have to be replaced (at least partly) by alternative ones. The development of modern power production facilities are nowadays dominantly driven by more and more stringent emission regulations, especially for nitrogen oxides (NOx), carbon monoxides (CO) and hydrocarbons (HC). At the same time, gas turbines have found their way into heat and power generation. Today, combustor performance is in the single-digit NOx region (in ppm) when using natural gas as a fuel, which represents a decrease of several orders of magnitude over the last decades.

Biomass has become a promising alternative for power production [Bridgwater, 1995; Klass, 1998; Forsberg, 2000]. For a gas turbine application, this solid fuel source has to be converted into a gaseous one, gasification is one possible way for this conversion. Typically gasified biomass has a low heating value, which is about 4-7 MJ/kg or roughly 10% of conventional fossil fuels. Maintaining stable combustion is a difficult task. Also, gasified biomass has a potentially high level of fuel-bound nitrogen in the form of ammonia (NH3). Under the aspect of low emission levels (especially low NOx emission levels), gasified biomass is a rather unattractive fuel for conventional flame combustion.

Catalytic combustion offers an elegant way to circumvent this difficulty. During the last few years, catalytic combustion of gaseous fuels has gained interest due to the fact that it offers a possibility for a stable combustion of low heating value gases, resulting in low conversion rates of fuel nitrogen to nitrogen oxide [Zwinkels et al., 1993]. By decreasing the activation energy, when compared to flame combustion, lean fuel-to-air mixtures can be burnt below the flammability limit. This avoids high peak-temperatures, which lead to the formation of thermal nitrogen oxides formed from the nitrogen contained in air. By choosing adequate catalysts, a high combustion efficiency can be achieved which in turn reduces emissions of CO and HC. A bottleneck may however be nitrogen compounds, which can be found in the fuel itself. Again, by choosing an adequate catalyst, a high conversion rate to molecular nitrogen may be achieved.

1.2 Background

1.2.1 The Role of Biomass in Power Generation

Public and commercial interest in renewable energy sources has steadily increased for several decades. International agreements such as the Kyoto Protocol, which was agreed upon in December 1997, have brought renewable sources for power generation
with the potential to reduce greenhouse gas emissions into the atmosphere to a wide public. Carbon dioxide is assumed to be one of the main contributors to the greenhouse effect. The emission reduction of this species is thus of major concern. Table 1-1 lists data from 1990, 1998 and the emission target for the some countries according to the Kyoto Protocol.

<table>
<thead>
<tr>
<th>Country</th>
<th>1990 emissions</th>
<th>Target according to Kyoto Protocol</th>
<th>1998 emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂ only Mt CO₂</td>
<td>Total GHGs Mt CO₂eq.</td>
<td>% 1990 Mt CO₂eq.</td>
</tr>
<tr>
<td>Austria</td>
<td>62</td>
<td>78</td>
<td>-13</td>
</tr>
<tr>
<td>Germany</td>
<td>1014</td>
<td>1215</td>
<td>-21</td>
</tr>
<tr>
<td>The Netherlands</td>
<td>168</td>
<td>219</td>
<td>-6</td>
</tr>
<tr>
<td>Spain</td>
<td>227</td>
<td>302</td>
<td>15</td>
</tr>
<tr>
<td>UK</td>
<td>584</td>
<td>720</td>
<td>-12.5</td>
</tr>
<tr>
<td>Rest of EU</td>
<td>1252</td>
<td>1601</td>
<td>-1.1</td>
</tr>
<tr>
<td>Total</td>
<td>3307</td>
<td>4135</td>
<td>-8</td>
</tr>
</tbody>
</table>

Table 1-1: Greenhouse gas (GHG) emissions of a several EU countries in 1990 and 1998. Kyoto emission targets in % of 1990, CO₂ equivalent, metric million tons [Grummer et al., 2000].

As a consequence from the Kyoto Protocol, several national programs have been launched in the European Union countries. One of these is the ALTENER 2 program that aims to increase the share of renewable energy sources in the power generation industry in the EU to 12 % by the year 2010 [Grummer et al., 2000]. This would save the amount 400 mio. metric tons of CO₂ per year by 2010. This shows the great potential biomass has to dramatically reduce the net emission of CO₂ from power generation processes. The carbon fixed in the plant matter has previously been absorbed from the earth atmosphere. A source of anthropogenic biomass related CO₂ emissions is associated with the transport of the raw material. An issue not to be forgotten.

This work focuses only on biomass, this term includes a wide selection of raw organic materials, such as wood and forest residues, by-products from the pulp industry, bagasse, straw, peat and agricultural waste. A large difference exists between the use of biomass in industrial and development countries. Biomass stands for about one third of the total energy consumption in Africa, while it is less than 1.5% of the total energy consumption in Europe (based on data from 1990) [Klass, 1997]. However this biomass is used inefficiently for cooking and heating purposes in rural area of developing countries [DIT, 1998]. By means of modern technologies, biomass can also be converted into a gaseous energy carrier. According to Hall [1993], the prospects are good that these energy carriers can be produced from biomass at competitive costs under several circumstances. From Fig. 1-1 the potential for the use of biomass in the generation of heat and power becomes clear. In the consumption of electricity, biomass plays already a significant role, seen on the right hand side of Fig. 1-1.
A similar diagram shows the role of biomass in energy supply for Sweden in Fig. 1-2. As already mentioned, a difference in the use of biomass exists both on an economical as well as a regional level. It is obvious that Scandinavian countries are in a fortunate situation for the implementation of alternative energy sources into the power generation.

Even though the potential to partly replace fossil fuels by biomass exists, this transition will not take place at an envisaged pace if the present market conditions for heat and power production remain unchanged [Kelly et al., 1993]. The financial benefit of such a conversion is too unrewarding for commercial companies to be of any appeal to make all necessary investments for further developing the renewable technologies. Kelly et al. [1993] have set up a number of policy initiatives in order to encourage the necessary investments and innovations for intensified use of renewable energy sources:

1. National straightening of institutions involved in the implementation of renewable energy programs.
2. International development funds for the energy sector should be directed to renewable energy sources.
3. Activities to encourage the development of a biomass industry have to be closely coordinated with the existing national agricultural development for restoring degraded lands.
4. Renewable energy technologies should be subsided at equivalent levels as competing fuel or subsidies for non-renewable fuels should be slowly decreased.

5. Taxes, regulations and other regulation instruments should be such that their evaluation is based on the full costs of the particular energy source, including environmental and external costs that are normally not reflected in the market price for fuels.

6. National government regulations of electric utilities have to be reviewed to ensure that investments made for new generating equipment in the “renewable” energy sector are consistent with an intensive sustainable future and that utilities are involved in programs to demonstrate new energy technologies in their service sector.

7. Finally, international corporation between various national research facilities as well as in the private sector should be intensified in order to increase efficient use of renewable energy sources.

It becomes clear from the above list that several of these issues have a strong political background and thus cannot become effective within a short period of time. As an example for issue 5), a CO$_2$ tax could be mentioned. Such a tax, as being applied in several countries world-wide, must be based on the net emissions of CO$_2$. If woody biomass is grown sustainably, this would be beneficial for the overall reduction of carbon dioxide emissions into the atmosphere. The amount of CO$_2$ emitted into the atmosphere during a combustion process is approximately equal to the amount that was absorbed from the atmosphere during growth by photosynthesis [de Jong et al., 1998]. This is a feature with a strong environmental significance in the strive of reducing CO$_2$ emission to combat the enhanced greenhouse effect. Transport issues must however be included in such a balance. The low energy content of biomass has to be compensated by increasing the amount of raw material used in the generation of heat and power.

It is obvious that industrialized countries should make use of their potential in the energy sector to provide development countries with knowledge and experience in this field. It is rather improbable that renewable energy technologies will be investigated in developing countries as problems like achieving a stable economy have a higher priority.

From the above, one can see that the issue of introducing biomass into the every day life is more complex than one might expect. Thus research and feasibility studies have to be intensified in order to clear the path for biomass.

1.2.2 Biomass Preparation and Thermochemical Conversion for Use in Power Generation

The combustion of solid fuels for a gas turbine application will inevitably cause severe problems in the turbine. Without any preparation solid fuels are not an option for gas turbines. In order to be able to use solid biomass as a fuel, this matter has to be converted into a combustible gas. This thermochemical conversion can be divided into three main groups, shown in Table 1-2.
Thermochemical conversion

<table>
<thead>
<tr>
<th>Combustion</th>
<th>Reactolysis</th>
<th>Pyrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partial oxidation gasification</td>
<td>Solvolysis</td>
<td>Hydrogenation</td>
</tr>
</tbody>
</table>

Table 1-2: Three groups of thermochemical conversion processes [Warnecke, 2000].

Gasification is part of the reactolysis section. For gasification, air or pure oxygen can be used as the oxidizing agent; hydrogenation (also called hydro-pyrolysis) is operated in a hydrogen atmosphere; if steam is used, the process is called solvolysis; for special processes, molten salts bed for example are used. Depending on the oxidizing agent, certain product gas characteristics are the result. These are listed in Table 1-3.

<table>
<thead>
<tr>
<th>Oxidizing agent</th>
<th>Pro</th>
<th>Contra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>Cheap</td>
<td>Low heating value of product gas</td>
</tr>
<tr>
<td>Oxygen</td>
<td>High heating value of product gas</td>
<td>Expensive</td>
</tr>
<tr>
<td>Steam</td>
<td>Cheap</td>
<td>Low carbon conversion</td>
</tr>
</tbody>
</table>

Table 1-3: Pro and contra of different oxidizing agents.

Due to its low costs, air is most commonly used as an oxidizer. The drawback of the low heating value has to be compensated by gasifying larger quantities of raw material.

Bridgwater [1991] has given the following statement to describe the driving force behind biomass gasification: “The objective is to convert or upgrade the biomass into a more useful and hence more valuable energy product which, in turn can be converted into an even more valuable end-product such as electricity or a motor fuel, and in all cases the carboniferous energy products are eventually converted into carbon dioxide in order to release the maximum amount of energy.”

Fig. 1-3 shows a process diagram for the conversion of wood-based biomass to electricity. It covers the full cycle, from harvesting and the biomass preparation, to the gasification and the final use as a fuel in a steam power plant.

The harvesting is a quite significant cost factor in the commercialization of biomass energy crops for use in power generation. Studies performed in the mid-80s have shown that cost effective harvesting should be done using equipment which can handle large amounts of small diameter trees (approx. up to 20 cm in diameter), i.e. resulting in fast growing trees as a biomass source [BIN, 1998]. Conventionally, an area within a 50-100 km radius around the gasification plant is considered to be a reasonable catchment area to keep transport costs at an acceptable level [Maier et al., 1997]. As large amounts of biomass may have to be supplied on a daily basis, this transport may have a strong environmental impact. Consequently, the gasification unit should be
placed in area with high occurrences of biomass in order to reduce transportation efforts. From this it becomes clear that a cost efficient use of biomass is only feasible in geographical regions with high availability of biomass. This issue is often neglected in the literature.

Fuel preparation includes such tasks as shredding the biomass to smaller particle sizes, and drying. As the water content of biomass can be up to 50%, e.g. freshly cut trees [BIN, 1998], the biomass has to be dried before entering the gasification process as water has a strong decreasing influence on the heating value of the biogas. Drying of the biomass is very often done by recovering waste heat from the power plant. More detailed information can be found at Salo et al. [1998] or Kopetz [1997]. If the raw biomass is not hacked, it is too inhomogeneous for a smooth and quick gasification or combustion [Mory, 1998]. Uniform size of the biomass feedstock improves gasification efficiency, so the raw material may have to be reduced in size. Obviously for material like sawdust, this is not necessary. Fuel feed systems include all types of conveyors (screw, drag, belt, pneumatic) and elevators, depending on the gasification type. Zefferer [1997] has reported severe damages done to the burner caused by rocks, wires and other iron parts, showing the need for intensive fuel preparation. The biomass may have to be pre-processed a second time before being fed into the actual gasification unit. This however depends on the requirements of the gasifier type for smooth operation.

Several types of difficulties have to be considered when storing biomass. Zefferer [1997] has reported problems in the long term storage of bark. In this case, bark was used as a fuel in a 6.5 MW\textsubscript{th} boiler for district heating purposes. The bark was delivered during summer months and had to be stored over the heating period up to one year. Biological processes in the bark piles lead to an ignition of the bark leading and possibly resulting in severe fires. He estimates that even without fires, biological processes in the bark piles cause an energy loss of 15% per year.

Schmidt et al. [1998] have reported difficulties with respect to the working environment during storage of wood chips. The growth of microflora (fungi and bacteria) can take place quickly after building up a pile of wood chips. Fungi propagate via microspores with a diameter of about 5 µm,

![Fig. 1-3: Process diagram for conversion of biomass to energy [BIN, 1998].](image-url)
inhalation of large quantities may result in affecting the respiratory system and cause allergic reactions. The total number and the growth rate of fungi and bacteria are the result of very complex structure and have to be considered carefully. Furthermore temperatures as high as 90°C could be measured in the wood pile only a few days after unloading. Similar problems occur during the storage of straw. Warnecke [2000] suggested that wood chips should not be stored longer than 14 days before final usage. It can be seen from this that storage is an important factor, which has to be regarded with attention. Other issues of concern with respect to storage are:

− storage size has be to be large enough to provide fuel for several days to overcome short periods like weekends, etc.,
− physical properties of the biomass,
− back-up capacity for storage,
− seasonal weather condition.

Various techniques exist for the gasification process, one characteristic criterion is the pressure as the process can take place, either at atmospheric or under pressurised condition. Capital costs are clearly higher for pressurised systems due to higher equipment and construction costs for the pressure equipment. Advantageous of pressurised systems is however that the product gas does not need to undergo any compression to enter the combustion system of a gas turbine for instance. Working pressure can be as high as up to 30 bar [Salo et al., 1998]. For certain applications, e. g. co-combustion of gasified biomass in furnaces or boilers, the quality of the product gas does not need to be as high as for gas turbine application. In this case atmospheric gasification can be the optimal solution. The most recent development in gasification technology is the fluid bed gasification. This has the advantage of excellent mixing between the biomass and the fluidizing material. Bed material is usually a silica sand. Warnecke [2000] compared a fixed bed and a fluidised bed reactor in his paper, drawing the conclusion that none of these types have any significant advantages over the other. Further information on gasification technologies can be found in Bain et al. [1995], Paisley et al. [1997], Waldheim et al. [1998], Klass [1997] and Bridgwater [1995].

The last step in the fluidised bed gasification procedure is the gas cleanup. A cyclone separates larger particles from the gas which are then returned into the bed. The tar which is created during the gasification process may be cracked to decompose heavy condensable hydrocarbons into lighter [Johansson, 1998]. This procedure improves the fuel gas properties. A common tar cracking catalyst is dolomite.

Hot gas cleanup by mechanical filters in pressurised gasification systems is a cleaning method at a near-commercial status [Newby et al., 1999]. Ceramic and metal candle filter are being used in several units, [Bridgwater, 1995]. Cold gas cleanup by water scrubbing removes aerosols and tars at the same time [Tidow, 1994]. The scrubbing has to cool down the product gas significantly in order to reach the condensation temperature of the tars between 200 and 500°C [Rensfelt, 1997]. Tars and particles can almost be completely removed with water scrubbing. Disadvantageous of this method is the handling and disposal of waste water, an issue not treated any further in this work.

Ash from conventional coal fired power plants is recycled in the building industry as an additive to cement. It has to be investigated in the future in how far ash from
biomass combustion can be used for this as well. Another option for ash disposal is the use as a fertilizer in the forest industry. However ash composition varies largely in its main elements Ca, K, Si, Na and Al. The main component CaO is usually present with 40%wt. Ashes resulting from gasification of agricultural products on the other hand usually contain silicates and alkalimetals. The final use of ashes therefore depends strongly on its composition, no general rule can be given on this issue.

1.2.3 Typical Fuel Properties of Gasified Biomass

Fuel gas properties depend heavily on the type of gasification as well as the raw biomass material. A typical composition of the product gas obtained by pressurised, fluidized bed gasification is given in Table 1-4 [Salo et al., 1998; McClosky, 1997]. For comparison reasons, the composition of solid bituminous coal, which is most commonly used for power station application, is given as well. The coal composition is given on a dry ash free basis. The product gas has a heating value in the range 4-7 MJ/m³, a typical value for gasified biomass. This rather low value can be explained by the high content of non-combustible components in the product gas, such as nitrogen, water vapour and carbon dioxide. Carbon conversion was between 83 and 99%. This pilot plant converts up to 13.3 MW of thermal input into a combustible gas, suitable for gas turbine combustion. The gasifier operates at pressures between 7 and 19 bar and at temperatures between 700°C and 900°C.

<table>
<thead>
<tr>
<th></th>
<th>Gasified Biomass (example only)</th>
<th>Bituminous coal a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>-</td>
<td>87.8 vol%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>-</td>
<td>10.5 vol%</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>9-18 vol%</td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>9-15 vol%</td>
<td>4.5 vol%</td>
</tr>
<tr>
<td>Methane</td>
<td>4-8 vol%</td>
<td></td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>15-19 vol%</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>46-57 vol%</td>
<td>1.9 vol%</td>
</tr>
<tr>
<td>Water vapor</td>
<td>9-20 vol%</td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>400-20000 ppmv</td>
<td>0.4 vol%</td>
</tr>
<tr>
<td>Total reduced sulphur</td>
<td>100-600 ppmv</td>
<td>0.4 vol%</td>
</tr>
<tr>
<td>HCl</td>
<td>10-460 ppmw</td>
<td></td>
</tr>
<tr>
<td>Alkaline (after filtering)</td>
<td>0.05-0.1 ppmw</td>
<td></td>
</tr>
<tr>
<td>Dust (after filtering)</td>
<td>&lt; 5 ppmw</td>
<td></td>
</tr>
<tr>
<td>Heavy tars</td>
<td>&lt; 140 ppmw</td>
<td></td>
</tr>
<tr>
<td>Light tars</td>
<td>4500-14000 ppmw</td>
<td></td>
</tr>
<tr>
<td>Lower heating value</td>
<td>4-7 MJ/m³</td>
<td>~24 MJ/kg b)</td>
</tr>
</tbody>
</table>

a) Example of Australian Blair Athol coal, dry ash free basis
b) based on ultimate coal analysis

Table 1-4: Typical product gas composition from pressurised, fluidized bed gasification using wood, forest residue, paper mill residue and straw as a fuel, reference for the coal [Salo et al., 1998; McClosky, 1997].
1.3 Combustion Emissions

The combustion process has been used to generate heat for several thousands of years. The chemical process behind combustion is probably one of the most studied reactions in chemistry. Problems arising with emissions have been known for a long time. Only during the last few decades however, public concern for reducing these emissions has risen.

Nitrogen oxides, carbon monoxide, hydrocarbons and soot are species of high interest to combustion. The term nitrogen oxide includes two different compounds: NO and NO₂. Both are conveniently merged to NOₓ. Sometimes, nitrous oxide (N₂O) is mistakenly counted as NOₓ. These species trigger reactions in the atmosphere that result in the production of ozone and acid rain. Nitrogen oxides are produced via different pathways. Thermal NOₓ is described by the Zeldovich mechanism, prompt NOₓ by the Fenimore mechanism and NOₓ resulting from fuel-bound nitrogen, called fuel-NOₓ [Prasard, 1984], see also Fig. 1-4. Formation of thermal NOₓ becomes significant at temperatures above 1500°C. Thermal NOₓ is avoided in catalytic combustion by keeping the temperature below critical values. Prompt NOₓ is formed by the formation of nitrogen oxide via fast radial reactions between hydrocarbons from the fuel and atmospheric nitrogen in hydrocarbon flames. Catalytic combustors commonly use well-premixed lean fuel/air mixtures to limit the maximum combustion temperature, no prompt NOₓ is formed. The third and last route, fuel-NOₓ, is of special importance for gasified biomass. This type of nitrogen oxide is formed via the oxidation of nitrogen-containing compounds of the fuel. These fuel-bound nitrogen species react via several intermediate reactions further, described by Glassman [1996]. It is assumed that these intermediate steps start with the thermal decomposition of fuel-N species upstream of the combustion zone [Johansson, 1998]. Most common fuel-N species are: NH₃, NH₂, NH, HCN and CN. In contrast to thermal NOₓ, there is only a weak dependency on temperature. Five major pathways exist for the formation of fixed nitrogen, sum of NHi and NOₓ [Prasad, 1984], shown in Fig. 1-4. For the sake of completeness, thermal and prompt NOₓ pathways are also shown in the figure.

Fig. 1-4: Major path for fixed nitrogen formation and conversion [Prasad, 1984].
Hydrocarbon emission is a direct result of incomplete combustion, which lowers the overall efficiency.

Emissions of CO are another direct result of incomplete combustion. Thus by optimizing the combustion efficiency, CO emissions can be kept at acceptable levels. Poor burner design or badly chosen air-to-fuel ratios are often the cause for high emission levels. Another option to decrease CO levels in the exhaust gases is to increase the combustion temperature, which has a negative effect on the emissions of thermal NO\textsubscript{x}. A tradeoff is necessary for acceptable CO and NO\textsubscript{x} emissions. This tradeoff is illustrated in \textit{Fig. 1-5}.

\begin{center}
\textit{Fig. 1-5: Schematic concentration of thermal NO\textsubscript{x} and CO in arbitrary units vs. combustion temperature \cite{Zwinkels, 1996}.}
\end{center}

As the combustion temperature increases, the level of CO in the emissions decreases while the amount of thermal NO\textsubscript{x} present in the exhaust gases increases. This diagram has to be understood in a schematic way, it should only illustrate that a temperature zone exists, at which acceptable levels of thermal NO\textsubscript{x} and of CO may be achieved. The intersection of the two lines varies depends of course on the scaling factor of both ordinates. The conclusion from the above figure that the optimum working point in terms NO\textsubscript{x} and CO emission for this specific combustion system lies at an adiabatic flame temperature of 1600 K cannot be drawn. In a further discussion of the environmentally harmful effects of both NO\textsubscript{x} and CO, their toxicity should be included.
2. OVERVIEW OF CATALYTIC COMBUSTION

2.1 Introduction

The CRC Handbook of Chemistry and Physics [1981] gives the following definition of a catalytic agent: “A substance which by its mere presence alters the velocity of a reaction, and may be recovered unaltered in nature or amount at the end of the reaction.” The benefit of catalysis for combustion application lies in one of its characteristics. Since a catalyst establishes a different reaction pathway at a lower activation energy, the reaction can take place at lower temperatures. Hence combustion can take place at temperatures lower than in a homogeneous gas-phase reaction.

Catalysis can be classified in several ways. Either by the phase in which the catalyst and the reactants are present or by the nature of the catalyst. Homogeneous catalysis implies that the catalyst and the reactants are present in the same phase. Homogeneous catalytic processes in the chemical industry are most commonly of the liquid-liquid type with water being the solvent for the catalyst and the reactants. This type of catalysis has relatively little significance in industrial processes. In heterogeneous catalysis, the system consists of two or more phases. The latter form is the one applied within this project, therefore homogeneous catalysis will not be treated any further. Enzymes are a type of catalysts that do not fit in neither class, they represent an intermediate class. In the following the term catalysis always refers to heterogeneous catalysis unless stated otherwise.

2.2 Some Fundamentals of High Temperature Catalysis for Gas Turbines

Prasad et al. [1984] has summarised the requirements for the application of catalytic combustion in a gas turbine to be the following:
- ignition of the fuel/air mixture at typical compressor outlet temperatures,
- high catalyst activity to maintain complete conversion of fuel into thermal energy,
- low pressure drop over the catalyst,
- thermal shock resistance,
- retention of high specific surface area and catalytic activity under high temperatures of operation.

A single substance is not able to fulfill all the above mentioned demands. A typical high temperature catalyst used in gas turbine combustion applications usually consists of three main components: the support, the washcoat and the active material.
The support
A mechanical support is the base for a high efficiency catalytic combustion system. In order to minimize the pressure drop over the system, usually a honeycomb structure is used in gas turbine applications [Zwinkels et al., 1996]. Honeycombs offer large area to volume ratios, allowing high throughputs at low pressure drops. Further requirements of the support are a high thermal shock resistance, low thermal expansion and chemically inert to combustion gases. The monolith material should have a porosity of 30-40% with large pores of a diameter of 5-15µm to obtain the proper surface for adhesion of a washcoat (see next section) [Thevenin, 1997]. Table 2-1 gives an overview of the most commonly used materials for supports.

<table>
<thead>
<tr>
<th>Material</th>
<th>Properties</th>
</tr>
</thead>
</table>
| Cordierite (2MgO•2Al₂O₃•5SiO₂) | - low thermal expansion  
                          | - low costs for the material  
                          | - high thermal shock resistance |
| Alumina (Al₂O₃)       | - high temperature stability  
                          | - suitable for operation below 1000 K, as large specific surface area decreases above that temperature |
| Mullite (3Al₂•2SiO₂)  | - good thermal stability at higher temperatures |
| Magnesia (MgO)        | - good thermal stability  
                          | - high specific surface area |
| Zirconia (ZrO₂)       | - high thermal stability, can even be used above 1300 K |
| Silicon Carbide (SiC) | - high temperature stability |
| NZP (Na₂O-Zr₂O-P₂O₅-SiO₂) | - low thermal expansion  
                          | - good thermal shock resistance |
| FeCr Alloy            | - allow low pressure drop  
                          | - low sensitivity to vibrations  
                          | - allow even temperature distribution inside the catalyst due to high conductivity  
                          | - maximum operating temperature approx. 1300 K |

Table 2-1: Overview of most commonly used support materials [Johansson, 1998].

Corderite and mullite based catalysts are most commonly used for high temperature catalytic combustion due to their low costs and relatively good thermal stability. The melting temperature of Corderite is specified by the manufacturer to be approximately 1350°C [Corning, 1996]. Trimm [1983] gives the maximum allowable temperature of mullite to be approx. 1350°C. Fig. 2-1 shows a schematic of monolithic catalyst.

![Fig. 2-1: Schematic of a monolithic catalyst [Jackson, 2001].](image-url)
Metallic monolith materials have been used for automotive catalytic systems. The advantages of metallic monoliths are the high heat conductivity and the strong resistance to mechanical stresses. Problematic however is the application of a washcoat and the active material as well as the operation at temperatures above 1300°C [Zwinkels, 1996].

The washcoat and the active material

The washcoat is applied onto the surface of the mechanical support to provide a large specific surface area that has to be maintained at high temperatures. Thermal expansion of the washcoat must not differ much from the support material as this would cause separation of the components under combustion conditions [Berg, 1996].

