

Mitigation strategies for hydrogen safety in the confined environment: CFD modelling and validation

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“When we give someone our time, we actually give a portion of our life that we will never take back.”

— Unknown

SOLEMN DECLARATION

I, Alexander A. Malakhov, declare that the thesis entitled:

“Mitigation strategies for hydrogen safety in the confined environment: CFD modelling and validation”,

submitted in fulfillment of the requirements for the degree *Doctor of Philosophy in Engineering with Chemical Engineering*, is my own research work except where acknowledged in the text and has not been previously submitted to any other tertiary institution in whole or in part.

Signed at North-West University (Potchefstroom campus)

Signature: 

Date: 25/11/2021

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ABSTRACT

This research is based on experimental evaluation and computational fluid dynamics (CFD) modelling validation. Full-scale tests to investigate unintended hydrogen release were conducted at the HySA Mining Platform Test Facility for Green Mining. A PAR (passive autocatalytic recombiner) cylindrical-type catalyst unit has been tested in an in-house developed recombiner section testing station. Hydrogen concentrations were measured by means of high-precision H_2 sensors, while the temperature of PAR catalyst has been evaluated utilizing a high-resolution infrared camera. Detailed three-dimensional calculations have been performed utilizing the STAR-CCM+ software package to simulate each experiment.

Over the last twenty years, the importance of hydrogen as a prospective energy source has significantly increased. Utilizing hydrogen offers advantages in reducing carbon emissions generated by transportation systems. The current hydrogen economy growth is owed to the rapid development and employment of hydrogen fuel cell technology. Moreover, in efforts to achieve zero-carbon emission in the mining industry, they are looking for more perspective technologies in terms of clean and environmentally friendly energy carriers. Hydrogen fuel cell technology can make zero-carbon emissions a reality. However, due to specific combustion properties, the usage of hydrogen energy is accompanied by a risk of unintended leakage, dispersion, ignition, and deflagration inside a confined space. In this regard, mitigation strategies for hydrogen safety need to be investigated. The emergency hydrogen removal systems must be deployed to guarantee that the H_2 concentration is diluted below the minimum flammability limit, even under severe accidents.

One of the widely applied hydrogen safety technologies is utilizing a ventilation system. Forced ventilation can promote the removal of hydrogen from a confined space by means of mixing and diluting a flammable gas below the ignition limit. Another important approach that goes toward mitigation strategies for hydrogen safety is PAR. The spontaneous exothermic chemical reaction between hydrogen and oxygen leads to the heating of the catalyst surface and then activates natural convection inside the PAR. Eventually, by means of autocatalytic recombination reaction, the concentration of hydrogen reduces to lower than the flammable limit.

Related to this, the CFD simulations method can be very helpful in terms of hydrogen safety research. However, there is an urgent need to develop and validate numerical models of hydrogen distribution processes in confined environments. Hydrogen release and subsequent dispersion, as well as a multi-step reaction of hydrogen autocatalytic recombination, can be investigated using commercially available CFD software.

Keywords: renewable energy, hydrogen safety, three-dimensional CFD simulations, hydrogen distribution, hydrogen leakage, forced ventilation (FV), passive autocatalytic recombiner (PAR), physical-chemical processes modelling, STAR-CCM+

PREFACE

I, Alexander Malakhov, have chosen to submit my thesis in article-based format, as permitted by the North-West University under the General Academic Rules of 2017. The tables, figures, and general outline of the thesis were adapted and formatted to ensure uniformity throughout the thesis, with the technical content of the published articles remaining the same. Therefore, the format of the manuscripts may appear slightly different from what is presented in this thesis. All co-authors have granted their permission for the articles to be used in this thesis, and the author consent forms are attached in Appendix D.