Certain types of washcoats already have a catalytic activity, such as hexaaluminates. These are promising types of materials for washcoating a support for a combustion application. Even though they are disadvantageous with respect to a high thermal expansion, they are advantageous in terms of their resistance to sintering and their activity. Hexaaluminates can be described by the general formula \( AB_xAl_{12-x}O_{19} \) with the A being possibly an alkali, alkaline earth or a rare earth metal and the B being a metal with similar characteristics to Al in size and charge as the Al-ion [Johansson, 1998]. A good review of the present state of the art in the use of hexaaluminate is given by Groppi et al. [1997]. Several ions have been investigated for the A and B position in the general formula for hexaaluminates. Machida et al. [1989] has found that the B position seems to have the stronger effect on the activity of the hexaaluminate materials. For a BaMA11O19 (M being a transition metal) the trend

\[
\text{Mn} = \text{Cu} > \text{Fe} = \text{Ni} = \text{Cr} = \text{Co}
\]

(Mn and Cu having higher activity than Fe, which has a higher activity than Ni, etc.) was found for methane combustion, the effect was measured at a temperature corresponding to 10% conversion. This could be reproduced also for LaMA11O19. The influence of the A position has been investigated by Inoue et al. [1996], Ramesh et al. [1997] and Machida et al. [1990]. These research groups have found that addition of Pr, Nd, Sm or Gd can improve the catalytic activity for methane combustion in the low temperature region of a Sr1-xLnxMnAl11O19 washcoat.

If the catalytic activity for methane oxidation of any hexaaluminate is compared to the one of a noble metal such as Pd (see below), it is found to be rather low. However the reactivity for other fuels such as CO and H2, which are a component of gasified biomass, is high. As the ignition temperature for these compounds is at typical compressor outlet temperatures, hexaaluminate becomes an attractive material for catalytic combustion of gasified biomass.

Platinum metals group (PMG), Ru, Rh, Pd, Os, Ir and Pt have shown a high performance in oxidizing typical components of gasified biomass, such as CO, HCs and H2. This high activity makes them preferable for high temperature catalytic combustion in gas turbines. The activity chain for PMG is the following [Prasad et al., 1984]:

\[
\text{Pt} > \text{Ir} > \text{Os} > \text{Pd} > \text{Rh} > \text{Ru}.
\]
Disadvantageous is the volatility of several of these elements, so that only Pt, Pd and Rh can be used as active materials in catalytic combustion. Pd is most commonly used in catalytic combustion due to its enhanced thermal stability compared to Pt and its high reactivity for CH$_4$ combustion. At temperatures below approx. 970 K, palladium is present as PdO. As the temperature increases, a reversible reduction to metallic Pd takes place, resulting in a decrease of activity [Johansson, 1998]. As the temperature increases further, the activity of metallic Pd exceeds that of PdO. Pt on the other hand has a higher activity for CO and saturated hydrocarbons. It could rashly be concluded that a combination of Pd and Pt would be the optimal solution. However, problems with these two elements occur in the form of sintering (loss of active surface area) and evaporation at high temperatures resulting in a deactivation of the catalyst. This is a main obstacle in the development of catalytic combustor and intensive research is being performed to solve this problem. Additionally, platinum and palladium also are expensive noble metals, a fact that has to be kept in mind by catalyst developers. In January 1996, one gram of Pt was priced at US$13, about the price of gold at that time. Palladium was sold at a price of US$4.5 per gram [CRC Handbook of Chemistry and Physics, 2001]. Due to the demand of palladium from the chemical industry, the prices of these noble metals have approached each other.

Single-metal oxides have been investigated for combustion of methane. Advantageous of this type of active material is that they maintain a high surface area at temperatures of about 950°C [McCarty et al., 1997]. The activity of the compounds decreases in the following order:

$$\text{PdO} > \text{RuO}_2 > \text{CoO}_4 > \text{CuO} > \text{NiO} > \text{Mn}_2\text{O}_3 > \text{Cr}_2\text{O}_3.$$  

These single-metal oxides could be an alternative to PMGs, however if these oxides are chosen, care has to be taken to avoid vaporization by keeping the catalyst temperature below 1000°C.

Another group of materials which can be used as actives materials are perovskites. These can be described by the general formula ABO$_3$. The A and B positions have to be filled with a cation, with A usually being Sr, Ca or Al and B being Mn, Ti or Al. A and B differ in their position in the lattice structure. Their high catalytic activity and high thermal resistance makes them attractive catalyst in combustion applications. However, as Lowe et al. [1994] have found out, the surface area of these materials is not high enough for an application in high temperature combustion. Also, thermal stability is not as good as the one of hexaaluminates.

Literature on this subject is numerous, more detailed information can for example be found in Johansson, [1998], Zwinkels et al. [1993], Thevenin [1997] and Berg [1996].
2.3 Catalyst Deactivation

One of the key interests in the development and industrial acceptance of catalytic combustion for a gas turbine application is the lifetime of the catalyst. This issue is also one of the bottlenecks in the economy of catalytic combustion. One of the mechanisms for catalyst deactivation is sintering which can occur in either the active phase or in the washcoat. The second type of deactivation processes is poisoning.

In the case of sintering occurring in the active material, its crystal structure changes towards larger and better defined crystals [Heck et al., 1995] resulting in fewer active sites being exposed to the reactants. Consequently, the catalyst activity decreases. Certain rare earth oxides can be used for active material stabilization. Cerium dioxide (CeO₂) and La₂O₃ have successfully been used to suppress sintering of Pt [Heck et al., 1995]. In the case of pore sintering a formerly chemically controlled reaction will become controlled by the mass diffusion into the pore resulting in a continuous decrease of the activity of the catalyst. If a pore is completely sintered, i.e. the pore is completely enclosed, the active material is no longer accessible for reactants.

Catalyst poisons act directly on the active phase, either by directly reacting with the active material (selective poisoning) or as deposits onto the carrier (e.g. burying the active material underneath). Selective poisons react with the active site to form a catalytically inactive species (e.g. Pb, Hg, Cd) while other adsorb onto an active site and block this site from further reactions (e.g. SO₂ on Pt). These poisons are often present in the fuel. Masking results from deposits of aerosols or other high molecular weight compounds present in the fuel, e.g. soot onto the washcoat. Masking can become so distinct, that the bulk mass transfer is obstructed.

2.4 Catalysis in Gas Turbines for the Generation of Heat and Power –
State of the Art

The application of catalytic combustion in the generation of heat and power is versatile. Three main groups can be distinguished [Forzatti et al., 1999].
1. Non-adiabatic premixed systems, these are under development for domestic burners and smaller compact chemical reactor heaters.
2. Non-adiabatic diffusive catalytic combustion systems used in radiative heaters
3. Adiabatic lean premixed catalytic combustion for power generation in gas turbines.
This work focuses on the last group of these three.

If a catalyst is to be used for a combustion application in a modern gas turbine, it has to satisfy several requirements to be competitive in today’s energy market. Forzatti et al. [1999] have summarized the requirements a gas turbine combustion chamber has to fulfill.
Design criteria and operating conditions

<p>| | | |</p>
<table>
<thead>
<tr>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet temperature</td>
<td>550-750 K</td>
<td>Residence time</td>
</tr>
<tr>
<td>Outlet temperature</td>
<td>1300-1500 K</td>
<td>Pressure drop</td>
</tr>
<tr>
<td>Operating pressure</td>
<td>10-20 bar</td>
<td>Catalyst lifetime</td>
</tr>
<tr>
<td>Mass flow</td>
<td>100-200 kg/s</td>
<td></td>
</tr>
</tbody>
</table>

Table 2-2: Operating conditions and design criteria for a combustion chamber of a conventional stationary gas turbine [Forzatti et al., 1999].

Its ability to ignite the fuel / air mixture at compressor outlet temperatures is crucial for successful catalyst operation. This implies high catalytic activity to start up the oxidation process. If a pilot flame has to be used to reach the ignition temperature at which the oxidation is initiated by the catalyst, careful design of the pilot flame is needed as this can produce a significant amount of thermal NOx, nullifying the low-emission potential of catalytic combustion. The maximum allowable turbine inlet temperature limits the combustor outlet temperature. In a gas turbine equipped with a flame combustion system, the combustor exhaust gases have to be cooled in order to decrease thermal loading of the nozzle guide vanes and turbine blades.

The design of a catalytic combustion chamber can be divided into two main groups as schematically shown in Fig. 2-2. Type I consists of a combustion chamber that is based on complete oxidation of the fuel only by means of one or several catalysts. Type II is a so-called hybrid combustion chamber in which the combustion process is completed by homogenous gas phase reactions downstream of the last catalyst segment. In the following a short description and some examples of these two main groups is given.

- **Type I: Fully catalytic combustion by multiple segments.** The premixed air / fuel stream is oxidized by a set of catalytically active monoliths. No noteworthy fuel oxidation should occur downstream of the last segment. Sadamori et al. [1995] and Sadamori [1999] demonstrated such a system using natural gas as the gas turbine fuel. In their study, highly active noble metal catalysts have been used as the first segments in order to initiate the oxidation at a low inlet temperature. The implementation of a pilot flame for start-up procedure is hence unnecessary. A prototype catalytic combustion chamber was tested in a 160 kW gas turbine test rig. During a total of 200 h of running time, NOx emissions between 10 and 17 ppm were demonstrated. Maximum combustor outlet temperatures of 1200°C were achieved. Such temperatures are however too low for today’s high-efficiency turbines which require turbine inlet temperatures of at least 1300°C. The difficulty of finding suitable materials maintaining high catalytic activity and thermal stability under prolonged exposure times above 1300°C has yet to be solved. Still, such an approach would be favourable one due to its low complexity once the obstacle of the lifetime can be solved.

- **Type IIa: Hybrid combustion using inactive channels.** Similar to Type I, fuel and air are premixed before entering the first segment. Selected channels of the monolith support have not been supplied with active phase. This feature limits
the heat release inside the catalyst and thus its operating temperature. The unburnt fuel is oxidized downstream of the last segment in a homogeneous reaction zone. Results of such an arrangement have been reported by Cutrone [1997] in a General Electric gas turbine using catalysts manufactured by Catalytica Combustion System Inc. In this case the catalysts were in form of metallic nets. Combustor outlet temperatures of up to 1400°C and at the same time keeping the catalyst temperatures below 1000°C were demonstrated. Clearly, this configuration has the advantage of reducing the operating temperature of the catalyst, thus increasing the lifetime of the catalyst.

- **Type IIb: Hybrid combustion using secondary fuel / air.** Furuya [1995] has proposed this design. In difference to Type IIa, secondary fuel / air is introduced into the region downstream of the last catalyst segment. Furuya [1995] injected pure fuel downstream of a Pd / Al₂O₃ cordierite catalyst. The disadvantage of such a design is the difficulty of achieving a homogeneous mixture of fuel and air in the post-catalytic reaction zone. Advantageous is again the possibility to keep the catalyst temperature low enough to avoid deterioration. In a similar arrangement Ozawa et al. [1998] report tests using a 10 MW multi-can gas turbine using liquid natural gas as fuel. Using a secondary fuel / air mixture, catalyst bed temperature could be kept between 700 and 800°C with the ignition temperature being 360°C. Combustor outlet temperatures as high as 1390°C at 13 bar pressure could be realized. A Pt/Pd/Rh-based cordierite honeycomb catalyst has been used in those tests. NOₓ levels below 5 ppm were measured.

![Fig. 2-2: Different catalytic combustor design concepts [Johansson, 1998].](image)

As catalytic combustion for gas turbine application has been commercialized only recently, rather little information on the commercial state of the art is available in the literature. A few examples can be listed.

Catalytica Combustion Systems Inc. (CCSI) should be mentioned here. They introduced a catalytic combustion system called Xonon. Intensive tests on a 1.5 MW Kawasaki gas turbine have demonstrated NOₓ emission levels of less than 3 ppm and less than 10 ppm CO and HC over a wide range of operating conditions [Yee et al., 2000]. Dalla Betta [1998] concludes that for gas turbine application with less than
5 ppm NO\textsubscript{x}, catalytic combustion should be the lowest cost and hence the preferred technology. This result was achieved by comparison of total costs including capital and operational cost over a 15 year period for lean premixed combustion, water and steam injection and selective catalytic reduction (SCR).

General Electric [Cutrone et al., 1997] has performed catalytic combustion tests on a MS9001E gas turbine, also using CCSI’s Xonon combustion system. The combustor has been operated at base load with an outlet temperature of 1190°C. At base load, 3.3 ppm NO\textsubscript{x}, 2 ppm CO and 0 ppm HC were achieved. The combustor consisted of a multi segment combustor with full burn out in a post-catalytic reaction zone. The homogeneous reaction zone allowed low temperatures in the metallic catalyst while enabling the intended turbine inlet temperature. Combustor dynamics were reported to be of negligible magnitude.

Solar Turbines Inc. is developing in the research program titled “Advanced Turbine Systems” a high thermal efficiency gas turbines with emission level in the single digit ppm-region [Dutta et al., 1997]. Similar to the General Electric approach Solar Turbines uses a multi segment catalytic combustor with complete burn out of the fuel in a post-catalytic reaction zone. Dutta et al. [1997] report emission levels of less than 5 ppm NO\textsubscript{x}, 8 ppm CO and 5 ppm HC in a medium pressure ratio, 9 bar recuperated gas turbine.

Pratt & Whitney Canada has given out a press release in April 1998 stating the planned tests of the CCSI’s catalytic combustion Xonon system in a ST18 and a ST30 gas turbine. These systems are to be introduced in year 2001 [Pratt & Whitney Canada, 1998].

Lipinski et al. [1998] have reported successful tests of a catalytic combustor for an automotive application. Those tests were performed as part of Allied Signal efforts for a hybrid electric vehicle to meet the ULEV standards. A small-scale gas turbine has been used for these experiments. It was shown that the NO\textsubscript{x} emission level was purely a function of the amount of fuel-bound nitrogen. Diesel fuel DF-2 was used for engine testing. The combustor is designed as multiple discs mounted in series, each one supported on a ceramic honeycomb structure. No information about the washcoat and the active material was reported. For DF-2, at a combustor outlet temperature of 1013°C, 6 ppm NO\textsubscript{x}, 97 ppm CO and 1 ppm HC were measured at the outlet. Emission measurements in a combustor test rig showed higher levels, revealing that CO and HC oxidized in the ducts of downstream of the turbine inlet.
3. OBJECTIVES

As the potential of biomass as a fuel source has gradually been recognized, various techniques have been developed for the efficient use of biomass in the power generation industry. Advance gasification techniques allow converting the solid biomass into a gaseous energy carrier. By means of catalytic combustion this gaseous fuel can be oxidized. The technique allows shifting the fuel-to-air ratio beyond the limits of flammability. A stable reaction process can thus be established under conditions at which a conventional flame combustion system could not be operated in a controllable manner. As a consequence, pollutant production can be reduced. By carefully choosing the proper catalysts, emission levels of nitrogen oxides, carbon monoxide and hydrocarbons can be kept at ultra-low levels, i.e. in the single digit region. Furthermore, engine dynamics in the form of vibration and noise is reduced substantially (compared to flame combustion).

The overall objective is to investigate the feasibility of firing a gas turbine equipped with a catalytic combustion chamber using a low heating value gas obtained from gasification of biomass. If a catalytic combustion system should replace a flame combustor, the catalyst must have certain characteristics.

The detailed objective of the present study is to manufacture a pilot-scale test facility suitable for investigating different catalyst arrangements. One of the aims is to develop and test promising catalyst compositions in a laboratory bench-scale rig under atmospheric conditions. A detailed objective is to study catalytic combustion at atmospheric and pressurized conditions. A suitable data acquisition system is needed for gas analysis, temperature and pressure measurements. A non-reacting, ambient condition test facility is required for achieving the objective of a spatially uniform flow field at the inlet of the catalyst segment(s). The catalytic segments must be able to initiate the combustion process without the use of a pilot flame, i.e. high catalytic activity is required. The fuel gas should resemble a fuel derived from wood gasification. One of the typical features of such a fuel is a low heating value.

A further objective is whether or not low emission levels for nitrogen oxides, carbon monoxide and hydrocarbons can be achieved by catalytic combustion is, and to investigate the lifetime of the catalyst in terms of its activity.
4. APPROACH

In order to achieve a maximum catalytic combustion efficiency, a uniform velocity profile over the cross-section of the flow tube is required. Non-uniform spatial velocity profiles, which should be minimized, would cause non-uniform thermal loads in the monolith. An inhomogeneous mixture of fuel and air at the catalyst inlet would cause the same consequences.

A cold flow test facility was designed to investigate and optimize the flow field in the mixing zone to meet the above mentioned requirements. The test facility had to be suitable for velocity measurements using laser-Doppler anemometry as well as measurements of the mixing quality using a mass spectrometer and a tracer gas to simulate the fuel. An optical access enabled using an available 2D-LDA for velocity measurements in the mixing zone between the fuel injection head and the installed catalyst monolith. A first design of the fuel injection head was made. Tracer gas concentration measurements were performed to investigate the mixing quality of the simulated fuel and air.

In parallel, CFD calculations were performed to study:
- the mixing process of fuel and air in the fuel injection system,
- the auto-ignition of the air / fuel mixture,
- the flow field in the mixing zone between the fuel injection head and the catalyst inlet.

Based upon these results, a combustion test facility has been designed and manufactured. The combustion rig is instrumented with thermocouples and pressure taps to obtain information of the flow properties. Gas sampling devices both upstream and downstream of the combustion chamber provide the necessary gas samples to study emission levels and fuel composition.

As manufacturing of the catalyst is both time and money consuming, the following iterative procedure was chosen to minimize the risk of damages:
- mount one catalyst intended to work as the first segment in a staged combustor and place several thermocouples inside the segment for close monitoring
- run first atmospheric and then pressurised tests under varying conditions; ignition of the catalyst can be triggered by increasing the air temperature with electric preheaters
- mount a second catalyst into the test facility and repeat the procedure
- increase the number of segments and repeat the procedure

Since the total number of thermocouples in the combustor is limited, a compromise has to be made between placing them inside a segment, between two segments and / or downstream of the catalysts.

The fuel gas composition has to be closely monitored during the experiment in order to associate temperature and / or emission composition changes of the catalytic combustor with the corresponding fuel gas.
5. TEST FACILITIES AND IMPLEMENTATION

5.1 Introduction

Two test facilities have been designed and manufactured. An ambient temperature test rig to investigate the flow field under non-reacting conditions has been designed as one of the first steps during this study. The objective of the cold flow test facility was to optimize the velocity profile at the inlet of the catalyst and to achieve a homogeneous mixture of fuel and air. Both these parameters strongly determine the combustion efficiency and have therefore to be investigated with great care. Reynolds similarity and geometrical similarity assure transferability to the final combustion rig. Uneven conversion rates of the fuel in the catalyst would lead to thermal stresses in the brittle support material.

The combustion test facility allows testing various catalyst arrangements and compositions under different operating conditions. This will give detailed information about the possibility to use a low heating value fuel gas for catalytic combustion systems.

In the following, the design calculations with respect to auto-ignition and flashback risk are being explained, after that the two test facilities and the applied measurement techniques are described.

5.2 Weak Flammability as Design Criterion

The flammability limits for a mixture of \( n \) combustible components \((i=1,\ldots,n)\) can be calculated by applying Le Chatelier’s law [Heffington, 1978]:

\[
F_{\text{lean}} = \frac{100}{\sum_i \frac{c_i}{F_{i,\text{lean}}}} \quad (5-1)
\]

where \( c_i \) is the concentration and \( F_i \) the flammability limit of the species \( i \). With this equation the lower flammability limit has been calculated for two different fuel compositions, listed in Table 5-1. Johansson [1998] used the gas composition listed in the second column of the table for catalyst development in bench-scale in a previous work. The fuel gas composition listed in the fourth column should be seen as the upper limit in terms of content of combustible species for the fuel used in this investigation.
<table>
<thead>
<tr>
<th>Species</th>
<th>$c_i$ [%]</th>
<th>$F_{i,\text{lean}}$ [%]</th>
<th>$c_i$ [%]</th>
<th>$F_{i,\text{lean}}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_2\text{H}_2$</td>
<td>1</td>
<td>2.5</td>
<td>1</td>
<td>2.5</td>
</tr>
<tr>
<td>$\text{CH}_4$</td>
<td>4.6</td>
<td>5</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>CO</td>
<td>14.7</td>
<td>12.5</td>
<td>18</td>
<td>12.5</td>
</tr>
<tr>
<td>H$_2$</td>
<td>10.2</td>
<td>4</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_8$</td>
<td>2</td>
<td>2.1</td>
<td>3</td>
<td>2.1</td>
</tr>
<tr>
<td>$F_{\text{lean}} = 16.67 %$</td>
<td>$F_{\text{lean}} = 10.56 %$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Table 5-1*: Lower flammability limits of main fuel species and for two different compositions [Glassman, 1996].

Heffington [1978] investigated the flammability limits of a low heating value gas derived from coal gasification of subbituminous coal (black lignite) in an air blown gasifier. The resulting fuel gas consisted of 17.3% H$_2$, 14.7% CO, 3.3% CH$_4$, 0.6% HC, 0.1% H$_2$S, 51.6% N$_2$-Ar, 12.4% CO$_2$ resulting in a higher heating value of 5.33 MJ/Nm$^3$. This value is somewhat lower but similar to the value for the fuel gas in this study. Heffington [1978] obtained the lower limit of flammability to be 17% and the upper limit to be 62% assuming the validity of Le Chatelier’s law.

Since all experiments will be performed at conditions leaner than the lower flammability limit calculated in *Table 5-1* and also given for a similar fuel by Heffington [1978], no difficulties with auto-ignition are to be expected.

### 5.3 Auto-Ignition Time and Flashback Risk as Design Criteria

The work presented in this paragraph has been performed as part of a diploma thesis. Therefore only a summary is given here. Detailed information on this issue can be obtained in Hopmans [1997].

Auto-ignition and flashback present serious safety risks for the operation of any combustion facility. In term of flashback the turbulent flame speed is of interest.

The bulk velocity of the flow has to be high enough to prevent a flame from stabilizing in the mixing section between the fuel injection point and the inlet of the catalyst. Furthermore the residence time of the fuel in the mixing section has to be lower than the auto-ignition time. Also, the bulk flow velocity has to be low enough in order to assure both homogenous mixing of the fuel with the air and an adequate residence time of the fuel inside the catalyst. Due to the lack of experimental data, an approximation for calculating the spontaneous auto-ignition delay time according to equation (5-2) was used [Lefebvre, 1983]:

\[
\begin{align*}
\tau_{\text{ignition}} = & \frac{4.66 \cdot 10^8 \cdot \exp \left( \frac{9160}{T_{\text{mixture}}} \right)}{\rho_{\text{Air}} \cdot \Phi}.
\end{align*}
\]  

(5-2)
This equation was derived for gaseous fuels with fuel equivalence ratios $\phi$ not less than 0.5. In the present project, however, ratios around 0.3 and 0.4 were intended to be used. Hence eq. (5-2) can only serve as a rough approximation. The calculated auto-ignition delay time after eq. (5-2), estimated for a temperature of the fuel / air mixture of 623 K, is shown in Table 5-2.

<table>
<thead>
<tr>
<th>Fuel equivalence ratio</th>
<th>$t_{\text{ignition}}$ [s]</th>
<th>Residence time [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>0.168</td>
<td>0.012</td>
</tr>
<tr>
<td>0.4</td>
<td>0.126</td>
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</tbody>
</table>

*Table 5-2: Estimated auto-ignition delay time at design point.*

The residence time of the fuel / air mixture has been calculated with a bulk velocity of the flow of 12 m/s and the constraint of a short mixing length of 15 cm. As the residence time is one magnitude smaller than the auto-ignition delay time, no auto-ignition difficulties are expected.

A calculation of the turbulent flame speed has been made using a turbulent flame propagation model described by Andrews et al. [1975]. Based upon a turbulence level of 5% (see next section), a macroscopic length scale of turbulence of 1.7 mm (diameter of an open passage in the fuel injection system, see next section) and thermodynamic data for the fuel / air mixture, the turbulent flame speed was calculated to be 2.0 m/s. The bulk flow velocity is clearly above this value. Hence it could be expected that flame stabilization was not possible. Again it has to be kept in mind that also this result can only be seen as a rough approximation.

### 5.4 Cold Flow Test Facility

Three different scenarios have been considered to transfer experimental results obtained in the cold flow test facility to the combustion test facility:

- Bulk flow velocity similarity
- Reynolds similarity
- Constant pressure drop

Based upon fixed parameters such as the diameter of the flow tube (due to monolith manufacturer specifications), maximum available mass flows delivered by the wind tunnel facility and pressure, the different scenarios were used to estimate the operating conditions for the cold flow test facility. All calculations were performed with air properties and the ideal gas assumption. This led to Reynolds similarity criterion to ensure transferability of the test results between the two test facilities. Also, as the dominating mixing process of fuel and air is turbulent mixing, Reynolds similarity is the preferred criteria.

A schematic view of the cold flow test section can be seen in Fig. 5-1. The cold flow test rig is connected to a fan, which sucks laboratory air through the test section.
Fig. 5-1: Schematic and photo of the cold flow test section.

Note the terms ‘fuel flow’ and ‘fuel supply tube’ in Fig. 5-1. As no combustion tests were performed in this test facility, air was blown by a separate fan through the fuel supply tube. The term ‘fuel’ in this context is used to improve clarity and comprehensibility. An orifice was used to measure the mass flow through the fuel supply tube.

A turbulence grid, calculated after Roach [1983], provides the inflowing air with a 5% turbulence level. This value has been chosen as it represents a typical value for the turbulence intensity at the compressor outlet of a gas turbine. The air passes through the fuel injection geometry, in which the fuel is introduced to the flow in the combustion test facility. After passing through the mixing section, the air enters the catalytic monolith.

The test facility is equipped with a traversable gas-sampling probe, which is connected to a gas analysis system, allowing measurements of mixing quality of fuel and air. A tracer gas was added to the flow through the fuel supply tube. By gas sampling at different radial positions, a profile for the relative tracer gas concentration was obtained, revealing information how fast mixing takes place. Helium and methane were used as tracer gases. These two gases were chosen in order to take different diffusivities into account.

The influence of the angular setting of the fuel injection system could be studied by rotating the fuel head. By moving the fuel head along the main axis, the mixing length could be changed. More information about this test facility is given in the following section as well as in Jacoby et al. [1998].