Peer-reviewed articles related to this study are listed below:

- Malakhov, A.A., Avdeenkov, A.V., Du Toit, M.H. and Bessarabov, D.G., (2020). CFD simulation and experimental study of a hydrogen leak in a semi-closed space with the purpose of risk mitigation. *International Journal of Hydrogen Energy*, 45(15), pp.9231–9240.
- Malakhov, A.A., du Toit, M.H., Du Preez, S.P., Avdeenkov, A.V. and Bessarabov, D.G., (2020). Temperature profile mapping over a catalytic unit of a hydrogen passive autocatalytic recombiner: an experimental and computational fluid dynamics study. *Energy & Fuels*, 34(9), pp.11637–11649.
- Kozhukhova, A. E., du Preez, S. P., Malakhov, A. A., Bessarabov, D. G. (2021). A Thermally Conductive Pt/AAO Catalyst for Hydrogen Passive Autocatalytic Recombination. *Catalysts*, 11(4), 491.
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NOMENCLATURE

ABBREVIATIONS

3D Three-dimensional
AAO Anodized aluminum oxide
Al Aluminum
CFD Computational fluid dynamics
CHC Catalytic hydrogen combustion
EDX Energy-dispersive X-ray
HFC Hydrogen fuel cell
HySA Hydrogen South Africa
FIB Focused ion beam
FC Fuel cell
IEA International Energy Agency
IR Infrared
LFL Low flammability limit
NPP Nuclear Power Plant
NTP normal temperature and pressure
PAR Passive autocatalytic recombiner
PEM Proton exchange membrane
PRD Pressure relief device
SEM Scanning electron microscopy
SS Stainless-steel
SSM Stainless-steel mesh
Pt Platinum
Pd Palladium
TEM Transmission electron microscopy
XPS X-ray photoelectron spectroscopy

DEFINITIONS, SUBSCRIPTS & SUPERSSCRIPTS

Å angstrom
atm atmosphere
°C Celsius degree
 B temperature coefficient
 A pre-exponential coefficient
 $C[H_2]$ hydrogen concentration
 D_p diameter of pores
 D_c interpore distance
 E_a activation energy
 K Kelvin degree
 p porosity
 S_0 surface site density
 s sticking coefficient
in inlet
 T Temperature
 $T_{initial}$ initial temperature
 τ time
out outlet
 n pore density
vol % volume percent

CHAPTER 1: INTRODUCTION AND OBJECTIVES

This chapter provides background to the research carried out in this study – *Mitigation strategies for hydrogen safety in the confined environment: CFD modelling and validation* – motivation for the study, the overall aim and specific objectives, and the research methodology followed. The background highlights the critical situation of global energy demand coupled with human-induced global warming, and then the development and application of hydrogen energy in electricity generation as a proposed solution. Associated with this, safety is an essential issue towards evolution of the hydrogen industry—investigations into strategies for hydrogen safety are of great importance. Here, forced ventilation (FV), as a generally applied hydrogen removal system is assessed. A passive autocatalytic recombiner (PAR) is introduced as an alternative advanced technology to mitigate unintended hydrogen leakage. Finally, computational fluid dynamics (CFD) methods are proposed to numerically analyse hydrogen emergency scenarios in detail.

1.1 Background

The continuous growth in world energy consumption coupled with rapid population growth has resulted in an increase in global energy demand. The Intergovernmental Panel on Climate Change reports, with concern, that “human-induced warming reached approximately 1°C (likely between 0.8°C and 1.2°C) above pre-industrial levels in 2017, increasing at 0.2°C (likely between 0.1°C and 0.3°C) per decade (high confidence).” (Allen *et al.*, 2018). Moreover, a human environmental impact study reveals a real concern over the past 25 years (Ripple *et al.*, 2017). Human activity leads to exceeding the ability of ecological systems to ensure living conditions for humanity on Earth. Furthermore, the ways in which we utilize fossil fuels has caused a huge increase in the levels of CO_x, SO_x, NO_x, heavy metals, ashes, etc. in the atmosphere and oceans of the world. In this regard, hydrogen is considered as a potential vector to address energy demand and to establish the era of renewable energy sources (Züttel *et al.*, 2010).

Over the past twenty years, the importance of hydrogen as a prospective energy source has increased significantly. Utilizing hydrogen offers significant advantages in terms of reducing carbon emissions generated by transportation systems, for example: furthermore, hydrogen has a higher efficiency than traditional fossil fuels (Hord, 1976). Recent research into hydrogen technology has revealed that it holds possibilities for various industrial and domestic applications, such as electrical generation, car fuelling, fertilizer production, mining, metallurgy, and domestic applications (such as in gas cookers).

Current progress in the hydrogen industry is owed to rapid advances in fuel cell (FC) technology (Sharaf and Orhan, 2014). A hydrogen fuel cell (HFC) is a device that converts electrochemical energy directly to electrical energy, bypassing second messengers (in comparison to the multi-step conversion in a diesel engine, internal combustion engine, and turbines).

FCs employing polymer electrolyte membrane (PEM) technology have been reported to offer sufficient capacity to be used in underground mines, replacing diesel power (Bessarabov *et al.*, 2017). The mining sector is an energy-intensive industry. In its efforts to control costs, one of the priorities of mining companies is energy reduction. Another important priority is, of course, to reduce employees' risk in underground mines. Machines that are used by the mining industry currently run on diesel fuel. The World Health Organization classifies diesel engine exhaust as "carcinogenic to humans", based on sufficient evidence to suggest that it is associated with an increased risk of lung cancer and related diseases (Iordache, 2016). Considering the above, the underground mining sector lends itself to HFC implementation, coupled with associated safety research and development. The gradual replacement of diesel vehicles with HFC vehicles will go a long way towards making the mining industry much cleaner.

No less important are hybrid renewable energy systems that employ HFCs combined with solar/wind/hydro power energy. A hybrid power plant can produce clean power—the only products are water and heat. The combination of HFCs and electrolyzers (as an additional system) can produce clean electricity and, moreover, the extra hydrogen produced could be stored and then transported to another location where the energy source is needed. Currently, there are more than fifteen pilot hybrid projects completed/underway, worldwide. One of the most progressive pilot plants was built on the Norwegian island of Utsira (Widera, 2019). The Utsira pilot plant is an autonomous hybrid wind–hydrogen–FC system equipped with a flywheel (5 kWh), Ni-Cd battery storage, and a hydrogen engine that supplies power (~300 kW) to the residents of the island. This plant (within a long-term project undertaken by Norway) is demonstrating significant efficiency, as the first full-scale renewable power plant combining wind and HFC energy generation. This ambitious development marks a very promising beginning to the way forward, to reduce worldwide air pollution.

A renewable energy cycle comprises several stages, depending on the complexity of the hybrid energy system. Figure 1-1 gives a schematic representation of the hydrogen energy cycle in a hybrid power plant. The electricity is generated by means solar energy panels, then the reserved energy is used to dissociate water into hydrogen and oxygen in an electrolysis facility. Here, only hydrogen produced directly from solar, wind, hydro, or geothermal is considered as green and renewable (Züttel *et al.*, 2010). In turn, as a result of the dissociation reaction, oxygen is released

into the atmosphere while the hydrogen is stored for future use (further transportation and distribution among customers). Finally, hydrogen is available to be used by the customer to generate electrical energy (HFC), mechanical energy (for vehicles, based on HFC), or heat energy (for gas cookers), for the customers' own purposes.