5.4.1 Fuel Injection System

The design of the fuel injection head is decisive for meeting the two major flow criteria mentioned in section 5.1. The mixing of fuel and air should be fast and result in a uniform mixture at the inlet of the monolith. A large pressure drop across the fuel injection system assures good mixing of fuel and air. On the other hand, this is undesirable in a gas turbine as it lowers the efficiency. Second, the velocity profile at the inlet of the monolith should be spatially flat.
A first fuel injection head was designed and manufactured. As this design showed unacceptable velocity profiles, a redesign was made. A schematic of the fuel head and its working principle of radial fuel injection are explained in Fig. 5-2.

This geometry of the fuel injection head was chosen as it represents a compromise in terms of pressure drop and homogeneous mixing of fuel and air. The fuel injection head can be rotated around its main axis to investigate the influence of the angular setting. This had to be investigated as the distribution of the fuel holes in the air passages was not axis-symmetric. The fuel supply tube and the injection head can be moved along the main axis of the complete system to vary the mixing length, hence the residence time of the fuel in the mixing section.

During the experiments, five different types of geometrical modifications were tested in order to improve the flow field at the inlet of the catalyst. These modifications are discussed in section 7.1 and in Appendix B. The final solution, which produced a satisfactory velocity and mixing quality profile was a flap-solution. These flaps redirect the airflow through some of the passages slightly towards the centre of the flow.

![Fig. 5-2: Second design of the fuel injection head and working principle.](image)

### 5.4.2 Applied Measurement Techniques in the Cold Flow Test Facility

**2D Laser-Doppler Anemometer**

Laser Doppler anemometry belongs to a group of non-invasive optical measurement techniques. It allows measuring the local velocity of particles suspended (i.e. seeding) in the flowing medium. By choosing adequate particles, the measured particle velocity can be set equal to the one of the fluid if the moment of inertia of the particles is negligible. Detailed information on the working principle and the different setups of a LDA is for instance given in Durst [1987]. All measurements were performed using a two channel LDA-580 system supplied by Polytech GmbH [Polytech, 1998]. This system allows measurements of two velocity components, perpendicular to each other. The light sources are two laser diodes, emitting at a wavelength of 690 nm at 22.8 mW and 826 nm at 42.6 mW output power, respectively.
Error sources for LDA measurements can be caused by the following phenomena:

a) inaccurate optical adjustment
b) finite size of the measurement volume
c) inaccurate measurement of the fringe spacing
d) non-ideal particle tracking
e) electronic noise and errors in the signal processing

a) If the optical adjustment is inaccurate, both laser beams will not intersect with their smallest diameters. This results in non-parallel fringe patterns, which does not give a correct velocity reading. Precise adjustments are therefore essential. For the LDA system used here, all optical components are contained in the optical head, hence the user has no or little influence on the adjustment. According to Polytech GmbH, all adjustments are done to minimize this error.

b) If the particle is experiencing a high velocity gradient while being inside the measurement volume, the measured value can be too high. However, this error is of more concern in measuring the turbulence intensity when high velocity gradients are present, which is not the case for this study. The error can be limited by reducing the size of the measurement volume via beam expansion.

c) The manufacturer has measured fringe spacing, no value for this accuracy has been reported.

d) The ability of the particles to follow the flow instantaneously limits the maximum resolution of the LDA system. By choosing a proper particle material, it can be assured that the particle dynamic fits the measurement problem. For this study, the droplets of the synthetic oil are expected to fulfill this.

e) Intensive investigations were performed in order to determine the optimum filter and sampling rate settings for the given application. For this study, a SNR value of 0 dB produced high enough data rates for reliable readings.

A comparison measurement using a calibration unit (consisting of a wheel rotating at a constant speed) revealed a true relative error of the measured mean velocity by the LDA system to a value of 2%. A second measurement at a higher flow velocity was done and compared with the calculated velocity obtained from pressure measurements using a Pitot tube. Variations between the two evaluated velocities was less than 0.5 m/s. Taking the Pitot result as the true velocity, the maximum, true relative error is evaluated to be 0.8%.

**Pressure Measurement System**

The pressure measurement is used for experimental work with both test facilities. The pressure acquisition system is a PSI 8400. A conventional IEE-488 interface allows communication with a PC for online display using an in-house developed software.

The PSI 8400 system consists of three different sets of pressure sensors in the range of ±7 kPa, ±35 kPa and ±100 kPa relative to the atmosphere. Each sensor has a built-in
calibration unit of high accuracy. Calibration of the pressure sensors is done prior to each measurement. During the calibration, five predefined pressures are applied to the sensors. The pressure is then calculated with a fourth order polynomial. A separate portable compressor and a vacuum pump are used for the calibration procedure. The calibration units in turn are calibrated regularly. Accuracy of the calibration unit is stated by the manufacturer to be ±0.02% F. S. (full scale); the accuracy of the ±7 kPa pressure sensor is given as ±0.1% F. S. and ±0.05% F. S. for the ±35 kPa and ±100 kPa units.

The cold flow test facility is provided with several static pressure taps on the outer wall. Respectively three pressure taps are shifted by 60° around the circumference in each measurement plane. Measurement planes are located before and after the fuel injection system and after the monolith bed. All three pressure signals are pneumatically averaged and conducted via thin flexible tubes to the pressure system. Apart from this, a separate pressure tap is located in the fuel supply.

**Quadrupole Mass Spectrometer**

This measurement technique has been used for investigations of the mixing quality of fuel and air by means of a traversable gas-sampling probe.

A mass spectrometer is simply speaking an apparatus that ionizes a gaseous sample. The ions are then separated according to their mass-to-charge ratio and counted to reveal information about the composition of the sample. Advantage of a mass spectrometer is its ability to simultaneously detect all species present in the sample. Disadvantage is the fact that it requires a probe, hence it is an invasive measurement technique. Several physical principles can be used for the ion generation and separation. Ionization can be done by bombardment of the sample with electrons, atoms, or photons or by thermal energy. Independently of the ionization process, the outcome is a beam of ionized particles (positive or negative charges) which are then accelerated by an electric field into the mass analyser.

Within this project, a quadrupole mass analyser was used. The system can be operated such that only a small range of mass-to-charge ratio ions is transmitted. This simplifies detection of a specific species of interest. As it selectively removes ions by neutralizing them it is often called quadrupole mass filter. The quadrupole consists of four cylindrical rods, which are the electrodes of the mass filter. The ions coming from the ion source are injected into the space between the four rods. Each rod forms a dipole with its nearest neighbour, hence opposing rods are charged equally. By varying the electric field between the rods, only ions with a corresponding mass-to-charge ratio can pass and can be detected by the ion collector. The rods are usually less than 1 cm in diameter and about 15 cm long. More detailed information on the quadrupole mass analyser can be found in Skoog [1989].

In order to get information about the accuracy of the mass spectrometer, a continuous concentration measurement has been done. This test was done at a concentration level of the tracer gas similar to the one in the mixing quality measurements. Approximately 1500 samples were taken each having 2 seconds measurement time. Standard deviation around the mean value was found to be 3.6%,
which is acceptable for the purpose here. A second study has shown that the mass spectrometer shows distinct warm-up behaviour. Thus, during all experimental investigations, it was assured that the mass spectrometer had been running for at least 30 minutes before any data acquisition was started.

5.5 Combustion Test Facility

The combustion test facility, which has been designed and manufactured allows investigating in how far a catalytic combustor can fulfill the requirements of combusting a low heating value fuel gas at high combustion efficiency and low emission levels. The modular design of the test rig enables to exchange the catalyst arrangement without disassembling the entire system, various compositions can thus be tested. A schematic of the combustion test rig is shown in Fig. 5-3.

![Schematic view of the combustion test facility.](image)

A screw compressor with a maximum flow rate of 4.7 kg/s and a maximum pressure of 4 bar supplies the compressed air. A bypass and an inlet valve regulate the air mass flow into the test facility. A pressure reduction valve downstream of the test facility adjusts the pressure. The test facility is designed to run experiments at an absolute pressure of up to 4 bar as well as under atmospheric conditions. Table 5-3 shows the design point of the test facility.
The design is made such that the outer pressure vessel acts as the support, the actual test section is then pushed into the pressure vessel. Six circular and one centrally mounted 29 kW electric air heaters are used for preheating the combustion air to temperatures up to 600 K. The maximum achievable temperature varies with the mass flow through the heaters. The air preheaters are electronically controlled. As no settling chamber could be mounted upstream of the heaters due to limited space in the wind tunnel room, the velocity profile at the inlet of the test section is uneven. Individual control of the electric power input for each heater allows adjusting the temperature to achieve a uniform temperature profile downstream of the heaters. The air can be preheated to typical compressor outlet temperatures between 500 and 600 K.

A gas reactor is installed shortly downstream of the central air heater. The purpose of this reactor is to generate a fuel gas synthetically from a mixture of air, propane and carbon dioxide. Electronic mass flow controllers are used for regulating the supply of C\textsubscript{3}H\textsubscript{8} and CO\textsubscript{2}. An air inlet valve allows, within some limits, controlling the amount of air that enters the gas reactor. The gas reactor is a packed bed pellets type consisting of an insulated steel cylinder. Table 4-5 gives details about this catalyst type. The pellets are commercially used in steam reformers for the generation of synthesis gas. They are provided by Süd-Chemie AG under the trade name G-90-B™.

<table>
<thead>
<tr>
<th>Gas reactor catalyst pellets</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Active material</td>
<td>14wt.% NiO</td>
</tr>
<tr>
<td>Carrier material</td>
<td>CaAl\textsubscript{12}O\textsubscript{19}</td>
</tr>
<tr>
<td>Diameter / depth [mm]</td>
<td>16 / 6</td>
</tr>
</tbody>
</table>

Table 5-4: Gas reactor pellet specification and photo of a pellet.

The overall process of the partial oxidation of C\textsubscript{3}H\textsubscript{8} in air is exothermic. However, for starting up the process, pre-heating of the gas reactor is necessary. A spark plug has been installed shortly downstream of the air inlet valve of the gas reactor for this purpose, see Fig. 5-3. This spark plug ignites a mixture of air and propane and establishes a flame for pre-heating the pellets with hot air. As soon as the gas reactor outlet temperature has reached a certain level, approx. 850 K, the pre-heating flame is extinguished by briefly shutting off the fuel supply. For the remaining operation of the reactor, the spark plug is deactivated. By adjusting certain mass flows of C\textsubscript{3}H\textsubscript{8} and CO\textsubscript{2} the required fuel gas composition can be obtained. In theory, the use of such a gas reactor provides an efficient and cheap way to synthetically produce a gas, which resembles gasified biomass. Due to high costs of pre-mixed gas bottles, the approach using the gas reactor was chosen. The water gas shift reaction is expected to take place in the gas reactor at equilibrium conditions. No detailed work on this equilibrium reaction has been made in this study.
Practice has shown that the operation of the gas reactor is complicated. A stable operation of the gas reactor in terms of outlet temperature as well as the resulting fuel gas composition is difficult to achieve. Several problems have been observed while operating the gas reactor:

- Pellet breakage occurs. This drastically reduces the conversion of the propane to synthetic gasified biomass. As a consequence, the pellets have to be exchanged regularly.
- The gas reactor outlet temperature is not stable, this is also reflected in the product gas composition. Close monitoring of the fuel gas is thus essential and changes in the raw feed of air, $\text{C}_3\text{H}_8$ and $\text{CO}_2$ have to be done when needed.
- Liu et al. [2001] have reported that carbon deposition occurs on the pellets in the temperature range of 923 to 1123 K. However, this group used LiLaNiO/$\gamma$-alumina catalysts. The modification of the NiO by an alkali and a transition metal resulted in enhanced thermal stability of the catalyst. Coke deposition has also been observed in this study. It results in deactivation of the NiO catalysts and a reduced conversion of $\text{C}_3\text{H}_8$ to CO and H$_2$. During the experiment, the reactor outlet temperature was kept below approx. 900 K.

The resulting hot product gas contains little oxygen, usually below 2%. A high-temperature resistant tube-bundle type water cooler decreases the gas temperature to roughly the same temperature as the surrounding airflow, hence avoiding temperature differences between both mass flows when being mixed with air in the fuel injection head, described in 5.4.1. Gas sampling for the fuel gas analysis is done by a rake mounted downstream of the cooler. In order to study the conversion of fuel-bound nitrogen to NO$_x$, ammonia (NH$_3$) was added artificially to the product gas during several experiments.

A high-temperature resistant steel tube forms the outer shell of the catalytic combustor. Several mullite-based ceramic insulation tubes are placed inside the steel tube. These insulation liners also hold the catalysts, which are axially fixed with ceramic pins. These pins are manufactured of 99.7% pure Al$_2$O$_3$. An aluminum-silicate fibre mat is compressed between the mullite-ceramic and the catalytic segments. The catalytic combustor is in form of in-series arranged segments. A schematic is shown in Fig. 5-4. Up to six catalytic segments can be mounted into the combustor. The axial gap between the segments is fixed to 20 mm. Fig. 5-5 shows a photo of one mullite section with a mounted catalyst. An inactive monolith has been mounted upstream of the first catalyst to act as a radiation shield into the mixing section.

![Fig. 5-4: Schematic of the catalyst mounting, showing thickness of the catalyst segment and axial gap between two segments, catalyst height is not in true scale.](image-url)
A water-cooled gas sampling rake is installed at the outlet of the combustor tube. Cooling is necessary both for preventing melting of the rake as well as for quenching possible reactions of the exhaust gases. A water sprayer is mounted in the outlet cone of the rig.

Due to the design of the rig, a large amount air delivered by the compressor is used for cooling the rig and diluting the exhaust gases. This implies that the actual amount of air that that passes through the air heaters and enters the test facility cannot be measured. The air-to-fuel ratio therefore has to be calculated from the measurement of emissions and fuel composition. More information on this subject is given in the results chapter.

5.5.1 Temperature and Pressure Monitoring

Fig. 5-6 shows schematically where temperatures are being monitored and where the static pressures are monitored. Several thermocouples are mounted for redundancy. The pressure taps allow measuring pressure drops across the gas reactor, fuel cooler and the combustion section including the fuel injection head. Measurement results are displayed online on a screen using commercial software.

The test facility is equipped with type N thermocouples for temperature monitoring. This type has been chosen because of its enhanced thermoelectric stability relative to standard base-metal alloys (type E, J, K and T). Accuracy of these thermocouples is given by the manufacturer to be ±1.1°C [Omega, 1999]. Temperature monitoring is done via analogue-digital converters, each having 24 analogue channel inputs. Measurement interval is 1 Hz. Resolution of the ADC is set via selecting an adequate operating voltage. Pressure monitoring is similar to that described in 5.4.2.
Thermocouple measurements are not always an adequate solution for temperature measurements. For application in a monolith channel, the question arises what quantity is actually measured. Several reasons can be mentioned for this.

1) Differences in the axial position of the different thermocouples may result in different temperature readings. Even though, when instrumenting the catalysts, care was taken to equally place the instruments in the channels, these may relocate during the experiments due to vibrations, etc.

2) Each thermocouple blocks the channel in which it has been placed. This blockage effect may vary between the thermocouples. This results in different amounts of fuel that enter the channel and consequently a different heat release.

3) In addition, the questions whether the monolith wall or the gas temperature is measured and how important the radiative heat transfer is cannot be answered definitely.

Rankin et al. [1995] investigated the influence of centreline temperature probes in a monolith channel. However, as compared to the dimensions used in this work, in their study the diameter of the cylindrical channel was 1.5 cm while the probe diameter was 1.6 mm. They found radiative heat transfer to play a significant role in the wall temperature range of 700-1000 K. The indicated probe temperature tends to lie between the average gas temperature and the reactor wall temperature.

The gas reactor, being a crucial component of the test facility has been instrumented as described in Fig. 5-7. The figure shows the thermocouple instrumentation of the gas reactor. At the inlet, two redundant thermocouples act as a flame detector. At the outlet, three thermocouples are equally distributed on the circumference, separated by 120°. The indicated temperatures at these three locations should not differ from each other for more than roughly 50 K. This arrangement of thermocouples can be used to determine whether or not pellet breakage has occurred. If during pre-heating of the gas reactor as described in section 5.5 T_{12-1} shows a significantly higher temperature than T_{12-2} and / or T_{12-3}, breakage has occurred. The cylindrical volume of the reactor is then no longer completely filled out with pellets and an air space has opened at the top of the tube, allowing the hot pre-heating air to pass over the catalyst pellets. In this case, a substantial part of the catalyst pellets have broken, reducing the overall conversion rate.

**Fig. 5-6: Thermocouple and pressure tap locations in catalytic combustion test facility shown for the case of three catalysts mounted.**
During instrumentation of the monoliths in the combustion tube, it was tried to fill out the space between the thermocouple wire and the monolith wall with chemical cement to avoid fuel entering this certain channel. The cement turned out to be very brittle and vibrations in the mounting process loosened the fixing. On the other hand, the thermocouple shaft fills out the channel almost completely. An optical access for temperature and/or gas analysis measurements was not practicable to implement into the facility. However, for future application, non-intrusive temperature measurements should be considered.

The temperature measurement uncertainty has been investigated by a series of tests. A stability analysis was performed at two different reference temperatures: at room temperature and in boiling water. Changes in the room temperature during the stability analysis were neglected. Two type-N thermocouples were used for the analysis, the difference being the physical thickness of the shaft. Shaft losses were neglected in this study. Table 5-5 gives an overview of the thermocouples properties and the measured standard deviation of the two reference measurements. The lower standard deviation of the 3.2 mm thermocouple is not surprising due to its longer response time to temperature variations.

<table>
<thead>
<tr>
<th>Thermocouple type N shaft diameter [mm]</th>
<th>Ø 3.2</th>
<th>Ø 0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard deviation at room temperature [K]</td>
<td>0.11</td>
<td>0.19</td>
</tr>
<tr>
<td>Standard deviation at boiling water temperature [K]</td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td>Sum of max. and min. absolute error ((x-x_{\text{mean}})) at room temp. [K]</td>
<td>0.6</td>
<td>1.2</td>
</tr>
<tr>
<td>Sum of max. and min. absolute error ((x-x_{\text{mean}})) at boiling water [K]</td>
<td>0.6</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 5-5: Properties of the tested thermocouples and measured standard deviation at two reference temperatures.

The measurement at room temperature lasted for 16 hours. No drift tendency could be detected, surprisingly not even a drift connected to changes in the room temperature caused by day-to-night shift. The duration of the measurement in boiling water was of the order of a few minutes. Also here, no drift tendencies could be observed. All values lie well below the accuracy given by the manufacturer. It was therefore concluded that the accuracy of the thermocouple measurements is sufficient.
5.5.2 Gas Analysis Equipment

A set of single-component gas analysis systems was used to study the species that are of primary interest for this study. Table 5-6 lists the species that were monitored on-line with the respective equipment and the respective measurement principle. The setup of the analysers for monitoring the emissions and the fuel gas composition is shown in Fig. 5-8. For clarity the flow path of the zero gas and the calibration gases are not shown. Both the THC and the NO\textsubscript{x} analyser are equipped with an internal pump that supplies the analysers with the appropriate gas flow. These two analysers were not available for the first experimental tests. Whenever THC could be measured the results are given in the appropriate section. The THC has a built-in bypass that allows guiding excess sample gas.

![Diagram of gas analysis equipment setup](image)

**Fig. 5-8: Setup of gas analysis equipment for fuel gas and exhaust composition measurement.**

<table>
<thead>
<tr>
<th>Species</th>
<th>Measurement range</th>
<th>Resolution / Linearity</th>
<th>Measurement principle</th>
</tr>
</thead>
<tbody>
<tr>
<td>O\textsubscript{2}</td>
<td>0-100 % (both units)</td>
<td>0.1 % resolution</td>
<td>Paramagnetic</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>0-20 % (both units)</td>
<td>±1% F.S. linearity</td>
<td>NDIR</td>
</tr>
<tr>
<td>CO</td>
<td>0-5000 ppm (emission meas.)</td>
<td>±1% F.S. linearity</td>
<td>NDIR</td>
</tr>
<tr>
<td></td>
<td>0-20 % (fuel meas.)</td>
<td>±1% F.S. linearity</td>
<td>NDIR</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>0-20 %</td>
<td>≤1% F.S. linearity</td>
<td>TCD</td>
</tr>
<tr>
<td>THC</td>
<td>0-10/100/10\textsuperscript{3} ppm</td>
<td>1% linearity</td>
<td>FID</td>
</tr>
<tr>
<td>NO\textsubscript{x}</td>
<td>0-10/100/10\textsuperscript{3}/10\textsuperscript{4} ppm</td>
<td>±1% F.S. linearity</td>
<td>Chemilumin.</td>
</tr>
</tbody>
</table>

*Table 5-6: On-line gas analysis system, all values taken from equipment manuals.*

Calibration of the gas analysis system was done prior to each measurement once per day. Furthermore, the calibration is also done at conditions as close to the actual measurement condition as possible, i.e. calibration of the fuel analysis system is done using a gas that roughly resembles the fuel gas composition. The also minimizes the error caused by cross-dependencies of the different species. The same procedure is applied for calibration of the analysis system for the emission measurements. By doing so the bias error associated with the measurement chain can be reduced to the bias in
A set of measurements has been performed to investigate possible drift tendencies of the analysers. The data sets taken for the stability analysis were done in such a manner that either air or a calibration gas was used. At least 450 samples were taken, the resulting statistical uncertainty from the student-t-distribution is then at most 1.96% of the measured value from a series of repeated measurements. The following two tables give an overview of the measured and calculated characteristics.

**Table 5-7: Summary of measurement uncertainties of the fuel gas analysis system.**

<table>
<thead>
<tr>
<th>Species</th>
<th>Number of samples</th>
<th>Average output signal [V]</th>
<th>Standard deviation [%]</th>
<th>Width of 95% confidence interval [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>2430</td>
<td>0.00535</td>
<td>0.03</td>
<td>1.2936*10⁻⁵</td>
</tr>
<tr>
<td>O₂</td>
<td>2430</td>
<td>2.09211</td>
<td>0.36</td>
<td>5.2679*10⁻⁷</td>
</tr>
<tr>
<td>CO</td>
<td>2430</td>
<td>0.03040</td>
<td>1.16</td>
<td>5.3214*10⁻⁷</td>
</tr>
<tr>
<td>H₂</td>
<td>1983</td>
<td>0.11240</td>
<td>0.08</td>
<td>3.5557*10⁻⁵</td>
</tr>
</tbody>
</table>

**Table 5-8: Summary of measurement uncertainties of the exhaust analysis system.**

<table>
<thead>
<tr>
<th>Species</th>
<th>Number of samples</th>
<th>Average output signal</th>
<th>Standard deviation [%]</th>
<th>Width of 95% confidence interval [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>500</td>
<td>502.66 mV</td>
<td>2.22</td>
<td>0.191</td>
</tr>
<tr>
<td>NO</td>
<td>500</td>
<td>97.94 mV</td>
<td>0.39</td>
<td>0.173</td>
</tr>
<tr>
<td>O₂</td>
<td>4341</td>
<td>0.994 V</td>
<td>0.17</td>
<td>1.30*10⁻⁵</td>
</tr>
<tr>
<td>CO</td>
<td>2430</td>
<td>-0.59 mV</td>
<td>0.03</td>
<td>3.0389*10⁻⁹</td>
</tr>
<tr>
<td>THC</td>
<td>450</td>
<td>1.97 V</td>
<td>0.475</td>
<td>0.000928</td>
</tr>
</tbody>
</table>

Assuming linearity of the gas analysers and a proper daily calibration with adequate reference gases, the resulting accuracy of the analysis system is sufficient for reliable measurement results.

### 5.6 Summary of the Experimental Test Facilities

A test rig to study the non-reacting flow under ambient conditions has been manufactured. This cold flow test rig was made such that intensive experimental investigations of the velocity profile could be performed using a two dimensional laser-Doppler anemometry system. A pressure monitoring system gave information concerning the pressure drops in the system. By means of a tracer gas, a gas sampling probe and a mass spectrometer the mixing quality of simulated fuel (i.e. the tracer gas) and air could be investigated. Accuracy of the applied measurement technologies was determined.

The studies in the cold flow test rig led to the design and manufacturing of a combustion test facility for investigating the feasibility of catalytic combustion of a
low heating value fuel gas. The test facility has been designed for pressurised tests; the combustor air inlet temperature is comparable to that one in commercial stationary gas turbines. Several arrangements of catalysts can be tested under varying loads in terms of air mass flow, fuel to air ratio and inlet temperature. Gas analysis in the fuel gas stream and at the combustion chamber exit gives information on fuel conversion and emission levels.
6. NUMERICAL INVESTIGATION OF THE FLOW FIELD IN THE MIXING SECTION

Numerical investigations were carried for comparison with experimental results as well as for studying whether auto-ignition of the air / fuel mixture would occur or not. It is clear that this phenomenon has to be avoided under all circumstances. Furthermore it was studied in how far mixing already occurs inside the fuel injection head for a non-reacting case. A simulation of the flow field in the mixing zone was performed to compare theoretical results with experimental work and to improve the understanding of the physical phenomena in the mixing section.

6.1 The Numerical Model

The commercial code CFX 4 [AEA Technology, 1995] was used in this project. Two different solver versions were available, version 4.1 running on a CRAY J932, version 4.2 running on a dual Pentium PC. The figure below shows the structure of the software package.

![Fig. 6-1: Structure of the commercial CFX 4 software package.](image)

The flow solver is a fully implicit, finite volume 3D Navier-Stokes solver allowing steady and unsteady calculations. During this project, only steady state calculations have been performed. The code is an unstructured multiblock solver, which simplifies the geometry definition. As the code is a commercial one, it would be beyond the scope of this work to describe all features of the program. Interested readers are referred to AEA Technology User Manual [AEA Technology, 1995] to obtain further information.

Numerical investigations have been performed in order to:
- study the mixing process,
- study the flow field structure in the mixing section,
- investigate the risk of auto-ignition of the fuel

In the following, the numerical method applied within this project is described.
6.1.1 Turbulence Model

The system of mass and energy equations is extended to the turbulent flow by implementing the k-ε turbulence model after Spalding and Launder [1974]. Reynolds averaging the governing equations leads to the Reynolds stresses which are approximated using the Boussinesq eddy viscosity hypothesis to

\[
-\rho \frac{\partial u_i u_j}{\partial x_j} = \mu_T \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) - \frac{2}{3} \rho k \delta_{ij} \tag{6-1}
\]

with \(\delta_{ij}\) being the Kronecker delta. The turbulent viscosity \(\mu_T\) is expressed as

\[
\mu_T = C_\mu \rho \frac{k^2}{\varepsilon}. \tag{6-2}
\]

The k-ε turbulence model is a two-equation model. As this name already suggests, a set of two transport equations are needed for closure, one for the turbulent kinetic energy \(k\) and the other one for the energy dissipation \(\varepsilon\). These two equations are given to

\[
\frac{\partial (\rho k)}{\partial t} + \frac{\partial (\rho u_i k)}{\partial x_j} = \frac{\partial}{\partial x_j} \left[ \left( \mu + \frac{\mu_T}{\sigma_k} \right) \frac{\partial k}{\partial x_j} \right] - \rho u_i \frac{\partial u_i}{\partial x_j} - \rho \varepsilon, \tag{6-3}
\]

\[
\frac{\partial (\rho \varepsilon)}{\partial t} + \frac{\partial (\rho u_i \varepsilon)}{\partial x_j} = \frac{\partial}{\partial x_j} \left[ \left( \mu + \frac{\mu_T}{\sigma_\varepsilon} \right) \frac{\partial \varepsilon}{\partial x_j} \right] - C_1 \rho u_i \frac{\partial u_i}{\partial x_j} - \rho C_2 \frac{\varepsilon^2}{k}. \tag{6-4}
\]

\(C_1, C_2, C_\mu, \sigma_\varepsilon, \sigma_k\) are model constants with the values given in Table 6-1. These constants may be changed if necessary, however this was not needed for the work described here. This turbulence model has been validated for a large number of applications and is already implemented in the numerical code. The turbulent kinetic energy \(k\) and the eddy dissipation \(\varepsilon\) at the boundary conditions can be approximated by the following equations [AEA Technology, 1995]:

\[
k_{\text{inlet}} = 0.002 \left( u^2 \right)_{\text{inlet}}, \tag{6-5}
\]

\[
\varepsilon = \left( k^{1.5} \right)_{\text{inlet}} / 0.3 \cdot D. \tag{6-6}
\]

These two equations are recommended to be used as they are applicable for a wide range of cases [AEA Technology, 1995].
6.1.2 Boundary Conditions

All mass flow inlets are set to Dirichlet boundaries. For this type of boundary condition, a specification of the dependent variables along the boundary has to be given. At the mass flow outlet, a Neumann boundary condition is applied. In contrast to the Dirichlet condition, the derivative of the dependent variables has to be specified.

The walls of the domain were set to be adiabatic with no slip, i.e. \( v_{\text{wall}} = 0 \text{ m/s} \).

For the modeling of the flow field in the mixing zone, symmetry planes were introduced where possible to reduce the grid size and hence the calculation time. The boundary condition at a symmetry plane is easily defined. No diffusion across a boundary occurs, except for the normal component of the velocity, the Reynolds shear stress and the Reynolds flux involving the normal velocity.

6.1.3 Discretization Schemes

The convection terms are discretized using the Rhie-Chow interpolation formula, see AEA Technology [1995] for more details. A series of different schemes is available for the discretization of the advection term. All other terms in the equations are discretized in space using second-order central differencing.

For the simulation to be described in 6.2.2, discretization in space of the advection terms is done by a hybrid scheme. This scheme is a modification of the upwind scheme as it is a combination of central and upwind differencing. If the Peclet number, \( Pe \), becomes less than 2, central differencing is used, otherwise, an upwind scheme is applied. For the simulation described in 6.2.3, discretization in space of the advection terms is done by a second-order upwind scheme [Versteeg et al., 1995].

The choice of the discretization scheme was somewhat arbitrary and more or less controlled by the speed of convergence. As the hybrid scheme is the default discretization scheme in the solver, this was also the one used in the first place. The higher upwind scheme was applied when a higher accuracy was required. However, comparison of results obtained with either scheme show only very little differences.

Linear backward differencing was chosen for discretization in time.

6.2 Mixing Process of the Fuel / Air Mixture and Auto-Ignition of the Fuel

Auto-ignition of the fuel will occur only at locations where a sufficient amount of fuel is present at corresponding thermodynamic conditions. Therefore, auto-ignition could occur inside the fuel head, where fuel is injected into the surrounding air flow. A numerical 3D model has been set up to investigate mixing effects and reaction kinetics
inside the fuel injection geometry. In the following the applied numerical method will be explained.

### 6.2.1 Modeling of the Geometry and Grid Generation

For the investigations of the flow field inside the fuel injection head, a multiblock geometry has been set up, illustrated in Fig. 6-2. The structured, body-fitted mesh consists of 93200 cells in 19 blocks. The grid is generated using algebraic interpolation. Calculations have shown that no interaction between the discrete fuel injection streams takes place. In other words, fuel injected at location A does not mix with fuel injected at location B. It was therefore concluded, in order to save CPU time, that a two-dimensional geometry would be sufficient for studying the mixing behaviour of the fuel after being injected into air. This 2D grid has been developed using the same procedure as for the above mentioned geometry. This grid consists of 30800 cells and is shown in Fig. 6-3. The grid dependency was checked by reducing the number of grid cells by a factor of 2, the results showed to be grid independent.

*Fig. 6-2: Geometry and grid of one air passage of the fuel injection including all fuel injection locations.*

*Fig. 6-3: 2D geometry of the central plane of one air passage of the fuel injection.*
6.2.2 Non-Reacting Mixing Process in the Fuel Injection Head

For these calculations, the fuel had been modeled as a mixture of five different components being mixed with air. Table 6-2 lists these components. Calculations were performed using the 2D geometry shown in Fig. 6-3. Specifying a mass fraction $Y_i$ for each component, a transport equation of the form

$$\frac{\partial \rho Y_i}{\partial t} + \mathbf{V} \cdot (\rho \mathbf{U} Y_i) - \nabla \cdot (\Gamma_i \nabla Y_i) = 0$$

is set up. The zero on the right hand side indicates that no creation or destruction of species “i” is taking place due to chemical reactions or phase changes. Species are labeled by $i = 0, 1, 2...n$, so $n$ transport equations are being solved, obeying

$$\sum_{i=0}^{n} Y_i = 1$$

(6-8)

to determine the mass fraction of the carrier or background fluid, air is taken for this purpose.

The constant molecular binary diffusion coefficients $\Gamma_i$ are set by the user. They have been calculated after White [1974] and are also included in Table 6-2 below. The diffusion coefficient has to be multiplied by the gas density (a specific feature in CFX only), hence the unit kg/(m s).

<table>
<thead>
<tr>
<th>Species</th>
<th>Diffusion coefficient [kg/(m·s)]</th>
<th>Absolute mass fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>$8.443 \times 10^{-5}$</td>
<td>0.0285</td>
</tr>
<tr>
<td>CO</td>
<td>$7.752 \times 10^{-5}$</td>
<td>0.1589</td>
</tr>
<tr>
<td>CO₂</td>
<td>$6.072 \times 10^{-5}$</td>
<td>0.2344</td>
</tr>
<tr>
<td>H₂</td>
<td>$2.547 \times 10^{-4}$</td>
<td>0.0079</td>
</tr>
<tr>
<td>N₂</td>
<td>$7.881 \times 10^{-5}$</td>
<td>0.4812</td>
</tr>
</tbody>
</table>

Table 6-2: Calculated constant binary diffusion coefficient [White, 1974] and absolute mass fraction of the fuel components.

The choice of a discretization scheme has shown little influence on the results. Results of these calculations are shown in chapter 7.

6.2.3 Governing Equation and Chemistry Model for Investigation of the Reactive Flow

The Navier-Stokes equations given as a scalar advection-diffusion equation in index notation including the source term $S$ are given by
\[
\frac{\partial \rho \Phi}{\partial t} + \frac{\partial}{\partial x_k} \left( \rho U_k \Phi - \Gamma \frac{\partial \Phi}{\partial x_k} \right) = S, \quad (6-9)
\]

with \( k \) being a coordinate index. The source term \( S \) has to be modeled using the appropriate reaction kinetics. The species source term \( S_i \) for species “\( i \)” is summed over the contributions of the reaction rates, described by

\[
S_i = \frac{Y_i}{X_i} \sum_{j=1}^{NS} n_{ij} R_j = W_i \sum_{j=1}^{NS} n_{ij} R_j. \quad (6-10)
\]

For reactive flow calculations, seven additional chemical species equations are implemented in order to model turbulent hydrogen oxidation after a scheme developed by Eggels and de Goey [1995]. In this scheme, the components \( \text{O}_2, \text{H}, \text{OH}, \text{H}_2, \text{H}_2\text{O} \) and \( \text{N}_2 \) are applied to the following set of equations:

\[
\begin{align*}
\text{H} + \text{O}_2 &= \text{OH} + \text{O} \\
\text{O} + \text{H}_2 &= \text{OH} + \text{H} \\
\text{H}_2 + \text{OH} &= \text{H}_2\text{O} + \text{H} \\
\text{OH} + \text{OH} &= \text{O} + \text{H}_2\text{O} \\
\text{H} + \text{H} + \text{M} &= \text{H}_2 + \text{M} \\
\text{OH} + \text{H} + \text{M} &= \text{H}_2\text{O} + \text{M} \\
\text{O} + \text{O} + \text{M} &= \text{O}_2 + \text{M}
\end{align*}
\]

where \( \text{M} \) denotes a third body to participate in third-body reactions. In the calculations, the collision efficiency is taken from Eggels and de Goey [1995] to evaluate the third-body reactions. This scheme has been chosen because hydrogen has the highest potential for auto-ignition under the combustion test conditions.

The reaction rate of a reaction \( j \) is calculated as a function of the reactants and the product concentrations,

\[
R_j = k_{fj} \prod_{i=1}^{Ns} [X_i]^{x_{ij}} - k_{bj} \prod_{i=1}^{Ns} [X_i]^{y_{ij}}. \quad (6-11)
\]

The modified Arrhenius law (temperature dependent pre-exponential factor) evaluates rate constants for the forward and backward reactions, \( k_{fj} \) and \( k_{bj} \).

The command file for this calculation is given in Appendix A. This file gives the values taken for estimation of thermodynamic properties of the species. Information about the numerical method for this simulation, e.g. discretization scheme, equation solvers, etc. can be taken from this file as well.
6.3 Flow Field in the Premixing Zone

Fig. 6-4 shows the grid that has been used to calculate the non-reacting flow field in the mixing section. This is a 64-block, body-fitted grid using algebraic interpolation. By using symmetry boundary conditions on the two radial planes, this section can be expected to be sufficient for modeling of the full flow field. The inlet section was included in the model to calculate proper conditions in terms of velocity field at the inlet of the fuel injection head.

![Flow Field in the Premixing Zone](image)

Fig. 6-4: 3D mesh for numerical investigation of the mixing zone consisting of 310900 cells.

Incompressible flow, steady state calculations were performed using the k-ε turbulence model. A higher upwind scheme has been used for discretization of the advection term [Versteeg et al., 1995].

6.4 Convergence Strategy and Solution Algorithm

Several methods are available in the numerical code for influencing the solution strategy of the linearized transport equations. By choosing appropriate keywords in the command file, the user can take action over the solution procedure. The solution strategy of CFX 4 is given in the following.

An inner iteration procedure is used to solve the spatial coupling for each variable over the whole mesh. An outer iteration solves the coupling between the different variables. For each variable, regarding all the other variables as fixed, a linear transport equation is set up for each cell in the domain. A linear equation solver solves this equation and returns the updated value of the variable for each cell. Several linear equation solvers are available and can be selected by the user, these are:

- line relaxation,
- preconditioned conjugate gradients,
- full field Stone’s method,
– block Stone’s method,
– algebraic multi-grid,
– general version of algebraic multi-grid.

For almost all calculations performed in this project, the block Stone’s method has been used for all variables except for the pressure, which was solved using the preconditioned conjugate gradients method, see Appendix A and AEA Technology [1995]. These methods have shown satisfactory results for the time needed for convergence.

General criteria for the solution process are:
– maximum number of outer iteration
– tolerance on a residual, by defaults this residual is taken to be the mass source residual
– CPU time limit

It is worth to mention the mass source residual, which is the sum of the absolute values of the net mass fluxes into or out of every cell in the domain. This residual is not dimensionless but has the dimension kg/s [AEA Technology, 1995]. For all calculations performed, the required value for this residual was set to be $10^{-20}$ kg/s as to assure that the solution process is stopped by the maximum number of outer iterations. In practice, if the decrease in order of magnitude of the residual for each variable is five or more, the solution can be considered to be converged. Mass conservation is always ensured in a converged solution by CFX 4.

For the calculation described in section 6.3, convergence was difficult to achieve. In a small region of the mesh, i.e. at the inner corners of the symmetry planes and the centre tube (see Fig. 6-4) upstream of the fuel injection head large values of the turbulent viscosity and small values of the dissipation caused the solution to diverge. As the grid cells in this region are distorted and thus non-orthogonal it could be expected that the sudden divergence of the solution was caused by the cross-derivative terms in the equation for $k$ and $\varepsilon$. The software offers a possibility for under-relaxing these equations [AEA Technology, 1995]. By applying this method the cross-derivative diffusion terms, which caused the code to diverge in the $\varepsilon$-equation eq. (6-4) were omitted. This resulted in a converging solution. The under-relaxing also implies that the analytic equation for the eddy dissipation is no longer fully discretized. According to AEA Technology [1995], the error introduced should be small as the equation is not dominated by the cross-derivative diffusion terms. Further information on the under-relaxing method can be found in AEA Technology [1995].
7. COLD FLOW RESULTS AND NUMERICAL INVESTIGATION OF THE NON-REACTING FLOW

In the following, results obtained with the cold flow test facility and from the numerical investigation are presented. Starting with the cold flow tests, results from the optimized flow field are shown. Only the final solution is presented here while all other results from the complete flow field investigation are listed in Appendix B. Results from the numerical investigation are shown and discussed.

7.1 Experimental Flow Field Optimization in the Cold Flow Test Facility

Intensive experimental work has been performed in order to meet the requirements for the flow field described in section 5.4.1. As the first fuel head design did not produce satisfactory results in terms of the velocity profile, a redesign was made. The first fuel head design had the inner air passages angled towards the centreline of the flow tube. The idea was to avoid a recirculation zone downstream of the fuel injection head. The redesign had no angled passages. Another difference was a larger open frontal area of the second fuel head compared to the first one, reflected in the pressure drop measurement shown in Fig. 7-5. As a result of the lack of angled air passages, a strong recirculation zone could be detected in the centre region of the mixing section behind the fuel injection head. Such a recirculation zone represents an area of accumulated fuel which, by radiative heating from the hot catalyst, might trigger auto-ignition of the fuel. Several modifications of the fuel injection head and the mixing section were investigated. The studied mixing lengths varied between 10 and 20 cm. The mentioned modifications were:

− cone shaped centre piece on the fuel head
− two elliptic shaped centre pieces of different lengths
− small metallic plates (flaps) on the fuel head to redirect the air flow towards the centre of flow at the end of the fuel head
− honeycomb structure in the mixing section to act as a flow straightener, mounted at varying distances downstream of the fuel head
− combination of a centre cone and a honeycomb structure

A parameter had to be defined allowing a comparison of the evenness of the measured velocity profiles. A normalized standard deviation was defined as the ratio of the empirical standard deviation RMS (Root Mean Square) and the average velocity.

\[
\text{RMS} = \sqrt{\frac{n \sum x^2 - (\sum x)^2}{n(n-1)}} \quad [-]
\] (7-1)
\[
\overline{\text{RMS}} = \left( \frac{\text{RMS}}{\overline{u}} \right) \cdot 100 \text{ [%]} \quad (7-2)
\]

While \( n \) represents the number of measured values used, \( u \) is the measurement velocity and \( \overline{u} \) the arithmetic average.

The evenness parameter can be calculated for one traversing over the full flow tube diameter at a fixed angular position, denoted as \( \overline{\text{RMS}}_a \). To estimate this parameter for a full 360° flow field, denoted as \( \overline{\text{RMS}}_o \), the average of all calculated \( \overline{\text{RMS}}_a \) for this set of measurement is taken. Fig. 7-1 explains how each measurement plane is denoted. The angle is noted in a mathematical positive direction starting with the 0°-plane being horizontally.

The normalized standard deviation can be used in order to evaluate the smoothness of the measured velocity profiles. Table 7-1 below gives an overview of all \( \overline{\text{RMS}}_o \) for the measured profiles. Results from these measurements and their discussion can be found in Appendix B.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>( \overline{\text{RMS}}_o )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic Configuration</td>
<td>9.85</td>
</tr>
<tr>
<td>Centre Cone I</td>
<td>13.45</td>
</tr>
<tr>
<td>Centre Cone II</td>
<td>16.45</td>
</tr>
<tr>
<td>Centre Cone III</td>
<td>10.46</td>
</tr>
<tr>
<td>Flaps</td>
<td>5.36</td>
</tr>
</tbody>
</table>

*Table 7-1: Normalized standard deviation in % for various configurations of the fuel injection geometry.*

From these values it becomes clear that the flap configuration produces a velocity profile at the inlet of the monolith which fits best to the requirement of smoothness at the inlet of the monolith. By redirecting the flow through some of the air passages, the recirculation zone could be reduced in size, hence reducing the risk of auto-ignition due to an accumulation of fuel. The working principle of the flaps is explained in Fig. 5-2. A full 360° flow field traversing using four flaps is shown in Fig. 7-2. The four thick black lines in the figure denote the location of these flaps.
The normalized RMS value of 5.36 shows that the velocity in this profile has the lowest variations of all so far investigated configurations. Further experiments were made with varying deflection angles of the flaps. An angle of 10° with respect to the main axis was found to be the most efficient in producing an spatially flat velocity profile. This velocity distribution was hence chosen to be sufficient for a satisfying combustor performance. This configuration using four flaps will be used in the final testing of the combustor.

Mixing lengths of 10, 15 and 20 cm were investigated with this profile. It was found that a length of 15 cm is suitable. Increasing to 20 cm did not improve the evenness of the velocity profile significantly. Even though irregularities are still present, they are of a low level. It should be mentioned at this point that it might have been be possible to further improve the velocity profile. This setup of the fuel injection head was then further investigated with respect to the mixing quality. As already mentioned in section 5.1, air was used to represent the fuel flow in this test facility.

### 7.1.1 Experimental Investigation of the Mixing Quality of Fuel and Air

In Fig. 7-3, a 360° flow field measurement is shown measured 10 mm downstream of the catalyst. In the figure the normalized concentration is given, as the absolute value of the tracer gas concentration was of no direct interest. Methane was used as a tracer gas in this experiment, the length of the mixing section was 15 cm. As can be seen, the lowest concentration of tracer gas can be found in the centre of the flow at a normalized value of 0.96 increasing to a value of 1.05 in the left-hand region of the profile. It is not fully clear what causes the high concentration of tracer gas in this certain area. Using the same procedure as explained in the previous section to calculate the evenness parameter \( E_{\text{p0}} \), a value of 2.12 was obtained with this configuration. A variation of \( \pm 5\% \) in the normalized concentration of the fuel would result in a difference of \( \pm 29\text{K} \) in the adiabatic flame temperature. This temperature interval represents an acceptable risk in terms of thermal stresses for the catalyst support material. It can
be concluded that homogeneous mixing is achieved up to a level at which no difficulty for combustor performance is expected.

**Fig. 7-3:** Mixing quality profile 10 mm downstream of the catalyst using methane as a tracer gas.

A similar measurement was then performed using helium as a tracer to take the different diffusion behaviour into account. As the diffusion velocity is inversely proportional to the square root of the molecular mass, helium diffuses twice as fast as methane does. The result of this measurement is shown in **Fig. 7-4.** The profile was measured 10 mm downstream of the catalyst. The smoothness of the profile was calculated to $E_P = 2.03$. The same phenomenon of a region of higher normalized
concentration was detected. The difference in diffusivity showed no significant influence on the measured concentration profile.

In order to explain the rather unexpected region of higher normalized concentration visible in Fig. 7-3 and Fig. 7-4, the fuel injection head was inspected to find out whether or not the location of the fuel injection holes inside the air passages of the fuel head could have an influence. The fact that eight fuel holes are placed in each passage makes it improbable that this could have any influence. No obvious relation between the location of the fuel holes and the increase of tracer gas concentration could be found. However, it cannot be excluded that the fuel head geometry is the cause of this. Manufacturing tolerances for instance could have such an influence. As, already mentioned, the mixing is considered to be sufficiently homogeneous, it was consequently not essential to investigate the cause of this local tracer gas concentration in more detail.

7.1.2 Pressure Drop Measurement

The fuel injection head had to be designed to meet a compromise in enabling a homogeneous mixture of fuel and air while keeping the pressure drop at a low level. Fig. 7-5 shows the measured pressure drop over the fuel injection head as a function of the total mass flow. Also shown in the figure is the pressure drop over the catalyst support material. However, the pressure drop over the monolith during the combustion experiments will vary from the one measured in the cold flow rig due to the different properties of the fluid.

From Fig. 7-5 it is clear that due to the increased total open area of fuel head version 2, the pressure drop is significantly reduced. At a total mass flow of 0.25 kg/s, the pressure drop could be reduced by 66%. With the available air supply, the maximum achievable mass flow could, due to the larger open area, be increased to 0.34 kg/s with fuel head version 2. These experiments were performed at ambient temperature. From the point of view of the pressure drop, fuel injection head version 2 clearly is an improvement. The pressure drop over the ceramic monolith is also shown in Fig. 7-5. At a mass flow of 0.34 kg/s, a pressure drop of 1.5 kPa was measured. This value is lower than specified by the manufacturer.
7.1.3 Summary of the Results obtained with the Cold Flow Test Facility

The objectives for the investigations in the cold flow test facility were to obtain:
- a uniform velocity profile at the inlet of the monolith,
- a homogeneous mixing of fuel and air.

Several modifications to the fuel injection head and in the mixing zone were tested and led to a configuration which fulfills the above mentioned requirements. As no significant improvement of the velocity profile at a mixing section length larger than 15 cm was observed, this length was defined to be the minimum length. This reduced the residence time of the fuel in the mixing zone, hence reducing the risk of auto-ignition in the mixing zone.

Concluding, no difficulties in the operation of the catalytic combustor were expected to occur due to inhomogenities in the mixing or the velocity profile.

7.2 Results from the Numerical Investigations

The objective of the numerical investigations was to increase the knowledge about the mixing process of the fuel and the air inside the fuel injection head as well as the flow field in the mixing section. The second point of focus of the CFD part was investigating in how far auto-ignition of the fuel in the test rig under the intended test conditions represents a risk during the experiments.
7.2.1 Numerical Investigation of the Recirculation Zone Downstream of the Fuel Head

Fig. 7-6 shows a comparison of the axial velocity at the centreline of the system as measured with LDA and calculated. The recirculation zone can clearly be seen in both, the experimental and the numerical results. No reliable velocity measurements could be performed closer to the fuel injection head in axial direction due to bad signal quality in this area. From Fig. 7-6, it can be seen that experimental and numerical values have a similar shape. The main difference occurs in the prediction of the axial velocity in the recirculation zone. The abscissa in this figure shows the axial distance from the inlet of the test section. In the figure below, the fuel injection head is mounted 0.15 m downstream of the inlet of the flow tube, illustrated by the textured area.

![Fig. 7-6: Comparison of numerical and experimental data of the axial velocity profile in the mixing section.](image)

The numerical simulation underpredicts the axial velocity in the mixing section. The velocity at the position $x = 0.30$ m coincidences well with the experimental result. The tendencies of the axial velocity in the mixing section can be said to be well predicted.

A numerically calculated and measured axial velocity profile are shown in Fig. 7-7. Both diagrams show a 90°-sector of the flow field 15 mm upstream of the monolith inlet. Distinct differences in the profiles can be found. The numerical data shows a jet of high axial velocity while the axial velocity in the centre region is about 3 m/s. The measured velocity profile is more uniform. It is expected that the difference between these two profiles can be explained by the presence of the monolith. This blocking effect of the monolith has the tendency to even out the axial velocity profile over the flow tube diameter. The monolith was modelled in the numerical investigations as a porous body with a volume porosity of 0.74. This value corresponds to the open frontal area of the monolith.
7.2.2 Numerical Investigation of the Mixing Process Inside the Fuel Injection Head

As described in 6.2, the mixing process of fuel and air has been investigated in a numerical 2D model. No kinetic reaction model was implemented into the calculations, only the mass transport of the fuel components was studied here. In order to investigate possible inaccuracies in the determination of the diffusion coefficient, separate calculations with $\Gamma_i$ artificially falsified by one order of magnitude were made. These calculations have shown no noteworthy influence of the diffusion coefficient on the solution. The conclusion that no significant errors are made in the numerical study related to wrongly chosen diffusion coefficients can be drawn.

Due to the complexity of the experimental setup, measurement of inlet velocities at the fuel injection head was not possible. Instead these were calculated from the measured fuel and total mass flows and the area ratios of the fuel injection head. In order to get a more detailed understanding of the flow field and the transport processes inside the fuel injection head, several calculations with different inlet velocities for the fuel and the air were performed. The air inlet velocity that could be calculated from mass flow measurements was about 50 m/s at maximum mass flow, results of this calculation is shown in Fig. 7-11.

Fig. 7-8 explains briefly the nomenclature for the presented results. Flow direction is from left to right with the air inlet on the left-hand side. Fuel is injected perpendicular to the main flow direction.

In Fig. 7-9, the velocity along the main flow axis is displayed for the two different fuel inlet velocities of 20 and 40 m/s. In both cases, air inlet velocity was 40 m/s. Fig. 7-10 shows for the
same cases the mass fraction of methane.

Fig. 7-9: Velocity profile in the centre plane of the fuel injection head for two different fuel injection velocities.

Patankar et al. [1977] have shown that for the calculation of turbulent jets in a cross-flow, the standard k-ε turbulence model gives accurate results. This model has also been used for the calculations in this study. As can be seen from Fig. 7-9, the extent of the recirculation zone in the axial and perpendicular direction to the main flow increases with the fuel inlet velocity. This area of reverse flow cannot simply be avoided in the consideration of auto-ignition since it represents a zone with potentially high risk for auto-ignition. An understanding of the mass transport is of interest.

Fig. 7-10: Concentration profile of methane in the centre plane of the fuel injection head for two different fuel injection velocities.

At a fuel jet velocity of 20 m/s, the fuel jet cannot penetrate far into the main flow and quickly absorbs momentum in the x-direction. The concentration of methane in the recirculation zone is at maximum. A different situation is seen for a fuel inlet velocity of 40 m/s. In this case, the momentum of the fuel jet in y-direction is sufficiently large to penetrate the main flow above the recirculation zone. The diffusion of methane into the recirculation zone is then purely caused by concentration gradients. The concentration profile does not change considerably when looking at another species with a different diffusion coefficient. Hence it can be concluded that the mixing process is not controlled by mass diffusion process but by the momentum transport processes.
Increasing the velocities of both fuel and air to 50 m/s does not show any significant changes to the profiles which can be obtained at a fuel inlet velocity of 40 m/s, shown below in Fig. 7-11.