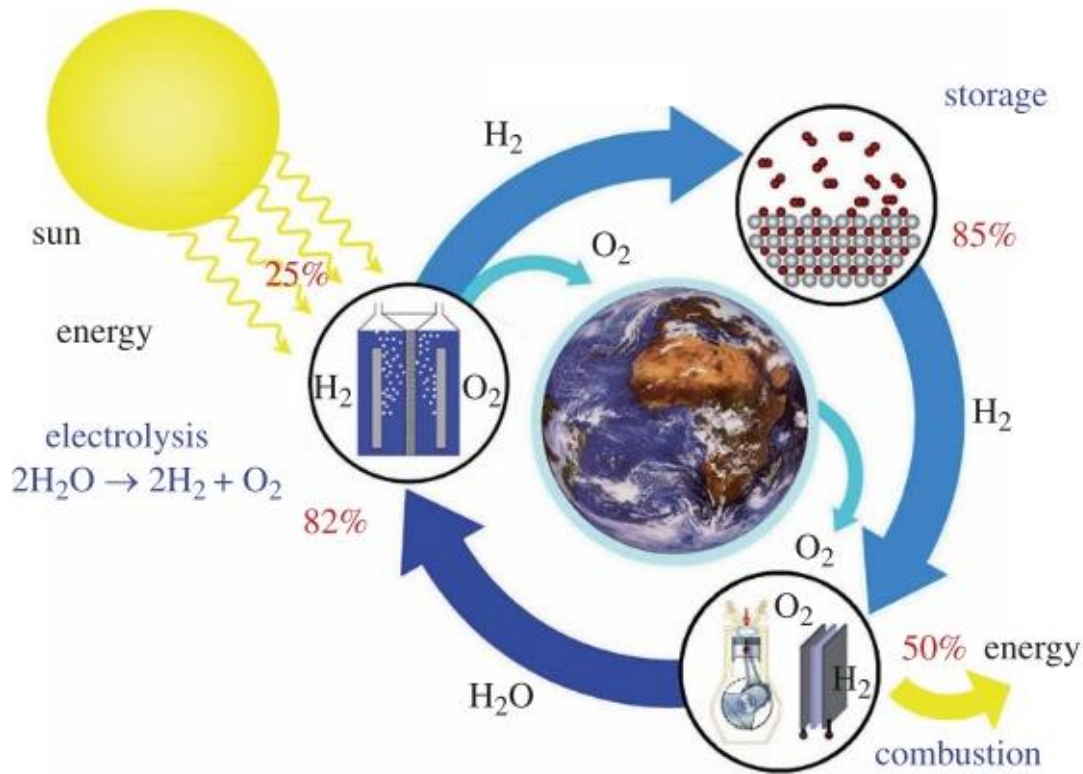


Figure 1-1: The hydrogen cycle employed in a hybrid renewable energy system (Züttel *et al.*, 2010).

However, there are associated safety concerns, mainly due to the following: the physicochemical properties of hydrogen, such as its wide flammability limit (4–75%), low-energy ignition (0.02 mJ), relatively low self-ignition temperature (~560 °C), high buoyancy (14× lighter than air) and the diffusion rate of hydrogen in air. Subsequently, safety technologies need to be carefully addressed (Rivkin *et al.*, 2015; Du Toit *et al.*, 2018). Research into hydrogen safety is important for preventing accidents and developing safety requirements for any concerns, including incomplete sealing of pipelines, system degradation, or human error. Hence, using hydrogen energy and the associated development of risk management strategies for associated hydrogen hazards, is essential for the long term.

In a recent overview of hydrogen production for energy, mention is made of a “hydrogen square”, which includes the production, storage, safety, and utilization as integral stages for hydrogen energy (Dawood *et al.*, 2020). Although here the safety aspect is prescribed in the third place, it is recognized as one of the most critical issues facing the promotion of wider hydrogen use. The importance of developing mitigation strategies for hydrogen safety has increased significantly and it continues to grow.

One of the widely applied hydrogen safety technologies is a ventilation system. Because hydrogen has a low density, when it is released it moves quickly towards a location above the leak point. This typical behaviour must be taken into account regarding the location of hydrogen safety sensors. Here, the safety sensors should be capable of detecting the leak within a short time, followed by the activation of emergency ventilation. The fresh air ventilation can be either passive or forced, depending on the shape of the enclosure or the amount of hydrogen in storage (Papanikolaou *et al.*, 2010; Hussein *et al.*, 2018).

Yet another important advanced approach towards mitigation strategies for hydrogen safety involves the use of a PAR (Bachelier *et al.*, 2003). A PAR is usually constructed as a vertical flow channel containing several catalytic units. The catalytic units can be of various geometric shapes, such as stainless steel (SS) plates coated with platinum (Pt) or palladium (Pd) (Klauck *et al.*, 2014), or a Pt/anodized aluminum oxide (AAO) catalyst (Kozhukhova *et al.*, 2021), or aluminum ceramic cylinders coated with a Pt-containing washcoat (Anpilov *et al.*, 2013). The operational performance of a PAR is maintained by means of the natural convection initiated when hydrogen passes through the PAR framework, usually from the bottom to the top (upward motion). The spontaneously exothermic chemical reaction leads to the heating of the catalyst surface and then activates natural convection inside the PAR. Eventually, by means of an autocatalytic recombination reaction, the concentration of hydrogen is reduced to lower than the flammable limit. A good ventilation system can provide efficient removal of hydrogen from a space or dilute it to below the flammable limit and, furthermore, in conjunction with a PAR, can prevent the formation of explosive mixtures in the accident localization zone.