![Fig. 7-11: Concentration and velocity profile at 50 m/s inlet velocity for fuel and air.](image)

In the left diagram, the diffusion of methane into the recirculation zone and the boundary layer can be seen, varying only slightly from the diffusion profile shown in Fig. 7-9 for a fuel inlet velocity of 40 m/s. As the mass flow into the domain is higher, the velocity of the reverse flow decreases. Hence the recirculation zone becomes larger. Cisible is the higher mass diffusion of methane from the main fuel stream into regions of lower flow velocities, i.e. towards the recirculation zone.

It can be concluded from the above shown results that fuel and air do not mix well inside the fuel head and that local regions of high fuel concentrations are present. This is of concern for the investigation of auto-ignition inside the fuel injection head, which is discussed in the next section.

### 7.2.3 Ignition Modeling

Determination whether or not ignition occurs can be done by looking at the temperature profile, the hydrogen mass fraction or simply by checking if water is produced as a reaction product.

The temperature of both air and fuel at the inlet was set to 623 K at a pressure of 4 bar. This corresponds to the planned combustion test conditions.

In Fig. 7-12, profiles for the hydrogen mass fraction, the temperature, velocity in main flow direction and density are shown. Inlet velocity for fuel and air was 50 m/s. As can be seen from the top-right diagram, no temperature change occurs that would indicate an established reaction chain to form water. The viscous shear layer causes the temperature change that occurs where the two gas streams interact. A separate calculation in a non-reacting, non-isothermal case has shown the same temperature variations. Hence these temperature variations are not due to chemical reactions. When comparing the axial velocity field in Fig. 7-12 with the one shown in the previous
figure, Fig. 7-11, one can see distinct differences. Compressibility effects do not cause these differences, as a separate calculation has shown.

The question is whether or not these results from the ignition modelling are reliable and do represent the actual flow field in the fuel injection head. From this study, it can be concluded that the implemented chemistry model is apparently not suitable for studying the ignition behaviour of hydrogen in this case.

Fig. 7-12: Flow field and thermodynamic property profiles in the fuel injection head using a 7-step reaction scheme for hydrogen, 50 m/s inlet velocity for fuel and air.

7.2.4 Summary of the Results obtained by Numerical Investigations

Numerical investigations were performed with the objective to improve the physical understanding of the flow field inside the fuel injection head as well as in the mixing zone. The studies of the flow field inside the fuel injection head were done with emphasis on the mixing process of fuel and air and as a second step, the risk of auto-ignition was studied. A number of different boundary conditions were studied to cover a range of operating conditions. It was found for all cases that momentum transport is the dominating procedure for the mixing process. The recirculation zone downstream of the fuel injection location, but still inside the fuel injection head, does not represent an area of accumulated fuel.
Investigations of the flow field in the mixing zone showed distinct differences from the measured results.

The implementation of a reduced reaction mechanism did not show the intended results. It has to be said that this mechanism seems not to be a suitable one for the intended study, hence the results from the numerical auto-ignition study are somewhat uncertain in terms of transferability to the experiments.

To conclude, it can be said that the CFD work performed has improved the knowledge about the flow field inside the fuel injection head. Nevertheless, this is not true for the ignition modeling. A more intensive study of the ignition behaviour, applying various reaction mechanisms would be necessary in order to get a deeper understanding.
8. CATALYST TESTING AND RESULTS

8.1 Catalyst Preparation

Three different sets of catalysts have been prepared, as shown in Table 8-1. All catalysts that have been tested within this project have been prepared and developed in bench-scale tests at the Chair of Chemical Technology at the Royal Institute of Technology with whom this project has been done in coorporation.

<table>
<thead>
<tr>
<th>Catalyst name</th>
<th>Washcoat (abbreviation)</th>
<th>Washcoat loading [wt%] b)</th>
<th>Pd loading [wt%] c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd / LHA</td>
<td>LaAl\textsubscript{11}O\textsubscript{18} (LHA)</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>Ba / Pd / LHA a)</td>
<td>LaAl\textsubscript{11}O\textsubscript{18} (LHA)</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>LMHA</td>
<td>LaMnAl\textsubscript{11}O\textsubscript{19} (LMHA)</td>
<td>20</td>
<td>0</td>
</tr>
</tbody>
</table>

a) layer of barium stabilized alumina coated over Pd / LHA, 3wt% Ba in Al\textsubscript{2}O\textsubscript{3}.
b) relative to monolith weight
c) relative to washcoat weight

Table 8-1: Catalyst composition and abbreviation.

The preparation of the catalyst is divided into three separate steps,
− synthesis of the hexaaluminate support
− impregnation with a Pd(NO\textsubscript{3}) solution
− preparation of the slurry
− washcoating the Cordierite monoliths

The hexaaluminate material was prepared according to the carbonate co-precipitation method, see Groppi et al. [1993] for detailed information. Ammonium carbonate was dissolved in an excess of water and the pH of the solution was adjusted to 9.0 by addition of an aqueous solution of ammonia. A water solution containing a stochiometric amount of aluminium, lanthanum and manganese nitrate was added drop-wise to the ammonium carbonate solution to form a precipitate. Mn was added only for the preparation of LaMnAl\textsubscript{11}O\textsubscript{19}. The intermediate precursor was a mixture of metal carbonate, hydroxicarbonates and aluminium hydroxide. The precipitate was then centrifuged, washed twice with acetone and dried overnight at 180°C. As the last step in the catalyst preparation, the material was calcined at 600°C and 1000°C for 4 hours. The powder was crushed and calcined at 1200°C for 12 hours. In the case of the noble-metal based catalysts, Pd was deposited by wet impregnation of an aqueous solution of Pd nitrate. The concentration of the solution was fixed in order to reach a Pd loading of 5 wt%. A slurry is produced by mixing the catalyst powder with ethanol (20% dry content) and then ball-milled for 24 hours. A dip-coating procedure based upon a method described in Zwinkels et al. [1993] has been utilized to coat the ceramic monolith with the washcoat and the catalytically active material. The monoliths are dipped in this slurry and air is blown through the channels to remove the excess of
slurry blocking the channels. The coated monoliths are then dried at 390 K. This procedure is repeated until the desired washcoat loading is obtained. The catalysts are calcined at 1470 K for 12 hours in air to obtain adequate adhesion of the washcoat onto the monolithic substrate. *Table 8-2* below gives a summary of the catalyst properties.

<table>
<thead>
<tr>
<th>Catalyst description</th>
<th>Diameter / length</th>
<th>Material</th>
<th>Cell density</th>
<th>Hydraulic channel diameter</th>
<th>Open frontal area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>150 mm / 25 mm</td>
<td>Cordierite / 2MgO-2Al2O3-5SiO2</td>
<td>400 cells per square inch (=cpsi)</td>
<td>0.11 mm</td>
<td>74 %</td>
</tr>
</tbody>
</table>

*Table 8-2: Summary of catalyst properties.*

**8.2 Catalyst Testing**

In the following, results from the experimental investigation of catalyst behaviour are presented. *Table 8-3* below shows the tested catalyst configurations. Catalyst Configuration IV is the one for which highest fuel conversion rates are expected. Segments 3 to 5 have been developed to achieve low level emissions of HC and CO that has not been oxidized in the first two catalysts. The selected testing procedure was to stepwise increase the number of catalyst segments to be able to characterize combustor performance at various configurations. The respective abbreviations are given in *Table 8-1*.

<table>
<thead>
<tr>
<th>Catalyst Configuration</th>
<th>Segment 1</th>
<th>Segment 2</th>
<th>Segment 3</th>
<th>Segment 4</th>
<th>Segment 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Pd / LHA</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>II</td>
<td>Pd / LHA</td>
<td>Pd / LHA</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>III</td>
<td>Ba / Pd / LHA</td>
<td>Pd / LHA</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>IV</td>
<td>Ba / Pd / LHA</td>
<td>Pd / LHA</td>
<td>LMHA</td>
<td>LMHA</td>
<td>LMHA</td>
</tr>
</tbody>
</table>

*Table 8-3: Investigated catalyst configurations.*

A common way to describe the catalyst throughput is the Gas Hourly Space Velocity, defined as:

\[
GSHV = \frac{\text{Volumetric gas flow through catalyst(s) per hour}}{\text{Volume of catalyst(s)}} \left[ \frac{m^3_{\text{fuel}}}{h \cdot m^3_{\text{catalyst}}} \right].
\]

The nomenclature being followed here for the definition of the equivalence ratio is after Warnatz et al. [1999]. The air equivalence ratio \( \lambda \) is defined as the molar ratio of air-to-fuel divided with its ratio at stochiometric conditions:
\[ \lambda = \frac{\text{air/fuel}}{\text{air/fuel}_{\text{stoichio}}} \]. \hspace{1cm} (8-1)\]

In such a system, fuel-rich conditions are characterised by a value of \( \lambda \leq 1 \) and a fuel-lean by \( \lambda > 1 \). Stochiometric combustion is characterised by \( \lambda = 1 \). The reciprocal value is called fuel equivalence ratio and symbolized by \( \Phi \). As already mentioned, the air-to-fuel ratio cannot directly be measured in the test facility. Spindt [1965] has presented a technique to calculate this ratio based upon information of the mass fraction of carbon and hydrogen in the fuel and the emission composition. This method is based on the proposition that the composition of a burnt mixture of air and fuel must reflect the air-to-fuel ratio of the original mixture. The validity of this calculation method has been demonstrated by comparing measurement results with calculated values. Because of its convenience, this method has been used here. For detailed information on the derivation of the equation, the reader is referred to the original paper by Spindt [1965]. Eq. (8-2) is used to calculate the air-to-fuel ratio:

\[
\begin{align*}
\frac{\text{air}}{\text{fuel}} &= F_b \left[ 11.492 F_c \left( \frac{1+R}{2+Q} \right) + \frac{120F_{H2}}{3.5+R} \right], \\
\end{align*}
\] \hspace{1cm} (8-2)

with \( F_c \) and \( F_{H2} \) being the mass fraction of carbon and hydrogen in the fuel. \( R, Q, \) and \( F_b \) are defined as ratios of emission concentrations:

\[
\begin{align*}
R &= \frac{\text{CO}(\%)}{\text{CO}_2(\%)}; \quad Q = \frac{\text{O}_2(\%)}{\text{CO}_2(\%)}; \quad F_b = \frac{\text{CO}(\%)+\text{CO}_2(\%)}{\text{CO}_2(\%)+\text{CO}(\%)+\text{HC}(\%)}. \\
\end{align*}
\]

In the following, the results from the catalytic combustion tests are being presented in the chronological order of the different configurations that were tested.

### 8.3 Catalyst Configuration I

This paragraph will present the results obtained with Catalyst Configuration I at atmospheric conditions, i.e. one single Pd / LHA segment mounted in the combustor. The aim of these experiments was to investigate the ignition behaviour of such a catalyst and to study in how far the product gas from the gas reactor can be used for these studies. Earlier component testing of the gas reactor had shown that the fuel composition is not stable over a prolonged period of time. It thus had to be investigated in how far this affects catalyst operation.

Fig. 8-1 shows a typical temperature profile in the catalyst during one. Five thermocouples were placed in the segment, one centrally and four equally distributed on the \( \frac{1}{2} \)-radius. Fuel ignition supported by the catalysts is achieved by stepwise increasing the temperature of the air/fuel mixture at the inlet of the catalyst. At an inlet temperature of 477 K at \( t = 2200 \) s, ignition occurred. At the time \( t = 4070 \) s, the
raw gas feed into the gas reactor was briefly shut off and increased to a larger raw fuel mass flow into the gas reactor. The lower heating value of the fuel changed from 6.31 MJ/kg to 7.78 MJ/kg, the calculated λ-value changed from 8.28 to 8.48. The increased lower heating value of the fuel explains the higher catalyst temperature at t > 4200 s. All five thermocouples show the same variations in the temperature. These minor peaks in the temperature profiles are most certainly caused by irregularities in the flow field upstream of the catalyst. The gas analysis system cannot resolve short-time variations, it could therefore not be measured if short-term variations in the fuel composition occurred that caused these minor temperature peaks. Several parameters were varied during this experiment, i.e. the catalyst inlet temperature and the amount of air that entered the gas reactor. The catalysts have been manufactured to operate at maximum temperatures around 1200 K. The temperature differences inside in the catalyst as shown in Fig. 8-1 do not give rise to noteworthy thermal stresses in the ceramic material, the same accounts for the profile shown in Fig. 8-4. However, these temperature differences show that thermally stable material is needed for the catalyst support (as local variations in the temperature cannot be excluded) in order to ascertain a sufficient safety margin for catalyst operation.

![Fig. 8-1: Typical temperature profile in the catalyst segment at different catalyst inlet temperatures during one experiment, \( \lambda \) between 8.28 and 8.48.]

During instrumentation of the catalyst, care was taken to mount all thermocouples in a similar depth into the catalyst. However certain variations in the mounting cannot be excluded.
Fig. 8-2: Time resolved profile measured ignition of the catalyst.

Fig. 8-2 shows a typical temperature profile development after the fuel ignition in the catalyst. A definition for the ignition temperature has been introduced such that ignition is stated to occur if the temperature gradient dT/dt is larger than 5 [K/s]. As no definition for the ignition temperature could be found in the literature, this value was decided. The depicted temperature profile is quite typical and has been observed frequently. As the catalyst temperature increases in axial direction and the mounted depth varies between the thermocouple (due to the tolerance in the mounting), the different profile shapes can be explained. Comparing Fig. 8-2 and Fig. 8-3, one can identify similar tendencies in the development of the catalyst temperature. As Zhu et al. [2001] explain, the differences in the temperature profiles can be caused by local different equivalence ratios and/or by the axial positions at which the temperature is measured. In the case of those results show in Fig. 8-2, these differences are most probably caused by the thermocouples that are positioned inside the catalyst channels. This results in a certain blockage effect of the specific honeycomb channel that may vary from one thermocouple to the other. This in turn results in different local fuel to air ratios, which then can be taken to be the cause of the non-uniform temperature profile. The right hand side of Fig. 8-3 gives temperature profiles of the channel flow at various axial locations and at different times. However, the monolith length in the study presented by Zhu et al. [2001] is 7.5 cm whereas the ones tested in this work are only 2.5 cm long. Because of the relatively short monoliths studied here, the effect of the axial location of the thermocouples can be assumed to be less important compared to local variations in the equivalence ratio. Still the axial position of the thermocouple is expected to have an influence on the measurement signal.
Fig. 8-3: Surface and gas phase temperature profiles along axial coordinate of the catalyst at different equivalence ratios at a fixed time (left-hand side) and at constant inlet flow velocity at different times and axial location, A=60 s, B=300 s, C=600 s; D=900 s, Zhu et al [2001].

Fig. 8-4a) shows the catalyst temperature at various catalyst inlet temperatures. Caution had to be taken to prevent overheating the electric heaters, which is why no inlet temperatures higher than 550 K were tested. Increase of the inlet temperature gives a linear response increase in the catalyst temperature. As seen before, the measured temperatures in the catalyst are not homogenous and differ between the minimum and maximum value by 150 K. The emission level of CO is reduced by approximately 48 % when increasing the average catalyst temperature from 650 K to 880 K, the change in the H₂ emission level for the same temperature increase is about 58%, see Fig. 8-4b). No significant change in the hydrocarbon concentration in the exhaust can be seen for this temperature increase. The average catalyst temperature at maximum is approximately 870 K, this is too low for noteworthy oxidation of hydrocarbons. Groppi et al. [1993] have calculated the apparent activation energy assuming first order dependence on fuel concentration for the kinetics and an isothermal plug flow reactor. Values of 54-62 kJ/mol for CO and H₂ and 92-100 kJ/mol for CH₄ were obtained. Verification experiments were performed using a LaMnAl₁₁O₁₉ catalyst. Experiments performed in this study are consistent with this, see section 8.3.1.

The fuel composition of the experiments shown Fig. 8-4 was the following: 23.99% CO; 4.43 eq.%CH₄ HC; 14.14% CO₂; 13.87% H₂; 1.37% O₂. Resulting in a lower heating value of 5.2 MJ/kg.
Fig. 8-4: a)–Change of catalyst temperature as a function of the catalyst inlet temperature at $\lambda=11.1$, b)–Change of exhaust composition vs. average catalyst temperature at $\lambda=11.1$. 

---

**a)**

- Catalyst Temperature [K]
- Catalyst Inlet Temperature [K]
- $T_{21-1}$
- $T_{21-2}$
- $T_{21-3}$
- $T_{21-4}$
- $T_{21-5}$

**b)**

- Exhaust Gas Concentration [%]
- CO
- HC [eq: % CH₄]
- CO₂
- O₂
- H₂
- Average Catalyst Temperature [K]
- O₂ Concentration [%]
Fig. 8-5: Average catalyst temperature at three different operating conditions.

The experiment summarised in Fig. 8-5 shows the average catalyst temperature at three different equivalence ratios. Due to instabilities in the gas reactor operation, the raw inlet fuel flow of C\textsubscript{3}H\textsubscript{8} and CO\textsubscript{2} had to be changed for each operation point in order to keep the fuel composition stable. This resulted in variations in the lower heating value of the fuel, as indicated in the figure. The fuel ignited at a catalyst inlet temperature of 440 K. OP 3 data series was recorded such that the catalyst inlet temperature was stepwise decreased. Stable catalyst operation at temperatures below the ignition temperature was achieved. This typical hysteresis behaviour is described in more detail in section 8.5. Due to the very lean mixtures, the change in heating value of the fuel is less reflected in the catalyst temperature than by variations in $\lambda$. The temperatures measured during OP 2 are approx. 40 K lower than the corresponding ones in OP 1. The temperature decrease of more than 100 K from OP 2 to OP 3 is due to an increased $\lambda$-value.

### 8.3.1 Comparison with Bench-Scale Experiments

Experiments in a bench-scale rig have been performed to study the fuel conversion in the catalyst under near isothermal conditions and to compare pilot-scale experiments with bench-scales. The rig consists of monolith catalyst (2 cm diameter and 1 cm length) mounted in an oven, i.e. external heating. In this type of reactor, the catalyst temperature is ideally the same as the oven temperature. A direct comparison between bench- and pilot-scale tests can reveal information in how far the scaling of the physical size of the catalyst influences its operation.
Premixed bottled fuel gas has been used for these experiments. The temperature ramp for the oven was 5 K/min from 370 K up to 1170 K. Exhaust gas composition analysis was done with a conventional gas chromatograph equipped with a TCD and a FID detector. The tested catalyst composition is the same as Catalyst Configuration I. The following fuel composition was used in this experiment: 31.8% CO₂, 23.7% H₂, 10.6% CH₄ and 33.9% CO. The dilution ratio of the fuel with air was 1:99. The stochiometric air/fuel ratio for this fuel is 2.38, which gives a \( \lambda \)-value of 4.5. The operating conditions in the bench scale tests were different in terms of the GHSV, which was by approximately a factor of 8 lower than in the pilot rig. The presented results have therefore a qualitative character.

![Graph](data:image/png;base64,iVBORw0KGgoAAAANSUhEUgAAAQAAADcCAYAAAAd1SuaAAAgAElEQVR42mC2Q1P...)

Fig. 8-6: Conversion of H₂, CO and CH₄ and outlet temperature profile over a Pd-LHA in a bench scale experiment on a catalyst, fuel composition 31.8% CO₂, 23.7% H₂, 10.6% CH₄, 33.9% CO, diluted in air by 1:99, lower fuel heating value of 9.28 MJ/kg.

Instantaneous ignition of CO and H₂ occurred at a \( T_{\text{inlet}} \) of 390 K, followed by a smooth ignition profile for CH₄ starting at a temperature of about 600 K, see Fig. 8-6. These results have confirmed earlier observations of higher temperatures required for CH₄ oxidation. Ignition is also visible in the right diagram of Fig. 8-6 by an increase of the slope in the catalyst outlet temperature. Above a \( T_{\text{inlet}} \) of 560 K, the slope of \( T_{\text{outlet}} \) decreased to its original value. Above this temperature, the heat production in the catalyst is overruled by the external heating, i.e. the reactor became isothermal again. No decrease of the conversion of CO and H₂ is observed at 100% conversion of CH₄ at temperatures above 800 K. The conclusion reached is that Pd impregnated catalyst is sufficiently active for complete combustion of CO and H₂ at temperatures at which high conversion of methane is achieved. The ignition temperature observed here is somewhat lower than the ones measured in the pilot-scale rig. The lower space velocity at which the bench scale experiments were performed can explain this. Pd impregnated hexaaluminate catalysts and Pd supported catalyst in general show a characteristic drop in catalyst activity in the oxidation of CH₄ at specific temperature of about 1000 K.
In the experiment shown in Fig. 8-6, complete conversion of methane is already reached at temperatures below 1000 K. The high conversion of methane is caused by a combination of the very high Pd loading (5wt% rel. to washcofat) of the catalyst and the relative low space velocity. Due to the design of the bench-scale test rig, test condition as in the pilot rig could not be achieved.

### 8.3.2 Conclusion of Catalyst Configuration I

These first catalyst tests have shown the applicability of the combustion test facility. The following conclusions from these catalytic tests can be summarised:

- The ignition temperature of the Pd / LHA catalyst lies below the intended region of 500-600 K. The highly active Pd-segments are thus adequate as a first catalyst in the case of a segmented catalytic combustor for ignition and enabling the combustion process.
- A linear relation between the catalyst inlet and the catalyst temperature has been found for this configuration. The temperature in the mixing section is an excellent control tool for the combustor outlet temperature and thus the conversion of the fuel species.
- With one segment mounted only, the CO emissions could be reduced by almost 40% to 0.5% by increasing the catalyst temperature from 650 K to 870 K. The design of the combustor is aimed towards the use of several segments. The fact that with one catalyst only, these relatively low emission levels are achieved is promising.
- In order to oxidize a significant amount of hydrocarbons (from an emission level perspective) temperatures above 900 K are required.

Furthermore, it can be shown that even with a varying fuel composition, which is common for the product gas of gasification systems, the catalysts can be operated. Measures have to be taken to protect the catalyst being exposed to temperatures above 1200 K. Volatilization of the palladium becomes significant above this temperature and results in a lower in catalytic activity.

### 8.4 Catalyst Configuration II

This configuration was intended to reveal some knowledge about the operational behaviour of two highly active, noble metals, supported on LaAl$_1$O$_{18}$ catalysts. Two identical Pd / LHA segments were mounted into the combustor.

Stable catalyst operation with this configuration was not possible. The catalyst temperature frequently rose above 1300 K, illustrated in Fig. 8-7. This figure shows a typical temperature profile, often observed with Catalyst Configuration II. The temperature peaks (peak 1 at $t = 2800$ s, peak 2 at $t = 2910$ s) within catalyst segment 2 above 1300 K led to an emergency shut off of the fuel. At these temperatures, volatilization of the Pd may become significant. The direct consequence is a more rapid monolith deactivation with a resulting reduced combustion activity.
Temperatures above 1000 K were not measured in segment 1. The temperature peaks can be explained by the very high activity of the catalysts in terms of Pd loading. The lower maximum temperature of peak 2 is explained by an earlier emergency shut off. Also visible in Fig. 8-7 is the onset of homogeneous gas phase reactions downstream of the catalysts at $t = 3250$ s, shown by the dashed line in the figure. This thermocouple is mounted 50 cm downstream of the last catalyst at the outlet of the combustor. The reason why no catalyst temperature peak was observed while the gas phase reactions occurred is not completely understood. One possible explanation is that the active material of both catalysts was reduced from active PdO to less active metallic Pd by temperature peak 1 and 2 and the time interval was too short in order to re-oxidize the Pd back to PdO (see also section 2.2 and section 8.8.3).

As these hot spots in the catalyst could not be avoided by adjusting the air-to-fuel ratio or the fuel composition, catalyst activity had to be reduced. It was expected that this would prevent hot spots in the catalysts. The procedure described in the following section was applied.

During the subsequent experiments it was observed that the temperature measured in the first segment did no longer reach levels above 500 K. A linear correlation between the emission levels for H$_2$ and CO and the catalyst temperature was calculated and the strength of the correlation was determined by the square of the Pearson product-moment correlation coefficient [Lowry, 2001]. For all data series the fuel composition was similar. The total time of catalyst operation increases with increasing data series index. Hence the catalyst has been operated for the longest time in data series five. The decreasing strength of the correlation, shown by the decreasing values of the coefficient of determination $r^2$, can be understood such that the catalyst activity has reduced.

![Fig. 8-7: Temperature profile of two identical Pd / LHA catalysts vs. time, indication of homogeneous gas phase reaction occurring downstream of the catalysts.](image-url)
Fig. 8-8: Coefficient of determination $r^2$ shown for different data series.

8.4.1 Conclusion of Catalyst Configuration II

No stable catalyst operation was possible with this configuration. Even with a fuel gas with small content of H$_2$ and CO, the catalyst turned out to be too active resulting in peak temperatures in the segments well above 1300 K. The amount of palladium on both segments with 5wt% proved to be too high. Furthermore, the excessive temperature peaks deactivated the first segment. This catalyst had to be exchanged for the subsequent investigations.

8.5 Catalyst Configuration III

A solution had to be found to reduce catalyst activity of the first segment. Such a limitation will not only avoid volatilization of the Pd but also limit the inlet temperature of the subsequent segment. Ahlström-Silversand et al. [1997] have reported that Ba is effective in restraining the solid diffusion process which leads to sintering. The presence of large ions such as Ba in the crystal structure of the catalyst reduces the atom mobility; crystal growth that is accompanied with a loss if surface area is thus inhibited. Alkali earth metals have the potential to act as thermal protection barrier. Other possibilities would have been to use Ce, La or Sr instead of Ba. From this, it was concluded that if a layer of inactive Ba-Al$_2$O$_3$ is applied on top of the palladium, maximum catalyst temperature will be limited and volatilization will hence be inhibited.
The photographs in *Photo 8-1* (taken with a transmission electron microscope), demonstrate the inhibiting effect of barium stabilized alumina (Ba-Al$_2$O$_3$) on sintering. This example is only to be seen representatively with respect to this work presented here, sintering of the catalyst support is inhibited, not of the active material. Photographs A and C show the catalyst after calcination at 500°C. Photo B shows the sintered Al$_2$O$_3$ catalyst after calcination at 1000°C. Sintering is recognized by the structural change of the catalyst support. This effect cannot be detected in photo D. The dark spot in photos B and D shows sintered metallic particles. Again, *Photo 8-1* illustrates the thermal protection of an inactive layer of Ba-Al$_2$O$_3$ on the catalyst support and not on the active material.