Due to the great progress made in computer simulations, we now have the potential to investigate hydrogen technologies through CFD (Dieguez *et al.*, 2013). Computer simulations play an important role in hydrogen energy research (Molkov *et al.*, 2008; Tolia *et al.*, 2019). Computational methods are increasingly used to perform analyses of hydrogen production, storage, transportation and utilization. Moreover, CFD has become an essential tool to investigate safety aspects.

1.2 Problem statement and motivation

Regarding the very promising technologies based on hydrogen as a future renewable and environment-friendly energy carrier, the safety aspect is of critical importance. The release and accumulation of hydrogen in confined spaces is potentially very dangerous. The low density of gaseous hydrogen coupled with its high buoyancy allows for the rapid release, accumulation and formation of flammable clouds near the ceiling. Emergency hydrogen removal systems must be employed to guarantee that the hydrogen concentration is diluted to below the minimum flammability limit, even under severe accidents. The dispersion of hydrogen into confined spaces, such as an underground tunnel, residential garage, or any confined space, depends on the many parameters associated with hydrogen release, for example, the release pressure, release direction, orifice size and the conditions of the space. To date, there are insufficient studies to mitigate the hazard of such scenarios for confined environments. In this regard, it is of great importance to obtain up-to-date knowledge in this field and to collect relevant databases for the study of mitigation strategies for hydrogen safety, both experimentally and numerically.

Hence, related to these safety concerns and risk mitigation, there is an urgent need to develop and validate numerical models of hydrogen distribution processes in confined environments. Hydrogen release and subsequent dispersion, as well as autocatalytic hydrogen recombination processes, can be investigated using available CFD software (Papanikolaou *et al.*, 2011; Klauck *et al.*, 2014). A simulation using CFD techniques can serve to provide detailed data such as the concentration of hydrogen (inlet/outlet) during experiments, the potentially flammable regions, the vectors of flow motion, the temperature related to the ignition or combustion, the spatial dispersion and other features.

However, the current state-of-the-art of CFD modelling of hydrogen leakage and the mechanisms of homogeneous/heterogeneous reaction kinetics require further development towards achieving a higher level of accuracy and predictability. Specifically, to provide a clear understanding of real hydrogen accident conditions, it is necessary to develop and validate 3D numerical models that can cover all potential scenarios. The existing numerical models for PARs are mostly based on the empirical correlations of various experimental results. In many cases, they are poorly applicable to real accident conditions. Furthermore, to date, experimental investigations into the temperature distribution on the catalyst surface as well as the hydrogen recombination efficiency have not been carried for cylindrical-type catalysts.

Thus, the ability to predict the PAR behaviour could surely be very useful to anticipate the self-ignition and explosion of hydrogen inside the PAR—addressing overall hydrogen safety. The

ability to predict all the physical phenomena that may occur following an accidental hydrogen release on an industrial or urban scale is mandatory for the safe use of hydrogen.

1.3 Literature analysis

Within the scope of hydrogen energy usage, the safety aspect is recognized as essential (Rivkin, et al., 2015). Indeed, many pathways of the hydrogen industry such as production, storage, transportation and utilization have to meet related safety strategies. These strategies may be based on novel technologies. There are two major methods accepted to mitigate the risk of a hydrogen leak, ignition, and explosion: the catalytic recombination process taking place in passive autocatalytic recombiners (PARs), and fresh air forced ventilation (FV).

The importance of FV to mitigate hydrogen release accidents has been identified in the relevant literature (Matsumoto and Shimizu, 2011; Papanikolaou *et al.*, 2010; Barley and Gawlik, 2009; Cariteau and Tkatschenko, 2012; Talias, et al. 2019). The potential leak from an HFC vehicle in a residential parking garage was studied numerically by Tamura *et al.* (Tamura *et al.*, 2014). The study confirmed that the FV can dilute unintended HFC leakage to below the LFL at an air velocity of 10 m/s. On the other hand, the same authors reported that FV at a flow rate of 2 m/s enlarged the cloud of flammable hydrogen concentration, increasing the detonation region (Tamura et al., 2012). Thereby, it was suggested in this thesis to carefully select the correct velocity of FV in order to dilute released hydrogen to a safe level. It is therefore very problem-specific and the required FV velocity needs to be determined for each unique case.

Several accident scenarios in underground private garages, semi-closed rooms, and other confined spaces were investigated (Gupta *et al.*, 2009; Choi *et al.*, 2013; Middha and Hansen, 2009). A CFD benchmark of vertical hydrogen release in confined space with natural ventilation was conducted by Giannissi *et al.* (Gianissi *et al.*, 2015). Numerical validation of hydrogen release and deflagration in the tunnels and open atmosphere has been carried out by Molkov et al. (Molkov, *et al.*, 2008; Molkov, et al., 2006; Bie and Hao, 2017). However, none of these studies have investigated the efficiency of FV to mitigate horizontally directed hydrogen releases in the full-scale tunnel. This highlights the importance of developing and validating CFD models that can be applied to various applications and scenarios. Specific to the release of hydrogen in an underground tunnel may be caused by the pipe//vessel/PDR damage and the release orifice can be of various sizes. It is therefore important to conduct a parametrical study of horizontally directed hydrogen release based on different inlet conditions.

A PAR is an advanced technology that has long been recognized in the nuclear industry to mitigate potential accidents with hydrogen release. In efforts to research and define the

characteristics of PAR, numerous experimental programs have been conducted in small- and full-scale recombiner facilities in the past (Reinecke *et al.*, 2004; Gardner *et al.*, 2021; Liang *et al.*, 2016). Relevant data have been collected within the scope of these experiments. However, the only plate-type catalyst has been studied in observed literature. In order to measure the temperature profile, only thermocouples have been applied along the catalyst plate length. It is therefore identified, the cylindrical-type catalyst requires attention. Moreover, advanced technologies should be considered to measure the temperature of cylindrical-type catalysts.

A one-dimensional numerical model of the passive autocatalytic hydrogen recombiner has been developed by Rożeń. A single-step reaction model of hydrogen recombination at the plate-type catalyst was used to simulate the chemical mechanism in Ansys Fluent software. (Rożeń, 2015, Rożeń, 2018). Numerical investigations of a plate-type recombiner catalyst section have been performed during a test series in the REKO-3 test facility (Jülich, Germany) (Reinecke *et al.*, 2005; Reinecke *et al.*, 2010; Reinecke *et al.*, 2013). Within the scope of that project, the REKO-DIREKT (JÜLICH/RWTH) two-dimension numerical code was developed to describe the chemical reaction processes inside a PAR. While most studies have been focused on the plate-type PAR catalyst, the developed one- and two-dimension numerical models have enough capability to predict the catalyst thermal profile, and gas composition along a single recombiner channel for low inlet hydrogen concentrations rather well. Nevertheless, in order to simulate much complex PAR catalyst geometry (i.e. cylindrical-type), a three-dimension model is required.

Analysis of other relevant literature demonstrates a comparison of different reaction kinetic mechanisms. The multi-step reaction kinetic is required to provide competitive and accurate simulation results and the single-step reaction mechanism is insufficient (Prabhudharwadkar, *et al.*, 2011; Klauck *et al.*, 2014; Rożeń, 2015; Meynet and Bentaib, 2012; Meynet *et al.*, 2014). It was therefore identified to use the multi-step reaction kinetics in complex CFD model development. Furthermore, the multi-step mechanism of hydrogen oxidation on Pt catalyst urgently requires verification and validation to be applicable for high inlet hydrogen concentrations (6 vol. % and higher).