*Fig. 8-9* shows a temperature profile during ignition of the fuel in both catalysts in Catalyst Configuration III. The lower ignition temperature seen in the second segment is due to its higher catalytic activity. This behaviour has been confirmed in different experiments with varying fuel composition. The Ba-Al$_2$O$_3$ layer works effectively in lowering the activity of the first catalyst. Ageing effects can be excluded from the explanation of the different ignition temperatures of the two segments. Radiative heat transfer from the second catalyst increases the temperature of the first segment and initiates its ignition. These tests were performed with bottled fuel gas, the gas reactor was not used here. Reason for the use of a bottled fuel gas was to see whether or not this would make the experiments easier to perform. This was, however, not the case. Although the tests turned to be shorter in time, the fuel costs on the other hand are much higher than with the gas reactor which nullifies the time advantage. For the test results shown here the fuel consisted of 15% CO, 14% CO$_2$, 10% H$_2$ and 4.5% CH$_4$. Background gas was N$_2$. The lower heating value of this fuel was 3.8 MJ/kg. The experiment was performed at very lean conditions of $\lambda=10.66$.

An observed temperature hysteresis for the ignition-extinguish loop of the catalyst temperature is shown in *Fig. 8-10*. The observed hysteresis behaviour is a characteristic for strongly exothermal reactions. Catalyst activity is not lost until the inlet temperature drops below 370 K. Dalla Betta [1997] has observed a similar hysteresis behaviour in a fully pressurised system at 11 bar. He reports that within a margin of 10 K, the ignition of the 4% CH$_4$-in-air mixture occurred. The catalyst temperature changed from 680 K to 920 K. Due to the higher required activation energy of methane compared to H$_2$ and CO, the observed ignition temperature was about 680 K, i.e. comparable to the ones seen in this study.
Fig. 8-9: Difference in ignition temperature of the two catalyst segments in Catalyst Configuration III.

Fig. 8-10: Observed hysteresis behaviour in the ignition / extinguish temperature.

Fig. 8-11 shows an enlargement of the extinction as part of the hysteresis curve in Fig. 8-10. Within 45 seconds, the averaged temperatures measured in the first segment dropped from 538 to 360 K. The second segment shows a temperature drop from 550 to 358 K, also during a time interval of 45 seconds.
Another test series was performed to study how the catalysts act in very lean mixtures. During this experiment, the catalyst inlet temperature had to be kept below 550 K to prevent damage to the electric air heaters. The reason for this was the limited mass flow of fuel that could be introduced into the rig and the resulting low air flow.

![Fig. 8-11: Enlarged section of the extinction temperature as presented in the hysteresis curve shown in Fig. 8-9.](image)

Fig. 8-11 shows the measured profiles of this experiment. Hydrocarbon emissions could not be measured during this experiment as the analyser was out of order. A \( \lambda \)-value of approx. 20 could be established. As can be seen from Fig. 8-12, at such lean conditions the temperature increase across the catalyst is relatively small. At a calculated air-to-fuel ratio of 20.5 and 20.9 respectively and a CO concentration in the mixing section of 0.730% and 0.718% respectively, the combustor outlet concentration
of CO is approx. 0.12%. The change in the CO emission level after changing $\lambda$ is not significant. This gives a CO conversion of 83%. It was thus shown that even at very lean mixtures and the resulting small $\Delta T$ over the catalysts, a high conversion rate of CO can be achieved. The observed temperatures are too low to achieve a significant conversion of hydrocarbons. The increase in catalyst temperature at $t = 2800$ s was not caused by an increase of the inlet temperature but by slightly reducing the total air mass flow through the test facility. This resulted in an increased residence time of the fuel in the catalyst and a successive increase of the catalyst temperature.

In the following, the gas reactor was again used as a source of fuel gas. In Fig. 8-13, the catalyst temperature against the catalyst inlet temperature for two different $H_2/CO$ contents of the fuel gas is shown. The operating conditions were otherwise similar.

![Graph showing catalyst temperature vs. inlet temperature for different fuel gas compositions.](image)
The bar diagram shows the ΔT from the first to the second segment on the right ordinate. The fuel composition was different in these two otherwise comparable tests. For the experiment shown in Fig. 8-13a), a content of 7.8% H₂ and 3.7% CO were measured in the fuel. The catalyst temperature is too low for hydrocarbon combustion to occur. The situation changes for the experiment shown Fig. 8-13b), 19.10% H₂ and 13.06% CO were measured in the fuel which results in far higher catalyst temperatures. The conclusion that can be drawn from this is that the Pd supported LaAl₁₁O₁₈ catalyst is suitable to catalytically support the ignition of a low heating value fuel gas. Stable catalyst operation was achieved for both high and low contents of H₂ and CO which resembles a main fraction of a fuel gas derived from biomass gasification.

![Average Catalyst Temperature vs. Combustor Outlet CO Level](image)

**Table 8.14:** CO emissions at combustor outlet for various operating points, displayed are average temperature in both catalyst segments, respective data given in the table.

<table>
<thead>
<tr>
<th>OP</th>
<th>λ-value</th>
<th>Hₘ [MJ/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.53</td>
<td>5.816</td>
</tr>
<tr>
<td>2</td>
<td>6.77</td>
<td>7.518</td>
</tr>
<tr>
<td>3</td>
<td>7.97</td>
<td>6.025</td>
</tr>
</tbody>
</table>

*Fig. 8-14 shows the measured CO content in the emissions for various catalyst temperatures. The catalyst temperature is the appropriate reference here since no gas phase reactions occurred during these experiments. Three different operating points are shown in the diagram, denoted by OP 1, 2 and 3. For each OP, the λ-value as well as the fuel composition changed due to the gas reactor characteristics, as listed in the figure. It is interesting to note that for OP 2 the lower heating value of the fuel is higher than for OP 1 and 3 and that λ is closer to stochiometric than for the other two OP’s. Reason for the lower catalyst temperature of OP 2 compared to OP 1, shown in Fig. 8-14, is the fact that the catalyst inlet temperature was deliberately kept lower for this test series. The hydrocarbon analyser was not available at the time these experiments were performed, they could however be estimated based upon measurement results obtained from later test series. The expected, non-ambiguous tendency was found: the higher the catalyst temperature for a certain operating point, the lower the CO level in the emission which is in agreement to the literature. Roughly the same temperature increase from the first to the second segment could as well be achieved for all three operating points.*
8.5.1 Pressure Effects

One of the objectives of the study was to investigate the effect of the pressure on the catalytic combustion of a low heating value fuel gas with respect to catalyst temperature and emission levels. During start-up gas turbines are pressurised at a constant volumetric flow rate, this cannot be achieved in the wind tunnel facility. Here, pressurizing can only be done via closing a pressure reduction valve mounted downstream of the test facility. At the same time, the amount of total mass flow entering the test facility can be changed. As a direct consequence of the different throughputs, the residence time of the fuel changes when pressuring the test facility. By measuring the pressure drop, the relative change in the velocity variation and thus the residence time of the fuel can be calculated as described below. The general expression for the pressure drop, neglecting friction, can be approximated as follows [VDI Wärmeatlas, 1977]:

\[
\Delta p = \frac{1}{2} k \rho \bar{u}^2. \tag{8-3}
\]

The ratio of two measured pressure drops, using the ideal gas assumption for the hot exhaust gases is thus:

\[
\frac{\Delta p_1}{\Delta p_2} = \frac{\rho_1}{\rho_2} \left( \frac{\bar{u}_1}{\bar{u}_2} \right)^2 = \frac{p_1 T_2}{p_2 T_1} \left( \frac{\bar{u}_1}{\bar{u}_2} \right)^2. \tag{8-4}
\]

In order to account for the density change due to the temperature change, the average of the inlet and the outlet temperature of the combustor was taken. From equation (8-4), the relative change in residence time can easily be estimated using the ideal gas assumption.

Table 8-4 gives the calculated, relative change in bulk flow velocity due to pressurizing the test rig from slightly below 2 bar to above 3 bar. The corresponding temperature profiles and emission measurements are shown in Fig. 8-15, the corresponding data table is given in Table 8-5. No data points at atmospheric pressure were obtained for this configuration due to the rather large changes in the fuel composition when the system was pressurised. Table 8-5 also gives the measured pressure drop across the combustor, which is less than 5% of the inlet pressure.
Table 8-4: Calculated change of bulk flow velocity due to pressure increase.

<table>
<thead>
<tr>
<th>Data point</th>
<th>Δp [kPa]</th>
<th>p_{in, rel} [kPa]</th>
<th>T_{in} [K]</th>
<th>T_{out} [K]</th>
<th>$\overline{T}$ [K]</th>
<th>Ratio of bulk flow velocities</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.64</td>
<td>102.9</td>
<td>481.5</td>
<td>910.1</td>
<td>695.8</td>
<td>$\overline{u}_2 / \overline{u}_1 = 1.71$</td>
</tr>
<tr>
<td>3</td>
<td>1.79</td>
<td>212.57</td>
<td>468.5</td>
<td>824.3</td>
<td>646</td>
<td></td>
</tr>
</tbody>
</table>

In Fig. 8-15, comparing data points 2, 5 and 6, one can see that for similar catalyst inlet temperatures, the corresponding catalyst temperature of the second segment decreases with increasing pressure. This is associated with an increase of CO emissions in the respective data points. In this test facility, a higher residence time of the fuel in the combustor, as explained in Table 8-4 could be expected to result in a higher conversion rate. This would then cause a higher heat release and the catalyst temperature to raise. The measurements do not support this. From a kinetic point of view on the other hand, interpretation of the pressure effect is more difficult. The adsorption rate of a gaseous species $A_g$ onto the catalyst surface is linearly proportional to its partial pressure $p$ in the gas mixture, the adsorption rate constant $k_a$ and the surface concentration of active sites $\Theta$, see also Appendix C

$$-\frac{d[A_{g}]}{dt} = k_a p (1 - \Theta) \quad (8-5)$$

In the case of bimolecular combination reactions, the pressure dependency becomes a function of both partial pressures. In this case, the two species are competing for free surface sites to bond to. At a higher partial pressure of the fuel species, more reactants compete for a constant concentration of active sites on the surface. Consequently, the amount of reactants that pass through the monolith channel without participating in a reaction increases. Schlosser [1972] derived an expression for the reaction rate of a bimolecular reaction including backward reactions (reactants desorb from the surface without reacting) for both species. The assumption of instantaneous desorption of the reaction product is made. For the desorption of the reaction products pressure effects are thus not included. The expression for the reaction rate shows that if the absolute pressure is increased with a constant ratio of the partial pressures of the reactants, i.e. no change in fuel composition, the reaction rate increases quadratically with pressure.

Detailed kinetic studies were beyond the scope of the study presented here. The pressure effect on the kinetics of the catalytic combustion of a low heating value fuel are not fully understood, also because the complexity of the gas-surface interactions. Very little research has been done on the kinetics of applied catalytic combustion especially with respect to pressure.
Fig. 8-15: a)–Catalyst temperature and b)–CO emission level at combustor outlet of Configuration III vs. the relative combustor inlet pressure.

Table 8-5: Data sheet for Fig. 8-15.
Fig. 8-16: Effect of pressure on the outlet temperature of a catalytic combustor, Groppi et al. [1993].

Groppi et al. [1993] published results of a numerically modeled hybrid catalytic gas turbine combustor. The pressure dependency on the combustor outlet temperature is shown in Fig. 8-16. Pure methane was used as a fuel in their studies. Three different flow regimes can be identified. The laminar flow regime is characterised by a linear decrease of the combustor outlet temperature with increasing pressure, the transition region is indicated by a less steep linear increase of the outlet temperature with increasing pressure. In the turbulent flow regime, the combustor outlet temperature is unaffected by the pressure. Several assumptions were made in this numerical model: i) steady-state conditions and uniform pressure along the monolith wall, ii) negligible homogeneous gas phase reactions, iii) irreversible first order kinetics in the fuel gas and zero order in O2 concentration at the catalyst wall, iv) combustion is limited to a thin layer near the monolith surface, no axial diffusion occurs, v) properties of air are taken for the properties of the air / fuel mixture.

The Re-number based on the hydraulic diameter of one channel, resulted in values below 1000. This value varied together with changes in other thermodynamic values, but no Re-number larger than 1000 was estimated. The flow inside the monolith is therefore assumed to be laminar. The proposed model shows a decrease of the catalyst temperature with increasing pressure. Similar trends in the pressure regime up to 4 bar were observed in this study.

Ozawa et al. [1998] have reported pressurised test results from a catalytically assisted gas turbine combustor. The catalyst studied consisted of Pd / Pt / Rh active phase on a Al2O3 / ZrO2 washcoat, liquefied natural gas was used as fuel. In their experimental study, a temperature decrease of about 100 K was observed when the operating pressure was changed from 3.5 to 4.5 bar. Different from the experiments performed in this study, Ozawa et al. [1998] kept the ratio of the air flow rate to inlet pressure, catalyst inlet temperature and combustor exit temperature constant while increasing the inlet pressure.

These results show the need for further research with respect to pressure effects in catalytic combustion.
8.5.2 Nitrogen Oxides from Fuel-Bound Nitrogen

NH₃ is added to the fuel stream downstream of the gas reactor to study the formation of nitrogen oxides from fuel-bound nitrogen. The planned test series were such that under stable catalyst operation, different amounts of NH₃ were to be added to the fuel flow. By varying the catalyst inlet temperature, conversion of ammonia to NOₓ and / or N₂ can be studied. During this test series, problems with the stability of the gas reactor occurred. The consequence of this was that the fuel composition could change drastically within a short period of time. However, some data was obtained and could be evaluated. It was decided in the following to abort this test series and to exchange the pellets in the gas reactor. This section presents the obtained results from the NOₓ studies.

The observed temperature profiles, shown in Fig. 8-17a) are comparable to the ones shown in the previous sections. Catalyst temperatures above 900 K were not reached below 500 K inlet temperature. The lower catalyst temperatures compared to Fig. 8-13 can be explained from the higher λ-value and a lower Hᶠᵗ.

As can be seen from Fig. 8-17b), the concentration of total hydrocarbons in the emission decreases with increasing combustor outlet temperature, which is consistent with the combustion theory. With two catalyst segments only, a substantial reduction of the THC to an outlet concentration of approx. 0.2 eq.% CH₄ at a catalyst temperature of close to 900 K could be reached. Carbon monoxide emissions of about 2000 ppm were measured. From this, it can be expected to reduce the emission levels further, once more catalytic segments are mounted into the test facility. NOₓ emissions of about 200 ppm were measured in the exhaust gas. These levels are too high to be acceptable for today’s gas turbine operators.

Several problems with the experimental hardware were identified during this test series. Besides the inconstancies in the fuel gas composition, the handling of the raw NH₃ caused difficulties due to condensation of ammonia in the mass flow controller. As a consequence of this, no pressurised experiments could be performed for the investigation of formation of fuel-bound NOₓ.
8.5.3 Conclusion of Catalyst Configuration III

Catalyst Configuration III has proven that ageing effects and/or sintering of the active material on the surface can substantially be reduced by the presence of a large ion, in this case barium in the crystal structure. The physical effect of the barium is that it reduces atom mobility of the metallic Pd on the catalyst surface. The Pd particles have thus a reduced ability to form surface islands. By limiting the maximum temperature of the first segment, the inlet temperature of the following segment is also limited. This results in a stepwise temperature increase from the 1st to the 2nd catalyst.
A hysteresis in the ignition and extinguish temperatures could be verified. The hysteresis width was measured to be about 80 K. Again because of the presence of a Ba-Al₂O₃ layer, different ignition and extinguish temperatures were observed for the two segments.

The catalyst could be operated under ultra-lean conditions, i.e. at $\lambda \approx 20$ with a correspondingly low $\Delta T$ across both catalysts. Operation of the catalytic combustor could be demonstrated over a wide range of H₂ and CO contents in the fuel. The potential for low CO and THC emissions could be shown at catalyst temperatures of about 1000 K under lean conditions. First measurements with focus on fuel-bound NOₓ were made, emissions of 200 ppm NOₓ were measured at the outlet of the combustor. More work is needed on this issue in the future.

The pressurised experiments indicated trends that are consistent with what has been reported in the literature. However, more research related to pressure dependencies of catalytic combustion is needed. Low pressure drops across the combustor of less than 5% inlet pressure were achieved.

8.6 Catalyst Configuration IV

In this arrangement three LaMnAl₁₁O₁₉ (LMHA) segments were mounted downstream of the two Pd-based catalysts. Due to the limited number of thermocouple fittings of the test rig, segments 1 to 4 are instrumented with two thermocouples. The last segment has three thermocouples fixed 2 cm downstream of the exit of the segment. Spacing between all catalysts is also 2 cm. Fig. 8-18 shows the obtained temperature and emission profiles with Configuration IV at atmospheric pressure. Several characteristics can be identified:

− The shape of the measured temperature profiles varies strongly between the Pd-based catalyst and the substituted hexaaluminates. The reason for the observed temperature drop in segment 1 & 2 is expected to lie in a change of fuel composition during the time interval. At $t = 3520$ s, the measured H₂ and CO contents in the fuel were 19.03% and larger than 20% respectively. At $t = 3700$ s, the respective H₂-value had dropped to 9.29% and the CO to 13.97%. As a consequence of the reduced formation of H₂ and CO in the gas reactor, it can be assumed that the amount of HC in the fuel rises simultaneously. The emission profile in Fig. 8-18b) shows no increase of the HC level at the combustor outlet. The conclusion that can be drawn is that this configuration including the LMHA catalysts can achieve a very high conversion of hydrocarbons.

− A combustor outlet temperature above 1100 K can be reached with this configuration.

− A decrease in catalyst inlet temperature of 30 K is not reflected in the outlet temperature.

− A rise in catalyst temperature from segment to segment can be seen. This is not true for the last catalyst segment. The measured temperature directly downstream of segment 5 is about 180 K lower than measured in segment 3 and 4 which are nearly identical. The reason for this is believed to lie in the fact that those thermocouples, that are mounted inside a monolith channel, do measure a
temperature that is composed of three different contributions: radiative heat transfer from the walls to the metallic thermocouple, convective heat transfer from the walls as well as gas phase temperature. The three thermocouples downstream of segment 5 cannot be influenced by the wall temperature of the monolith. Hence the lower indicated measurement value.

- The measured pressure drop over the combustor is 2.01 kPa. This is less than 2% of the combustor inlet pressure.

Fig. 8-18: a)–Temperature and b)–corresponding emission profile of Catalyst Configuration IV (two Pd-LaAl11O18 and three LaMnAl11O19 segments).

Fig. 8-19 shows the emission levels that can be reached using catalytic combustion of a low heating value fuel gas. For this experiment, performed at an equivalence ratio
of 6.95, the air-to-fuel ratio was estimated to be 14.81. Considering a concentration of 17% CO in the fuel gas, the resulting CO content in the mixing section can be calculated to 1.15%. Still, emission levels slightly below 100 ppm at a combustor exit temperature of 1175 K could be achieved. The corresponding HC level was below 100 eq. ppm CH₄.

![Graph showing THC and CO emission levels at \( \lambda = 7.08 \) and \( \lambda = 6.95 \) and two corresponding lower heating values of the fuel.]

The following figures illustrate the effect of varying hydrogen content in the fuel on the catalyst temperature. *Fig. 8-20a*) shows a nearly linear correlation between the amount of H₂ in the fuel and the catalyst temperature for all five segments. As the fuel concentration of hydrogen increases, so does the temperature of all catalysts. The similar trend is seen when the amount of CO in the fuel is considered. As the concentration of these two species decreases, the concentration of HC in the fuel, must, based upon a carbon mass balance over the gas reactor, increase. The maximum catalyst temperature of 820 K in segment is too low to oxidize any hydrocarbons. This picture changes in *Fig. 8-20b*) in which the variation in fuel concentration of H₂ is even larger than in case *a*). The temperature in the two Pd-based catalysts changes accordingly, consequently the inlet temperature of the third segment, i.e. the gas temperature between the second and third segment varies correspondingly. This variation in the inlet temperature of segment 3 is however not observed in the measured catalyst temperature itself. The reason for the lack of a temperature response lies in the fact that the temperature is sufficiently high to oxidize hydrocarbons. As the measured catalyst temperature of segment 3, 4 and 5 is above 1200 K, hydrocarbon oxidation takes place. The decreasing inlet temperature of segment 3 does not affect the reaction rate of the HC combustion. The effect of homogenous reactions that may occur in the short space between two segments has not been taken into consideration here.

With respect to operating a gas turbine on a fuel that is derived from biomass gasification, the illustrated results in *Fig. 8-20* have some relevance. They show that
the combustor outlet temperature is less affected by changes in the fuel composition if the catalyst temperature is sufficiently high that it can compensate the reduced content of one species by an increase oxidation of another compound. The temperature decrease noticeable in Fig. 8-20b) at H₂ concentrations of approximately 19% was caused by a reduction of the catalyst inlet temperature by the electric air pre-heaters.

The fact that no stable fuel composition could be obtained over a period longer than approximately 5 min made a more detailed investigation, including addition of NH₃ to the fuel impossible. It was therefore decided to continue these experiments with pre-mixed gas bottles in the future. These gas tanks allow studying the NOₓ formation under more specified conditions than are possible using the gas reactor.

Fig. 8-20: Catalyst temperature vs. content of hydrogen in the fuel at $\lambda = 6.95$. 
The temperature measured 2 cm downstream of the last catalytic segment, $T_{\text{ave cat 5}}$, is considerably lower than that one of segment 3 or 4, see Fig. 8-20. As mentioned earlier the question whether or not thermocouple measurements in the monolith channels are suitable for global catalyst temperature measurements arises. Differences in the axial position of the measurement are reflected in the signal. Channel blockage may be different for each thermocouple, this results in different amounts of fuel entering that specific channel which then in turn effects the heat release in that channel. Due to the lack of alternatives for this test facility, thermocouples were used. No optical access was practicable for the facility. For optical temperature and concentration measurements, windows would not only be needed in the pressure vessel, but also in the combustor tube itself. The stiff ceramic insulation inside the combustor shell would have to be removed, at least in some parts. The assumption of near-adiabatic conditions in the combustion chamber would no longer be valid. An optical access from the exit of the test facility would be hindered by the gas sampling device. In such an arrangement, only the outlet face of the last catalyst segment would be visible. These factors, besides the costs, made the implementation of spectroscopic or any other optical measurement equipment unrealistic for this study.

8.6.1 Conclusion Catalyst Configuration IV

Combustor outlet temperatures above 1100 K could be reached with this arrangement. Significant amounts of hydrocarbons were oxidized. Low CO emission levels of about 100 ppm could be achieved for a fuel that contained large amounts (> 15%) of this species. Hydrocarbon emissions were of the same order as the CO emissions. It could be shown that if the LaMnAl$_{11}$O$_{19}$ segments are at an operating temperature at which hydrocarbon combustion occurs, changes in the fuel composition, are not reflected in the combustor outlet temperature. The pressure drop measured during these experiments was less than 2% of the inlet pressure.

8.7 Comparison of the Different Catalyst Configurations

This sub-chapter is intended to give a brief comparison and summary of the experimental work performed in this study. Of the total number of experiments, only a certain amount has been done with focus on catalytic combustion. Others were performed in order to optimise the operation of the gas reactor in order to have better control over the fuel gas composition and / or to achieve stable boundary conditions for catalyst testing.

A representative set of the experimental data of the different configurations presented in this chapter has been summarised in Table 8-6. The listed data gives a comparison of the different arrangements tested at atmospheric conditions. The performed pressurised experiments and the studied literature on pressurised catalytic combustion have shown that knowledge of the pressure effects on surface chemistry is essential in order to fully understand pressure effects on catalytic combustion as a whole.
The combustion efficiency \( \eta \) has been calculated after eq. (8-6)

\[
\eta = 100 - \frac{\dot{m}_{\text{air}} + \dot{m}_{\text{fuel}}}{\dot{m}_{\text{fuel}} \cdot M_{\text{fuel}} \cdot H_{\text{lf}}} \cdot \left( c_{\text{CO}} \cdot M_{\text{CO}} \cdot H_{\text{CO}} + c_{\text{HC}} \cdot M_{\text{HC}} \cdot H_{\text{HC}} \right) \cdot 10^{-4}
\] 

(8-6)

with \( c_{\text{CO}} \) and \( c_{\text{HC}} \) being the emission concentration of the respective species in ppm. Hydrogen has not been included in eq. (8-6), since the assumption of complete combustion of \( \text{H}_2 \) is reasonable.

*Table 8-6* shows that the highest combustion efficiencies calculated after eq. (8-6) are achieved with Catalyst Configuration IV. The combustion efficiency is directly related to the combustion temperature. It could be shown that with Configuration IV, a stable combustion process using a low heating value fuel gas and at the same time achieving combustor outlet temperatures above 1100 K could be achieved. This fact makes Configuration IV the most suitable catalyst arrangement with respect to a gas turbine application.

Also shown in *Table 8-6* is the wide range of lower heating values of the fuel tested here. *Table 8-6* also lists the calculated Space Velocity at which the experiments were performed. At similar air and fuel mass flows through the rig, the Space Velocity decreases with increasing total volume of the catalyst reactor, i.e. the number of segments. As it was expected, the highest combustion efficiency can be obtained at those experiments operated under the lowest Space Velocity, i.e. longest residence time of the air / fuel mixture in the catalyst.

No results from Catalyst Configuration II are listed in *Table 8-6*. The unstable temperature profiles such as shown in *Fig. 8-7* and explained in section 8.4 aggravate the definition of a stable operation point of the catalytic combustion system. For this reason, this configuration has been omitted in the following table.
<table>
<thead>
<tr>
<th>Catalyst configuration</th>
<th>IV</th>
<th>IV</th>
<th>III</th>
<th>III</th>
<th>I</th>
<th>I</th>
<th>I</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. date yymmdd; Samples [s]</td>
<td>010531; 3550-3700</td>
<td>010531; 2818-3051</td>
<td>010329; 15400-17000</td>
<td>010329 7500-10000</td>
<td>000419; 6400-6600</td>
<td>000417; 4500-5500</td>
<td>000417, 4580-4700</td>
<td>000417, 5079-6378</td>
</tr>
<tr>
<td>Fuel input power [kW]</td>
<td>126.58</td>
<td>141.80</td>
<td>60.49</td>
<td>145.65</td>
<td>147.84</td>
<td>147.84</td>
<td>147.84</td>
<td>147.84</td>
</tr>
<tr>
<td>Combustor outlet temperature [K]</td>
<td>1116</td>
<td>1180</td>
<td>589</td>
<td>867</td>
<td>813</td>
<td>883</td>
<td>809</td>
<td>785</td>
</tr>
<tr>
<td>Combustion efficiency [%]</td>
<td>96.04</td>
<td>91.04</td>
<td>12.03</td>
<td>25.05</td>
<td>16.98</td>
<td>N/A&lt;sup&gt;a)&lt;/sup&gt;</td>
<td>8.97&lt;sup&gt;b)&lt;/sup&gt;</td>
<td>5.52&lt;sup&gt;b)&lt;/sup&gt;</td>
</tr>
<tr>
<td>Equivalence ratio [-]</td>
<td>6.95</td>
<td>7.07</td>
<td>&gt; 20</td>
<td>10.49</td>
<td>9.02</td>
<td>N/A&lt;sup&gt;a)&lt;/sup&gt;</td>
<td>8.96&lt;sup&gt;b)&lt;/sup&gt;</td>
<td>9.22&lt;sup&gt;b)&lt;/sup&gt;</td>
</tr>
<tr>
<td>Space velocity [h&lt;sup&gt;-1&lt;/sup&gt;]</td>
<td>168000</td>
<td>136000</td>
<td>337000</td>
<td>344000</td>
<td>565000</td>
<td>563000</td>
<td>563000</td>
<td>684000</td>
</tr>
</tbody>
</table>

<sup>a)</sup> THC not measured; <sup>b)</sup> THC approximated from correlating experiments
## 8.8 Miscellaneous Observations

This paragraph contains various observations that were made during the experimental investigation.