According to the literature, the other gap has been identified. Several fundamental studies only take into account surface reactions mechanism and neglect the gas-phase chemistry (Schefer, 1982; Prabhudharwadkar, *et al.*, 2011). Heterogeneous reactions mechanisms for the numerical simulation of hydrogen oxidation on Pt catalyst have been introduced by research groups (Ljungström *et al.*, 1989; Deutschmann, *et al.*, 1994; Rinnemo *et al.*, 1997), while homogeneous reactions mechanisms have been introduced by Warnatz *et al.* (Warnatz *et al.*, 1990). However, Appel *et al.* demonstrated that the simulation uses a conjugated approach with accounted both

gas-phase (homogeneous) and surface (heterogeneous) reactions can provide a higher level of simulation accuracy (Appel et al., 2002). The authors have tested four homogeneous and three heterogeneous mechanisms in the model against experimental homogeneous ignition characteristics. The best agreements found with the experimental measurements were the surface mechanism proposed by Deutschmann *et al.* (Deutschmann et al., 1996) and the gas-phase mechanism proposed by Warnatz *et al.* (Warnatz, et al., 1990). This conjugated approach combining both surface and gas-phase mechanisms has been identified for future use in complex CFD models. It is evident that accurate CFD models can be very useful in the development of new cost-effective, high-performance, thermally conductive, durable catalysts.

Several gaps were identified from the literature analysis in terms of mitigation strategies for hydrogen safety.

- Hydrogen leakage and dispersion are very case-specific and therefore require validated CFD models to evaluate emergency scenarios.
- Not much attention has been given to investigating the dilution effect of FV systems in terms of horizontally directed hydrogen release into a confined environment.
- The plate-type catalyst has been broadly investigated in terms of various initial parameters. In this concern, to fulfill the scientific database of PAR research, the cylindrical-type PAR Pt catalyst needs to be investigated
- Previous studies indicate that only one- and two-dimensional numerical models have been utilized to simulate the chemical mechanism of hydrogen autocatalytic recombination. However complex three-dimensions CFD models are required to consider all the interacting physical and chemical processes during a PAR operation.
- The single-step chemical mechanism of hydrogen recombination on a Pt catalyst is insufficient and the multi-step mechanism is more accurate. However, the multi-step mechanism remains to be validated, especially in terms of three-dimension simulations.
- Not much attention has been given to developing a CFD model that uses a conjugated approach with accounted both gas-phase (homogeneous) and surface (heterogeneous) reactions.

1.4 Aim and objectives

Hydrogen is now considered as one of the leading fuels for a future renewable and environmentally friendly energy carrier. The overall aim of this work is to investigate the mitigation strategies for hydrogen safety through the development and validation of innovative CFD models. The models for two safety technologies were considered: FV and the use of PARs. More

specifically, investigations focused on the following: the analysis of important parameters of hydrogen leakage in confined spaces in terms of various sizes of leaking orifice and the release pressure and the presence or absence of FV, the characterization of the hydrogen recombination processes, from the viewpoints of catalyst temperature and recombination efficiency.

The following specific objectives were defined:

- I. To identify the relevant literature on the experimental and computational investigations into hydrogen mitigation safety technologies: (i) the use of forced/natural ventilation systems for hydrogen removal from underground tunnels and residential garages, and (ii) the use of PARs as the generally accepted hydrogen safety device in nuclear power plants as well as others applications.
- II. To analyse the hydrogen distribution under a leakage accident in a confined space, with regards to the size of the leaking orifice and the hydrogen release pressure, and then to characterize the efficiency of forced and natural ventilation on hydrogen mitigation by performing a full-scale tests in the experimental facility and validate results through the CFD simulations.
- III. To develop and validate a 3D CFD model of a small-scale PAR by experimental evaluation of a PAR's cylindrical-type catalyst section in terms of temperature distribution and hydrogen recombination efficiency under low hydrogen inlet concentrations of 2–5 vol %.
- IV. To apply and validate an innovative 3D CFD model of the catalytic hydrogen recombination process by conducting experiments in a small-scale PAR with an in-house developed Pt/AAO plate-type catalyst.
- V. To develop and validate a detailed 3D CFD model and verify the surface and gas-phase mechanisms of hydrogen recombination reactions, by performing experiments in a PAR's cylindrical-type catalyst section under high inlet hydrogen concentrations of 6–7 vol %.

1.5 Research methodology

The research methodology followed in this work was directed towards obtaining and using experimental data and numerical simulations to investigate the mitigation strategies for hydrogen safety. The experimental data will be obtained utilizing different experiments/procedures, depending on the stated objectives. Further research will include developing and validating innovative numerical CFD models for hydrogen leakage and PARs. The numerical model will be created in the STAR-CCM+ software package (Siemens PLM Software, TX, USA), to better understand the hydrogen leakage process in confined spaces and to qualitatively analyse the effect of FV.