### 8.8.1 Fuel Composition and Ignition Temperature

Of crucial interest for the operation of a catalytic combustion chamber in a gas turbine is the ability of the catalysts to initiate the combustion process at typical compressor outlet temperatures. For catalyst arrangements I and II Fig. 8-21 shows the measured ignition temperature as a function of the hydrogen content in the fuel. Ignition was defined to occur as soon as the temperature gradient \( \text{dT/dt} \) exceeds 5 K/s. Hydrogen has been chosen as the reference firstly as it is a main component of the fuel and secondly as it diffuses faster into the catalyst pore structure than any other fuel component. It can hence be expected that H2 atoms are the first ones that react on the catalyst surface. A certain scatter in the measured ignition temperatures can be observed. The reason for this scatter lies in variations in both the air-to-fuel ratio and the fuel composition. The measured ignition temperature lies below 500 K. The conclusion can be drawn that the actual H2 content of the fuel has little or no influence on the ignition temperature.

<table>
<thead>
<tr>
<th>H2 Content in Fuel [%]</th>
<th>Ignition Temperature [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>300</td>
</tr>
<tr>
<td>7.5</td>
<td>350</td>
</tr>
<tr>
<td>10</td>
<td>400</td>
</tr>
<tr>
<td>12.5</td>
<td>450</td>
</tr>
<tr>
<td>15</td>
<td>500</td>
</tr>
<tr>
<td>17.5</td>
<td>550</td>
</tr>
<tr>
<td>20</td>
<td>600</td>
</tr>
</tbody>
</table>

**Fig. 8-21: Measured ignition temperature for Catalyst Configuration I and II vs. the H2 content in the fuel gas for a set of different experimental conditions.**
8.8.2 Hot Spots in the Catalyst

During several experiments performed under different operating conditions temperature peaks were measured at a discrete position in the catalyst, Fig. 8-22. This experiment was performed with a single segment mounted in the combustion chamber. Several possible explanations for the observed phenomenon have been considered:

− The temperature peaks were not constant with respect to the location in the catalyst, so a connection with the respective thermocouple can be excluded.
− Based upon the measurements in the cold flow test facility, homogenous mixing is assumed. Radial fuel concentration differences, that would cause different conversion rates, can therefore be excluded as well.
− Bruno et al. [1983] have reported that the catalyst wall temperature may quickly reach the adiabatic temperature of the reacting mixture. In cases in which the Lewis number Le is less than unity, the catalyst wall temperature may even exceed the adiabatic flame temperature. This effect was suspected to be the reason for the discrete temperature peaks. Taking the heat conductivity of the cordierite to 1.46 W/mK, density of air at 870 K as a first approximation and the heat capacity of the air / fuel mixture to 1327 J/kgK, the only uncertainty is the estimation of the diffusivity D. In order to circumvent this estimation of D, the Le-number was calculated a function of D. It was shown, that D has to be larger than 27.7 cm²/s in order for Le to become less than unity. Such a situation can physically not occur. The same could be shown with the hydrogen Le-number. Hence a Le-number effect at the cause for the temperature peaks can be excluded.
− The metallic tip of the thermocouple itself may act a catalyst and trigger certain reactions. Jones [1997] has reported such phenomena in connection with investigations in internal combustion engines. If this were the cause for the observed temperature peaks, it could be expected to happen more frequently than observed. Catalytic reactions on the thermocouple surface may very well occur within the experiments performed in this study. A more probable cause for the observed peak is given in the next point.
− It has been found that the fuel gas formed in the gas reactor contains soot particles. It is therefore probable that soot has agglomerated on the thermocouple inside the monolith channel. Carbon auto-ignites at temperatures around 670 K. The difference between 670 K and the temperature shown by the thermocouple at the onset of the peak can be explained by the relatively slow response time of the thermocouple compared to chemical time scales. The combustion of soot is highly exothermic. This cause is the most probable explanation to the observed temperature peaks.
8.8.3 Transition from Palladium Oxide to Metallic Palladium

A characteristic of Pd-based catalysts is a decrease of activity of CH$_4$ combustion at a temperature of about 1000 K. At normal conditions, the palladium on the catalyst surface is present as palladium oxide, PdO. At about 1000 K, the PdO is reduced to metallic palladium. This reversible transformation shows hysteresis behaviour and has been subject to intensive research as it, to some extent, enables a self-regulating effect in terms of CH$_4$ conversion over Pd-based catalysts, see McCarty [1995]. This phenomenon has also been observed in this work. Fig. 8-23 shows temperature profiles that were obtained during three different experiments. The circled areas can be understood as the reduction of PdO. These profiles were measured in the segments without the inactive Ba-layer. Dalla Betta et al [1994] and Forzatti et al. [1999] have reported similar observations for the PdO-Pd decomposition in air at atmospheric pressure. Forzatti et al. [1999] have furthermore reported that the temperature of decomposition of PdO increases with pressure. Whether or not the reduction of the PdO is the cause of the temperature oscillations mentioned in the following paragraph and illustrated in Fig. 8-24 is not fully clear. The detailed surface chemistry for the Pd-based catalysts as a whole is not well understood. The phenomenon described here has no direct impact on the applicability and operation of a catalytic combustor. For the sake of completeness, it should only be mentioned that the PdO-Pd transition has been observed in this study.
8.8.4 Temperature Oscillations in the Catalytic Combustor

Under various experimental conditions, fluctuations in the catalyst temperature occurred. An example of this phenomenon is shown in Fig. 8-24a). The temperature oscillations are stronger in the second segment than in the first one, suggesting that the Ba-Al$_2$O$_3$ layer has a damping effect on the temperature variations. The exact cause of these fluctuations is not known at this time. The oscillation shown occurs with a mean period of 138 sec and mean amplitude of 177 K. The inlet pressure of the combustor was constant. Pressure waves travelling into the test facility from the wind tunnel system were not recorded. The combustor pressure drop was constant at 1.9 kPa. Emissions and combustor outlet temperature show fluctuations corresponding to those shown in Fig. 8-24a). The changes in the combustor outlet temperature are however weaker with a mean amplitude of 87 K, their period matching that of the catalyst fluctuations. Emission variations reflect the temperature fluctuations. Minor variations of the raw C$_3$H$_8$ flow into the gas reactor have been measured during this experiment. Fig. 8-24b) shows the resulting catalyst temperature variation, which was clearly caused by a pulsating flow of propane into the gas reactor. The absolute variation of raw propane flow was about 9% in this case. The resulting temperature fluctuation in the catalyst is lower than the observed temperature oscillations shown in Fig. 8-24a). The damping effect of temperature fluctuations by the Ba-layer on the first catalyst segment can also be seen in Fig. 8-24b). In Fig. 8-24a) the absolute change in the raw C$_3$H$_8$ flow was about 2.8%, which is only one third of those seen in b). The catalyst temperature variation is however three times larger. The change of raw fuel mass flow into the gas reactor is therefore most certainly not the cause for the observed temperature oscillations. Fig. 8-25 shows an enlarged section of one period, which has its maximum amplitude at $t = 8980$ s and the corresponding change in combustor outlet concentration in NO$_x$ and HC. The temperature $T_{\text{down,cat}}$ depicted with diamond symbols in Fig. 8-25 is measured between the combustor outlet and the exit face of the...
last catalyst segment. It indicates the homogeneous gas phase combustion occurring downstream of the catalysts.

![Graphs](image_url)

**Fig. 8-24:** Fluctuations in the catalyst temperature measured with Catalyst Configuration III; a) exact cause not known, b) fluctuation caused by a pulsating raw C₃H₈ flow into the gas reactor at constant inlet temperature of T_{inlet} = 420 K.
The literature shows that other researchers have observed similar fluctuations. Ozawa et al. [1997] reported oscillations with a mean period of 35 sec and an amplitude of 60 K. No change in the emissions or in the combustor outlet temperature was observed. The pressure drop over the combustor did oscillate with the same period of 35 sec and an amplitude of 0.8 kPa at base load. No cause for these fluctuations was suggested in their paper. The investigated catalyst consisted of a stabilized Al₂O₃ / ZrO₂ washcoat on a Cordierite honeycomb, the active material consisted of a specific mixture of Pt, Pd and Rh.

Zhu et al. [2001] have developed a transient 1D model to investigate lean catalytic combustion of CH₄ on Pd-based hexaaluminate catalysts. They report that under
certain conditions, which are not further specified oscillatory behaviour in the outlet temperature can be caused by competition for active surfaces sites between O and OH radicals. This has been observed both in experimental and numerical tests.

Forzatti et al. [1999] have reported temperature self-control capability connected with the PdO-Pd transition in the catalytic combustion of CH₄. The high catalytic activity of the PdO leads to an increased conversion rate of CH₄. Once the PdO is reduced to metallic Pd at temperatures of about 1000 K, the conversion rate is reduced and the temperature decreases. The metallic Pd is then oxidized again to PdO, which leads to an increased conversion rate. The oscillation is complete. A more detailed cause of the observed oscillations is not known, more detailed research including the surface chemistry is needed to fully understand this phenomenon.

8.8.5 Decrease in Catalyst Temperature in Larger Time Scales

One of the experiments was performed with the objective to study the thermal stability of the catalysts over a longer time period. This test was done with Catalyst Configuration III. The result of this test is shown in Fig. 8-26a). All boundary conditions of the experiment were kept constant over a time period of 62 min. The observed slight decrease of the catalyst inlet temperature from 419 K to 411 K can be considered to be negligible in the explanation of the observed catalyst temperature drop. The fuel composition was monitored during this experiment, no noteworthy change in fuel gas composition was observed. Jackson et al. [2001] reported a similar temperature behaviour, shown in Fig. 8-26b). The cause of the long-term temperature drop is believed to lie in an imbalance between the mass transfer of unburnt fuel to the catalyst surface, heat transfer away from the surface to the bulk flow and the surface reaction rates. Two cases were reported, denoted by index 1 and 2. In case 1, a temperature profile comparable to the measurement in Fig. 8-26a) is seen. In case 2, however, the reactor temperature is stable over the entire time period. Zhu et al. [2001] studied the effect of bulk flow velocities on the reactor outlet temperature and reported similar temperature profiles for certain cases. With increasing inlet flow velocity, the outlet temperature decreased with time. The cause suggested was the convective cooling of the reactor inlet by the high flow velocities. This cooling pushed the ignition zone further downstream and thus reduced the effective volume available for the oxidation of the fuel. For the case observed in this study, the mass transfer of fresh fuel to the surface is thought to be too small to compensate the heat transfer away from the catalyst surface. Convective cooling causes the reactor temperature to decrease. Detailed kinetic investigations including estimation of the mass transfer and thermal diffusion coefficients for the observed system would be needed in order to precisely define under which conditions the catalyst temperature can be kept stable under longer time scales (> 60 min). This was beyond the scope of this work.
Fig. 8-26: a)–Temperature profile over a time period of 62 min under constant boundary conditions; b)–Measured temperature profiles reported by Jackson et al. [2001], case 1 showing a similar profile as in a), case 2 showing a stable outlet temperature.
9. CONCLUSIONS

This thesis attempts to combine two technologies in the field of power generation that have experienced an increased interest in research, namely catalytic combustion and gasification of biomass. Catalytic combustion has been investigated by numerous research groups in both academic and commercial fields as it offers high efficiency combustion at low emission levels, a feature which has become essential to meet today’s stringent emission regulations. Single-digit ppm-emission levels of nitrogen oxides, carbon monoxides and hydrocarbons have already been demonstrated in a gas turbine equipped with a catalytic combustion chamber using natural gas as a fuel source.

Biomass is in certain geographical regions an attractive fuel source due to its abundance. Through advanced gasification technologies, e.g. the circulating fluidized bed technology, a combustible gas can be extracted from the solid biomass. This gas can be used to fire a gas turbine. Gasified biomass as a fuel source offers the possibility for reducing net emissions of the greenhouse gas carbon dioxide. A reduction of nitrogen oxides (NO & NO₂) as a combustion product is of interest since it results in the formation of secondary pollutants in the atmosphere which are potentially more harmful than the precursor itself. Gasified biomass has some distinct characteristics resulting in specific demands on the combustor. Even though rich in hydrogen and carbon monoxide, its low heating value requires a technique to maintain a stable combustion, which is difficult to achieve via flame combustion. The purpose of the catalyst is to enable a stable reaction process of lean fuel-to-air mixtures below the flammability limit for conventional flame combustion systems. Furthermore gasified biomass has a potentially high level of ammonia, which may generate emissions of nitrogen oxide.

The overall objective of this work was to investigate the feasibility of catalytic combustion for gas turbine application using a low heating value fuel gas. This gas should resemble a fuel derived from gasification of biomass. A combustion test facility had to be designed and manufactured. A synthetic fuel was used for the combustion experiments.

Based upon design calculations with respect to auto-ignition delay time and turbulent flame speed, geometrical design parameters for a combustion test facility were defined. Applying Reynolds similarity, these parameters could be transferred for designing and manufacturing a non-reacting, ambient temperature test facility. The objective of this cold flow rig was to investigate the flow field in the mixing section. Experiments were conducted in order to find out in how far a uniform velocity profile across the flow diameter can be achieved with the designed fuel injection system. As this could not be done with the first version of the fuel injection system, a re-design was necessary. As this second version showed better but still not satisfying results, several geometric modifications were mounted onto the fuel head and/or in the mixing section and their influence on the flow field was tested. Intensive experimental work was performed investigating the flow field. By means of four flaps mounted on selected air/fuel passages, the flow could partly be redirected, thus depleting the
recirculation which led to a more uniform velocity profile at the inlet of the monolith section.

Thereafter a tracer gas was added to the air stream through the fuel supply system. By means of a traversable gas sampling probe and an adequate gas analysis, knowledge about the mixing of the tracer gas, resembling the fuel and air was obtained. Even though gradients in the relative concentration were present both in radial and in circumferential directions, variations were small enough to conclude that the mixture was sufficiently homogeneous.

Numerical investigations were performed to obtain a deeper understanding of the flow field and to study the risk of auto-ignition when mixing the fuel gas with combustion air. It was found that mixing of fuel and air inside the fuel injection head is not controlled by diffusion mass transport but by forced convection. A numerical investigation of the non-reacting flow field in mixing section showed some similarities with experimental results although the overall conformity was not satisfying. Calculations showed no sign that auto-ignition might occur. Nevertheless, this result had to be treated with caution, as the applied reaction scheme does not seem to be applicable for this specific case of ignition behaviour of gasified biomass.

The results obtained with the cold flow test rig and the numerical investigations were implemented into the construction and manufacturing of the final combustion test facility. The design of the combustion test facility was made such that different catalyst arrangements could be tested. A sequential testing procedure was introduced starting with the study of a single, highly active Pd-based catalyst (Configuration I).

The main conclusion that could be drawn from this first test series was that such a catalyst is suitable to support the ignition of lean mixtures of a fuel that resembles gasified biomass at temperatures well below typical compressor outlet temperatures. A range of operating conditions in terms of heating value and air-to-fuel ratios proved the feasibility of the Pd-based catalyst for a gas turbine application. The catalyst inlet temperature proved to be an effective control tool for the reaction temperature. Because of the low residence time of the fuel in the catalyst, complete oxidation of the fuel could not be reached, i.e. the total catalyst volume needed to be increased. It was shown that the catalytic combustor can be operated under varying fuel composition conditions. This has some relevance since a rather common feature of commercial gasification units is that the resulting product fuel gas composition may not be constant in time.

The combination of two active Pd-based (Configuration II) segments turned out not suitable for catalytic combustion due to the high temperatures reached in the segments. The palladium loading of 5 wt% relative to the washcoat weight was too high. The catalytic activity had to be decreased in some way. It was decided to apply a layer of barium stabilized alumina onto the palladium. The Ba-layer stabilizes the Pd particles on the surface of the hexaaluminate washcoat. This reduces sintering of the active material at high catalyst temperatures.

The combination of two palladium catalysts with the first segment having a reduced activity (Configuration III) proved to be an efficient way to initiate catalytic combustion. A segment-wise temperature increase from the first to the second catalyst
could thereby be achieved. A temperature hysteresis in the ignition and extinction temperature, also reported by other researchers could be verified. The potential for low emission levels of carbon monoxide could be shown. This catalyst configuration could be operated over a wide range of H₂ and CO contents in the fuel gas. Pressurised experiments have indicated trends that are consistent with what has been reported in the literature. The experiments have also shown the need for further detailed research on the pressure effects on catalytic combustion.

The final catalyst configuration consisted of the two previously investigated noble metal based catalysts and three substituted hexaaluminates. This Catalyst Configuration IV showed that catalyst temperatures up to 1400 K could be reached. Low emission levels of carbon monoxide were achieved for a fuel containing more than 15% of this species. Nevertheless, the CO emission level was at least one order of magnitude larger than single-digit ppm. This shows that further improvements need to be made for catalytic combustion to be competitive with conventional combustion systems. Changes in the fuel composition are not reflected in the combustor outlet temperature if the LaMnAl₁₁O₁₉ segments are operated at a temperature at which hydrocarbon combustion occurs. The measured combustor pressure drop was less than 2% of the inlet pressure. This configuration was also the only one at which combustion efficiencies above 95% could be reached. Further work is needed to improve the combustion process as to reach efficiencies above 99%, common in conventional combustion systems.

The combustion tests have shown that a low heating value fuel gas can be oxidized by means of catalytically active monoliths. When looking at the measured emissions, one can see that the achieved exhaust gas concentrations with respect to CO, THC and NOₓ are still far too high to be acceptable for commercial operation. Further research is needed. Emission levels well below 25 ppm NOₓ and 10 ppm CO / HC at base load have been demonstrated with advance burner designs in conventional gas turbines using natural gas as a fuel source.

To further investigate and continue the research that has been started here, it is essential to operate the catalysts at those temperatures that have been achieved with Catalyst Configuration IV. The amount of palladium as the active material on the first two catalyst segments should be reduced to limit the maximum catalyst temperature. This will decelerate the ageing process. If the outlet temperature of the Pd-based catalysts is limited to about 1000 K, the subsequent Mn-substituted catalysts have a sufficiently high inlet temperature to oxidize HC and CO present in the fuel. This could raise the combustor outlet temperature to about 1400 K. Emission levels of HC and CO below 25 ppm should then be possible to reach. The performed experiments focussing on the NOₓ issue must be continued and intensified to draw conclusions in how far the investigated catalyst compositions are suitable to oxidise fuel-bound nitrogen, such as NH₃ into N₂.

The main obstacle experienced was the supply of a fuel gas constant in temperature and composition. This must be improved for future studies in the test facility. The question whether or not the principle of a hydrocarbon reformer as a gas reactor should be used needs to be discussed. Suggestions for improvements that could simplify the experiments as well as the data evaluation and interpretation can be summarized as follows:
1. The principle of using a gas reactor to provide the fuel gas is a simple and cheap means to produce a low heating value fuel gas. The operation and the physical access to the gas reactor should be improved. External heating of the gas reactor would allow a better temperature control and thus fuel composition control. A sideways mounting in a separate pressure vessel would be the preferred solution to assure easy access. A separate air supply would allow influencing the air mass flow used for hydrocarbon recombination more accurately. The simplest solution, however, would be to use bottled fuel gas for the combustion tests. This would have the great advantage of a known and steady fuel composition. The obvious disadvantage are the costs associated with purchasing pre-mixed fuel gas.

2. The fuel gas analysis system should be capable of measuring all major species including the hydrocarbon content. Gas chromatography would be a suitable and cost effective measurement technique. With focus on the future investigation of the NO₅-issue, a separate NH₃ detector would be beneficial to investigate the ammonia slip as to estimate the conversion of fuel-bound nitrogen to molecular nitrogen.

3. The performed experimental work has shown the need for accurate monitoring of the air mass flow into the mixing section. This mass flow is needed for calculation of the λ-value and the space velocity, essential for describing the operating point of the catalyst.

4. The start-up of a gas turbine is achieved at constant volume flow. Such a possibility should be feasible with the test facility in order to simulate real gas turbines conditions better.

5. For the development of suitable catalysts for a gas turbine application, more knowledge of the surface chemistry and the kinetics of the combustion are needed to fully understand the involved processes.

These five issues should be seen as guidance to pinpoint the main difficulties that have been encountered during the experimental investigation of catalytic combustion.

9.1 Future Challenges in Catalytic Combustion

Natural gas combustion systems are receiving most attention in today’s developments of catalytic combustion. Their commercialisation has come furthest. For such systems, the catalysts would preferably make the need for pilot burners for pre-heating purposes unnecessary. Such burners could cause a significant amount of NOₓ and would increase the complexity of the combustion chamber itself. When considering gasified biomass as a fuel source the ignition temperature is substantially lower than the one of natural gas due to the high content of CO and H₂. Here, the need for a pilot burner to initiate the combustion can be avoided if suitable catalysts are being used.
Thermally stable catalyst materials are needed for extended operating times in gas turbine combustion systems. Today, materials are limited to a maximum temperature of about 1300 K due to sintering and volatilisation. The development of suitable high-temperature catalytic combustion materials will push this boundary further.

Various research groups focus on the numerical aspects of catalytic combustion to improve understanding of surface kinetics and the combustion process itself. The interaction between the reactions occurring on the catalyst surface and those in the free gas stream is not well understood today. Numerical tools can provide an insight that is difficult if not impossible to achieve by experimental methods. Advanced laboratory bench-scale reactors can provide the necessary experimental data for verification of the numerical models.

The development of catalytic combustion systems for fuels derived from biomass gasification or other alternative fuels such as ethanol will profit from an improved understanding of the physical and chemical processes involved in the combustion of natural gas.
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APPENDIX A – COMMAND FILES FOR THE NUMERICAL INVESTIGATIONS

This appendix contains the command files that were used in the CFD simulations. All relevant information, such as the discretization scheme, turbulence model and physical values at the boundaries can be taken from these files.

Non-reacting Mixing Process in the Fuel Injection Head

The following corresponds to the calculation described in section 6.2.2, that is a non-reacting case in which the mixing process of the fuel, modeled by a five-component mixture is simulated.

```plaintext
>>CFX4
>>OPTIONS
  TWO DIMENSIONS
  RECTANGULAR GRID
  CARTESIAN COORDINATES
  TURBULENT FLOW
  ISOTHERMAL FLOW
  INCOMPRESSIBLE FLOW
  STEADY STATE
  USE DATABASE
  MASS FRACTION EQUATIONS 5

>>MODEL DATA
>>DIFFERENCING SCHEME
  ALL EQUATIONS 'HYBRID'

>>MATERIALS DATABASE
>>SOURCE OF DATA PCP
>>FLUID DATA
  FLUID 'AIR'
  MATERIAL TEMPERATURE 2.9300E+02
  MATERIAL PHASE 'GAS'

>>PHYSICAL PROPERTIES
>>MASS TRANSFER PARAMETERS
>>DIFFUSIVITIES
  MASS FRACTION1 8.4430E-05
  MASS FRACTION2 7.7520E-05
  MASS FRACTION3 6.0720E-05
  MASS FRACTION4 2.5470E-04
  MASS FRACTION5 7.8810E-05

/* Table of Mass Fractions */
/* Fraction 1 CH4 */
/* Fraction 2 CO */
/* Fraction 3 CO2 */
/* Fraction 4 H2 */
/* Fraction 5 N2 */

>>TURBULENCE PARAMETERS
```
TURBULENCE MODEL
TURBULENCE MODEL 'K-EPSILON'

SOLVER DATA
PROGRAM CONTROL
MAXIMUM NUMBER OF ITERATIONS 4500
MASS SOURCE TOLERANCE 1.0000E-19

EQUATION SOLVERS
U VELOCITY 'BLOCK STONE'
V VELOCITY 'BLOCK STONE'
PRESSURE 'BLOCK STONE'

MODEL BOUNDARY CONDITIONS

SET VARIABLES

#CALC
NORM=50.0;
KINL=0.002*NORM*NORM;
DHYD=0.016;
EPSI=KINL**1.5/(0.3*DHYD);
#ENDCALC

PATCH NAME 'AIR_INLET'
NORMAL VELOCITY #NORM
K #KINL
EPSILON #EPSI
MASS FRACTION1 .0000E+00
MASS FRACTION2 .0000E+00
MASS FRACTION3 .0000E+00
MASS FRACTION4 .0000E+00
MASS FRACTION5 .0000E+00

#CALC
NORM=50.0;
KINL=0.002*NORM*NORM;
DHYD=0.0016;
EPSI=KINL**1.5/(0.3*DHYD);
#ENDCALC

PATCH NAME 'BOTTOM_FUEL'
NORMAL VELOCITY #NORM
K #KINL
EPSILON #EPSI
MASS FRACTION1 2.8500E-02
MASS FRACTION2 1.5890E-01
MASS FRACTION3 2.3440E-01
MASS FRACTION4 7.9000E-03
MASS FRACTION5 4.8120E-01

#CALC
NORM=50.0;
KINL=0.002*NORM*NORM;
DHYD=0.0016;
EPSI=KINL**1.5/(0.3*DHYD);
#ENDCALC

PATCH NAME 'TOP_FUEL'
NORMAL VELOCITY #NORM
K #KINL
EPSILON #EPSI
MASS FRACTION1 2.8500E-02
MASS FRACTION2 1.5890E-01
Reactive Case Using a 7-step Hydrogen Reaction Scheme

The following corresponds to the calculation described in section 6.2.3, that is a reacting case using a 7-step hydrogen reaction scheme for modeling the ignition process.

>>CFXF3D
>>OPTIONS
TWO DIMENSIONS
RECTANGULAR GRID
CARTESIAN COORDINATES
TURBULENT FLOW
HEAT TRANSFER
COMPRESSIBLE FLOW
STEADY STATE
CHEMICAL SPECIES EQUATIONS 7
MAXIMUM DEGREE OF POLYNOMIAL DEPENDENCE ON T 4

>>VARIABLE NAMES
SPECIES1 'O2'
SPECIES2 'H1'
SPECIES3 'OH'
SPECIES4 'O'
SPECIES5 'H2'
SPECIES6 'H2O'
SPECIES7 'N2'

>>UNITS
>>CHEMICAL SPECIES
MASS FRACTIONS

>>MODEL DATA
>>CHEMISTRY

>>CHEMICAL SPECIES PROPERTIES
>>REFERENCE STATES
>>ENTROPY REFERENCE TEMPERATURE
ALL SPECIES 2.7315E+02
>>ENTROPY REFERENCE PRESSURE
ALL SPECIES 1.0133E+05
>>HEAT CAPACITY REFERENCE TEMPERATURE
ALL SPECIES 0.0000E+00

>>DIFFUSIVITIES
ALL SPECIES 2.5857E-05

>>MOLECULAR WEIGHTS
O2 3.1999E+01
H1 1.0080E+00
OH 1.7007E+01
O 1.5999E+01
H2 2.0158E+00
H2O 18.015
N2 28.013

>>SPECIFIC HEATS
O2 0.95144E3 .56227 1.9657E-3 -1.8093E-6 5.4387E-10
H1 20.620E3 4*0.0
OH 1.7573E3 4*0.0
O 1.3695E3 4*0.0
H2 13.398E3 5.9207 -11.944E-3 10.648E-6 -30.503E-10
H2O 1.9150E3 -.79151 2.6287E-3 -1.9803E-6 5.1931E-10
N2 1.0685E3 -.26819 .64669E-3 -.31453E-6 .34926E-10

>>MOLAR ENTHALPIES OF FORMATION
O2 0.0000E+00
H1 2.1800E+08
OH 3.8900E+07
O 2.4920E+08
H2 0.0000E+00
H2O -2.418E+08

>>MOLAR ENTROPIES AT REFERENCE STATE
O2 2.0500E+05
H1 1.1460E+05
OH 1.8360E+05
O 1.6090E+05
H2 1.3060E+05
H2O 1.935E+05

>>CHEMICAL REACTION SCHEME
/*----------------------------------------------
REACTION SCHEME TAKEN FROM: EGGELS AND DE GOEY,
COMB. & FLAME, VOL. 100, 559-570, 1995
----------------------------------------------*/

>>LIMITS
MAXIMUM NUMBER OF REACTIONS 10

>>REACTION
>>REACTION NAME
NAME 'REACTION 1'
>>REACTANTS
O2 1.0
H1 1.0

>>PRODUCTS
OH 1.0
O 1.0

>>FORWARD RATE
PREEXPOSITIONAL FACTOR 2.0000E+11
ACTIVATION ENERGY 2.9400E+08
TEMPERATURE EXPONENT 0.0000E+00
>>BACKWARD RATE
PREEXPONENTIAL FACTOR 1.4600E+10
ACTIVATION ENERGY 8.7000E+06
TEMPERATURE EXPONENT 0.0000E+00

>>REACTION
>>REACTION NAME
NAME 'REACTION 2'
>>REACTANTS
O 1.0
H2 1.0
>>PRODUCTS
H1 1.0
OH 1.0
>>FORWARD RATE
PREEXPONENTIAL FACTOR 5.0600E+01
ACTIVATION ENERGY 1.1000E+08
TEMPERATURE EXPONENT 2.6700E+00

>>BACKWARD RATE
PREEXPONENTIAL FACTOR 2.2400E+01
ACTIVATION ENERGY 7.7000E+07
TEMPERATURE EXPONENT 2.6700E+00

>>REACTION
>>REACTION NAME
NAME 'REACTION 3'
>>REACTANTS
H2 1.0
OH 1.0
>>PRODUCTS
H2O 1.0
H1 1.0
>>FORWARD RATE
PREEXPONENTIAL FACTOR 1.00E+05
ACTIVATION ENERGY 5.77E+07
TEMPERATURE EXPONENT 1.6

>>BACKWARD RATE
PREEXPONENTIAL FACTOR 4.45E+05
ACTIVATION ENERGY 3.23E+08
TEMPERATURE EXPONENT 1.6

>>REACTION
>>REACTION NAME
NAME 'REACTION 4'
>>REACTANTS
OH 2.0
>>PRODUCTS
O 1.0
H2O 1.0
>>FORWARD RATE
PREEXPONENTIAL FACTOR 1.50E+06
ACTIVATION ENERGY 1.76E+06
TEMPERATURE EXPONENT 1.14

>>BACKWARD RATE
PREEXPONENTIAL FACTOR 1.51E+07
ACTIVATION ENERGY 3.00E+08
TEMPERATURE EXPONENT 1.14

>>REACTION
>>REACTION NAME
NAME 'REACTION 5'
>>REACTANTS
H1 2.0
>>PRODUCTS
H2 1.0
>>THREE BODY REACTION
H2O 0.65
H2 0.1
N2 0.05
O2 0.035
>>FORWARD RATE
PREEXPONENTIAL FACTOR 1.80E+13
ACTIVATION ENERGY 0.0
TEMPERATURE EXPONENT -1.0
>>BACKWARD RATE
PREEXPONENTIAL FACTOR 6.99E+16
ACTIVATION ENERGY 1.82E+09
TEMPERATURE EXPONENT -1.0

>>REACTION
>>REACTION NAME
NAME 'REACTION 6'
>>REACTANTS
OH 1.0
H1 1.0
>>PRODUCTS
H2O 1.0
>>THREE BODY REACTION
H2O 0.65
H2 0.1
N2 0.05
O2 0.035
>>FORWARD RATE
PREEXPONENTIAL FACTOR 2.20E+17
ACTIVATION ENERGY 0.0
TEMPERATURE EXPONENT -2.0
>>BACKWARD RATE
PREEXPONENTIAL FACTOR 3.80E+21
ACTIVATION ENERGY 2.09E+09
TEMPERATURE EXPONENT -2.0

>>REACTION
>>REACTION NAME
NAME 'REACTION 7'
>>REACTANTS
O 2.0
>>PRODUCTS
O2 1.0
>>THREE BODY REACTION
H2O 0.65
H2 0.1
N2 0.05
O2 0.035
>>FORWARD RATE
PREEXPONENTIAL FACTOR 2.90E+12
ACTIVATION ENERGY 0.0
TEMPERATURE EXPONENT -1.0
>>BACKWARD RATE
PREEXPONENTIAL FACTOR 6.81E+16
ACTIVATION ENERGY 2.08E+09
TEMPERATURE EXPONENT -1.0

>>CHEMISTRY SOLVER OPTIONS
BACKGROUND FLUID 'N2'

>>DIFFERENCING SCHEME
ALL EQUATIONS 'HYBRID'

>>PHYSICAL PROPERTIES
>>COMPRESSIBILITY PARAMETERS
WEAKLY COMPRESSIBLE
FLUID MOLECULAR WEIGHT 2.8013E+01
MINIMUM TEMPERATURE 2.8000E+02

>>FLUID PARAMETERS
VISCOSITY 4.2000E-05

>>HEAT TRANSFER PARAMETERS
THERMAL CONDUCTIVITY 3.0000E-02
FLUID SPECIFIC HEAT +
1.0685E3 -0.26819 0.64669E-3 -0.31453E-6 0.34926E-10

>>TURBULENCE PARAMETERS
>>TURBULENCE MODEL
TURBULENCE MODEL 'K-EPSILON'

>>SET INITIAL GUESS
>>SET CONSTANT GUESS
OH 1.000E-03
H1 1.000E-03

>>INPUT FROM FILE
READ DUMP FILE
FORMATTED
LAST DATA GROUP
>>SELECT VARIABLES FROM FILE
ALL RELEVANT DATA

>>SOLVER DATA
>>PROGRAM CONTROL
MAXIMUM NUMBER OF ITERATIONS 3500
MASS SOURCE TOLERANCE 1.0000E-19
ITERATIONS OF TEMPERATURE AND SCALAR EQUATIONS

>>EQUATION SOLVERS
U VELOCITY 'BLOCK STONE'
V VELOCITY 'BLOCK STONE'
PRESSURE 'BLOCK STONE'

>>REDUCTION FACTORS
PRESSURE 1.0000E-03
ENTHALPY 1.0000E-03
ALL SPECIES 1.0000E-03

>>UNDER RELAXATION FACTORS
U VELOCITY 3.0000E-01
V VELOCITY 3.0000E-01
W VELOCITY 3.0000E-01
DENSITY 1.0000E-01
K 3.0000E-01
EPSILON 3.0000E-01
ENTHALPY 3.0000E-01
ALL SPECIES 0.3
>>MODEL BOUNDARY CONDITIONS

>>SET VARIABLES
#CALC
NORM=50.0;
KINL=0.002*NORM*NORM;
DHYD=0.016;
EPSI=KINL**1.5/(0.3*DHYD);
#ENDCALC
PATCH NAME 'AIR_INLET'
NORMAL VELOCITY #NORM
K #KINL
EPSILON #EPSI
PRESSURE 3.0000E+03
TEMPERATURE 6.2300E+02
O2 0.22

>>SET VARIABLES
#CALC
NORM=50.0;
KINL=0.002*NORM*NORM;
DHYD=0.0016;
EPSI=KINL**1.5/(0.3*DHYD);
#ENDCALC
PATCH NAME 'BOTTOM_FUEL'
NORMAL VELOCITY #NORM
K #KINL
EPSILON #EPSI
PRESSURE 3.0000E+03
TEMPERATURE 6.2300E+02
H2 1.0

>>SET VARIABLES
#CALC
NORM=50.0;
KINL=0.002*NORM*NORM;
DHYD=0.0016;
EPSI=KINL**1.5/(0.3*DHYD);
#ENDCALC
PATCH NAME 'TOP_FUEL'
NORMAL VELOCITY #NORM
K #KINL
EPSILON #EPSI
PRESSURE 3.0000E+03
TEMPERATURE 6.2300E+02
H2 1.0

>>WALL BOUNDARY CONDITIONS
PATCH NAME 'WALL'
HEAT FLUX .0000E+00

>>OUTPUT OPTIONS
>>DUMP FILE FORMAT
FORMATTED
SINGLE PRECISION
>>LINE GRAPH DATA
EACH ITERATION
FILE NAME 'RESIDUAL'
ALL VARIABLES
Flow Field in the Premixing Zone

The following corresponds to the calculation described in section 6.3, that is a flow field calculation in the mixing zone between the fuel injection head and the inlet of the catalyst.

>>CFXF3D
>>OPTIONS
THREE DIMENSIONS
BODY FITTED GRID
CARTESIAN COORDINATES
TURBULENT FLOW
ISOTHERMAL FLOW
INCOMPRESSIBLE FLOW
STEADY STATE
USE DATABASE

>>MODEL DATA
>>DIFFERENCING SCHEME
ALL EQUATIONS ‘HIGHER UPWIND’
>>MATERIALS DATABASE
>>SOURCE OF DATA PCP
>>FLUID DATA
FLUID ‘AIR’
MATERIAL TEMPERATURE 3.0300E+02
MATERIAL PHASE ‘GAS’

>>TITLE
PROBLEM TITLE ‘90DEG TURBULENT CASE INFLOW2’

>>WALL TREATMENTS
WALL PROFILE ‘LOGARITHMIC’
NO SLIP

>>PHYSICAL PROPERTIES
>>TURBULENCE PARAMETERS
>>TURBULENCE MODEL
TURBULENCE MODEL ‘K-EPSILON’
>>LOGLAYER CONSTANT
VELOCITY 9.7930E+00

>>SOLVER DATA
>>PROGRAM CONTROL
MAXIMUM NUMBER OF ITERATIONS 2000
MASS SOURCE TOLERANCE 1.0000E-16
TRACE MAXIMUM RESIDUALS

>>REDUCTION FACTORS
PRESSURE 1.0000E-03

>>UNDER RELAXATION FACTORS
U VELOCITY 3.0000E-01
V VELOCITY 3.0000E-01
W VELOCITY 3.0000E-01
>>EQUATION SOLVERS
U VELOCITY 'BLOCK STONE'
V VELOCITY 'BLOCK STONE'
W VELOCITY 'BLOCK STONE'
PRESSURE 'ICCG'
>>DEFERRED CORRECTION
EPSILON START 2001
EPSILON END 2001
>>PRESSURE CORRECTION
SIMPLEC

>>MODEL BOUNDARY CONDITIONS
>>SET VARIABLES
#CALC
WINL=2.1E+01;
KINL=0.002*WINL*WINL;
DHYD=0.075;
EPSII=KINL**1.5/(0.3*DHYD);
#ENDCALC

PATCH NAME 'INLET'
W VELOCITY #WINL
K #KINL
EPSILON #EPSII

>>SET VARIABLES
PATCH NAME 'OUTLET'
PRESSURE -2.723E+03

>>OUTPUT OPTIONS
>>DUMP FILE FORMAT
FORMATTED
SINGLE PRECISION
>>LINE GRAPH DATA
EACH ITERATION
FILE NAME 'RESIDUAL.TXT'
ALL VARIABLES
RESIDUAL
>>STOP
APPENDIX B – MEASUREMENT RESULTS FROM THE FLOW FIELD OPTIMIZATION IN THE COLD FLOW TEST FACILITY

Axial Velocity Profile in the Mixing Zone using Fuel Head No. 1

Recalling that the two main requirements for the fuel injection geometry were to produce a uniform velocity profile over the flow field diameter and to mix fuel and air homogeneously, one can see in Fig. B-1 that fuel head 1 did not fulfill this first requirement. During this experiment the mixing length was 15 cm.

![Fig. B-1: Axial velocity profiles over the full flow diameter, fuel head design 1, 15 mm in front of the monolith and cross section of the fuel head geometry showing the angled inner air passages.](image)

Since this geometry has a 60° symmetry, six measurements rotating the fuel injection head by 10° were sufficient to determine the flow field. In the above figure, a higher velocity can be seen in the centre of flow region, caused by the inner six passages of fuel head 1 that were angled with 30° towards the centreline, also shown in the cross section of the fuel injection head.

A further investigation, with all of the six inner passages blocked, strongly decreased the maximum velocity in the centre region resulting in a uniform velocity profile at the inlet of the monolith. As the blocking decreased the open area by 33 %, the pressure drop increased by a factor of 2.2. From this was concluded that a second design of the fuel injection geometry should not have any angled passages. This conclusion led to the manufacturing of the second design of the fuel head.

All results that are mentioned in the following have been obtained using fuel head design 2.
Investigation of the Flow Field using Fuel Head No. 2

Intensive experimental work has been performed to characterize the flow field at the inlet of the monolith. The geometry is here indicated as the basic configuration.

Two 360° flow field cross sections, one 15 mm upstream of the inlet of the monolith and one 15 mm downstream of the fuel injection head are shown in Fig. B-2. The fuel head geometry is also shown in the figure. The mixing length was 15 cm in this experiment. In another study, this was extended to 20 cm to check whether or not an improvement of the velocity at the inlet of the catalyst could be achieved. This was not the case. Having in mind that the mixing section should be as short as possible in order to decrease the residence time of the fuel, it was concluded that a mixing length of 15 cm should be suitable for the combustion application.

![360° flow field traversing of basic configuration showing the axial velocity profile, downstream of the fuel injection head and 15 mm upstream of the inlet of the monolith.](image)

A strong recirculation zone can be seen in Fig. B-2 downstream of the fuel injection head, causing the value for $\overline{\Delta RMS_o}$ to be 16.18, see eq. (7-2) for the definition of $\overline{\Delta RMS_o}$. Due to viscous mixing this value decreases to a value of 9.85 towards the inlet of the monolith [Lakshminarayana, 1996], showing that the velocity profile evens out, as can be seen in the figure. This recirculation zone extends 65 mm in axial direction downstream of the fuel injection head. This recirculation is of importance as it represents an accumulation of combustible gas that may ignite. Radiative heat transfer from the hot catalyst could trigger an ignition of this air/fuel mixture. Therefore, this recirculation zone should be suppressed as much as possible.
From the geometry of the fuel injection head however, it becomes clear that this zone cannot completely be avoided, but only reduced in axial extension. In the following the efforts made to weaken the recirculation zone are shown.

**Influence of Centre Cones on the Flow Field**

A distinct jet of high velocity can be seen in Fig. B-3 at $x = 20$ mm downstream of the fuel injection head at a radial position of $r = -55$ mm, caused by gas flowing through an outer passage of the fuel head. A recirculation zone at a radial position of $r = -25$ mm and a downstream distance of 40 mm from the fuel head can be observed. Furthermore, it can be seen that the flow field is not symmetric. No significant change can be detected after an axial distance of $x = 60$ mm from the fuel injection head.

![Fig. B-3: Measurement of axial velocity profile in the 0° plane using centre cone I.](image)

*Fig. B-3: Measurement of axial velocity profile in the 0° plane using centre cone I.*

*Fig. B-4 shows the axial velocity profile in the mixing section using centre cone II, also measured in the 0° plane.*
Fig. B-4: Measurement of axial velocity profile in the 0° plane using centre cone II.

The same asymmetric flow characteristic as in Fig. B-3 can be observed. A strong recirculation zone downstream of the centre cone is visible. This causes large radial variations in the axial velocity downstream of the centre cone. The velocity profile at the monolith inlet is non-uniform across the full diameter. Traversing over 360° (i.e. measuring over the full 360° flow field by stepwise rotating the fuel injection head) and measuring 15 mm in front of the catalyst confirms that this profile does not fulfill the requirements with respect to smoothness.

Fig. B-5 below shows a measured profile of the axial velocity 15 mm upstream of the monolith using centre cone geometry no. III.
Radial variations in axial velocity at the catalyst inlet could be suppressed, but not completely abolished when using centre cone III. Of all tests using centre cones, version III showed the best results with respect to the velocity profile at the monolith inlet. An improvement compared to the previous centre piece versions has been achieved but no improvement compared to the basic configuration, as seen from the normalized value $\text{RMS}_o = 10.46$.

**Influence of a Honeycomb Structure on the Flow Field**

Another idea following the same objective as the centre cone tests was to insert a honeycomb structure into the mixing section, acting as a flow straightener. Measurements with this configuration were performed in the $0^\circ$ plane. A result can be seen in Fig. B-6.

A recirculation zone with strong radial gradients in the axial velocity can be seen directly downstream of the honeycomb structure. Even though these gradients are weakened at the inlet of the catalyst, the inhomogenities in the flow field are still present. A further flow field measurement was performed with the honeycomb structure moved to a distance of 60 mm downstream of the fuel head, see Fig. B-7.
No recirculation zone downstream of the honeycomb can be detected, but the axial velocity is still non-uniform at the monolith inlet. These gradients can be explained by large radial velocity components in the section between the fuel head and the honeycomb. In this situation, the honeycomb “filters out” radial components and
allows only the axial components to pass through. Since the axial components are small in the radial region from \( r = 25 \) to \( r = -25 \) mm at an axial distance of \( x = 20 \) mm from the fuel head, the honeycomb structure simply blocks all flow in this region, creating a second recirculation behind the honeycomb. Furthermore, the areas of high axial velocity show the location of air/fuel passages of the fuel head. These jets penetrate the honeycomb without any great interference. As the value for \( \text{RMS}_a \) was larger than 25 for this measurement, no 360° flow field has been measured for this configuration since no improvement was expected.

With respect to the prerequisite of a uniform velocity profile, these results, including the use of a centre cone, are not satisfying. However, this type of flow field certainly has properties that make such a profile attractive. Extrusion technology for manufacturing the support material is nowadays such that the cell size may vary across the diameter. Hence an uneven velocity profile can be compensated by more adequate cell sizes. Furthermore the catalyst inlet does not necessarily have to be flat as in this case. Corning Contura™ [Corning, 1999] manufactures monoliths with a cone shaped inlet profile. This may also reduce the overall length of the mixing section, thus reducing the weight of the combustor.

The subsequently tested geometrical modification was the flap solution. Results from these are discussed in section 7.
APPENDIX C – KINETICS OF CATALYTIC CONVERSION

The catalyst activity is conventionally defined as the rate of the consumption of the reactant(s). This appendix will give some background on the calculation of catalytic reaction rate. The information given here is based on the book by Bowker [1998].

Adsorption is the agglomeration of molecules onto the surface of the solid body. In the case of a chemical bond between the surface and the adsorbate, the process is called chemisorption, if only a weak van-der-Waals force is establishing the bond, the process is called physisorption. Chemisorption is the relevant phenomenon here. For catalysis, the rate at which this happens is of interest. Irving Langmiur derived the relationship given below for the adsorption rate. A gaseous molecule A, denoted by the index g binds with a surface site * to form the adsorbed A_a.

\[
A_g +* \rightarrow A_a
\]

\[
-\frac{d[A_g]}{dt} = S_0 p Z (1-\Theta)
\]

\[
= k_a p (1-\Theta)
\]

(C-1)

S_0 sticking probability of the gas on the clean surface
P pressure of the gas
Z Knudsen collision factor
k_a rate constant for the adsorbate (the to be adsorbed molecule)
\(\Theta\) fractional blocking of the surface by the adsorbate = surface concentration
\(\Theta=\frac{\text{adsorbed amount at a given pressure}}{\text{max. amount that surface can take up}}\)

The surface concentration \(\Theta\) can thus vary between 0 and 1. When the surface is filled with adsorbate, i.e. \(\Theta = 1\), the catalyst surface is no longer reactive and the adsorption rate equals to zero. In order for catalytic reactions to occur continuously, a dynamic equilibrium between the adsorption and desorption of the species must be established. For simplicity, this is shown here for a single component A with no chemical reaction occurring on the catalyst surface.

\[
A_a \rightarrow A_g + *
\]

The rate at which the adsorbed component A desorps from the catalyst is directly proportional to the surface concentration of A and can be expressed as:

\[
-\frac{d[A_a]}{dt} = k_d \Theta
\]

(C-2)

with \(k_d\) being the desorption rate constant. At equilibrium the adsorption rate and the desorption rate are interchangeable, hence:
\[
\frac{-d[A_a]}{dt} = -d[A_a] \quad \text{(C-3)}
\]

\[
k_a (1 - \Theta) p = k_d \Theta
\]

\[
\frac{k_a}{k_d} \frac{1 - \Theta}{\Theta} p = 1 \quad \text{(C-4)}
\]

with the adsorption equilibrium constant ‘a’ being the ratio of the adsorption and desorption rate constant

\[
a = \frac{k_a}{k_d} \quad \text{(C-5)}
\]

Combining (C-4) and (C-5), an expression for the surface concentration can be obtained.

\[
\frac{1 - \Theta}{\Theta} = 1 ap \quad \text{or} \quad \frac{1}{\Theta} = \frac{1}{ap} + 1 \quad \text{or} \quad \Theta = \frac{ap}{ap + 1} \quad \text{(C-6)}
\]

The adsorption equilibrium constant ‘a’ can be expressed using the Arrhenius equation for \( k_a \) and \( k_d \),

\[
a = \frac{k_a}{k_d} = \frac{A_a e^{\frac{-E_a}{RT}}}{A_d e^{\frac{-E_d}{RT}}} = \frac{A_a}{A_d} e^{\frac{\Delta H_a}{RT}} \quad \text{(C-7)}
\]

with

- \( A_a \) Pre-exponential factor, to be estimated experimentally
- \( A_d \) Pre-exponential factor, to be estimated experimentally
- \( \Delta H_a \) Heat of adsorption

The equilibrium surface coverage of the catalyst has to be measured experimentally. Such experiments are normally done at a constant temperature over a range of pressure. The resulting curve is called a Langmiur isotherm. The curve can be linearised, the resulting slope is 1/a. From this the heat of adsorption can be calculated.

**Bimolecular reaction**

A simplified reaction mechanism for a bimolecular reaction with A and B as reactants and C as the reaction product can be divided into four main steps, not regarding any mass transport from the bulk through the washcoat of the catalyst.
The convenient assumption of the adsorption occurring fast and the desorption occurring instantaneously, step 3 becomes the overall rate limiting one. A major simplification here is the assumption that the reverse pathway of step 1 and 2 does not occur. In this case the derived equation for the reaction rate becomes difficult and is not given here. Detailed information on that derivation of the reaction rate can be found amongst others in Schlosser [1972]. (C-6) has then to be adjusted to calculate the surface concentration of A and B,

\[ \Theta_A = \frac{a p_A}{1 + a p_A + b p_B} \]

\[ \Theta_B = \frac{b p_B}{1 + a p_A + b p_B} \]  

with ‘a’ and ‘b’ being the adsorption equilibrium constants for the reactants. The resulting equation for the production rate of C is called Langmuir-Hinshelwood equation and has the following form

\[ \frac{d[C_3]}{dt} = k_3 \Theta_A \Theta_B \]

\[ = k_3 \frac{a b p_A p_B}{(1 + a p_A + b p_B)^2} \]  

with \( k_3 \) being the rate constant for the chemical reaction step 3. Below in Fig. C-1, some conclusions from (C-10) are shown.

**Fig. C-1**: Rate dependency of the surface coverage for a bimolecular Langmuir-Hinshelwood reaction.
At low partial pressures, (C-10) is approximately first order in each of the two reactants. If one of the two reactants is only weakly adsorbed to the surface, the consequence is that the other species is thus adsorbed strongly. In the case of B adsorbing weakly (i.e. \( \rho_B \approx 0 \)) and A strongly the denominator in (C-10) can be reduced to \( (\rho_A)^2 \) and the equation approximated as:

\[
\frac{dC}{dt} = k_3 \frac{b \rho_B}{a \rho_A}.
\]  (C-11)

In this case, the order for species A is negative and first order while positive first order for the weakly bound species B. If both components are weak adsorbates, the denominator of (C-10) becomes unity and the reaction is first order for both components.

Another mechanism is commonly mentioned together with the above described Langmuir-Hinshelwood mechanism, i.e. the Eley-Rideal mechanism. The characteristic of this case is that one adsorbate is not at all bound to the surface. If A is to be adsorbed, then B reacts by collision with A to form the product C. The production rate of C is thus first order in B but has Langmuir form in A, as shown below

\[
\frac{dC}{dt} = k_1 \frac{a \rho B \rho_A}{1 + a \rho_A}.
\]  (C-12)

There exists relatively little evidence on this type of catalytic reaction.