In order to collect relevant data for hydrogen leakage and distribution in confined spaces, a full-scale ventilation facility (HySA Mining Platform Test Facility for Green Mining) was built at HySA Infrastructure, South Africa (<https://hysainfrastructure.com>). The test facility is a standard size container with one open side—it represents part of an underground mining tunnel equipped with a ventilation tube. Measurements of hydrogen concentrations inside the facility were conducted utilizing twenty hydrogen sensors.

Furthermore, for the purpose of investigating the safety performance of a PAR from the points of view of the catalyst temperature and hydrogen recombination efficiency, a small-scale test set-up was also built at HySA Infrastructure. The recombiner section testing station is a small vertical channel that includes one catalyst section extracted from a commercial PAR (RVK-500, CJSC INPK RET, Russia). The catalytic section is a stainless-steel (SS) frame that can hold fourteen ceramic cylinders coated with Pt. To measure the inlet and outlet gas composition, thereby enabling estimation of the hydrogen recombination efficiency, gas sensors will be employed in the experimental set-up. An infrared (IR) camera (M100hd, Telops, Ontario, Canada) was placed in front of the recombiner channel to measure the catalyst temperature. The front side of the channel is made of synthetic sapphire glass to provide optical and thermal visibility of the catalyst section. At this stage, the CFD model will be created to validate the experimental data and to provide more details on the hydrogen recombination process on the Pt catalyst.

For the final stage of this study, namely, to investigate the cylindrical-type catalyst's safety performance in terms of high inlet hydrogen concentration, the recombiner section testing station will be upgraded. The number of hydrogen sensors will be increased to control the inlet and outlet gas composition, as well as to evaluate the catalyst start-up performance. Based on envisaged study requirements, the IR camera will be fitted with another filter that captures thermal images in the temperature range 147–600 °C. Finally, the STAR-CCM+ will be used to develop and validate a detailed CFD model that includes both the gas-phase and surface reaction mechanisms of H_2/O_2 oxidation on the Pt catalyst.

1.6 Thesis outline

The thesis comprises seven chapters.

Chapter 1, the introductory chapter, provides an overview of hydrogen as an energy carrier, as motivation for this research work, it states the overall aim and the specific objectives, and describes the methodology followed.

Chapter 2 presents a literature survey of the topic (*Mitigation strategies for hydrogen safety in the confined environment: CFD modelling and validation*). Relevant technologies in hydrogen safety that are widely recognized to mitigate unintended hydrogen release are described. The following related topics are included: work carried out to date on the use of forced/nature ventilation in underground tunnels and residential garages, PAR designs and their application in hydrogen safety, and PAR catalyst element configurations. Recent approaches to using CFD modelling for hydrogen dispersion and PAR operation, as well as the theoretical background of diffusion kinetics and numerical solution methods, are also addressed.

Chapter 3 presents a combined ‘experimental and modelling chapter’, published as a research article [Malakhov, A.A., Avdeenkov, A.V., Du Toit, M.H. and Bessarabov, D.G. (2020). *CFD simulation and experimental study of a hydrogen leak in a semi-closed space with the purpose of risk mitigation. International Journal of Hydrogen Energy*, 45(15), 9231–9240]. It describes the validation of the CFD model of hydrogen distribution in a confined environment with and without FV. The model was based on full-scale tests in a ventilation facility, applicable to use in underground tunnels and residential garages.

Chapter 4 presents another combined ‘experimental and modelling chapter’, published as a research article [Malakhov, A.A., du Toit, M.H., Du Preez, S.P., Avdeenkov, A.V. and Bessarabov, D.G. (2020). *Temperature profile mapping over a catalytic unit of a hydrogen passive autocatalytic recombiner: an experimental and computational fluid dynamics study. Energy & Fuels*, 34(9), 11637–11649]. It describes the performance of a recombiner section testing station under 2–5 vol % of inlet H₂. The following topics are addressed: evaluation of the catalyst temperature and H₂ recombination efficiency, as well as the development and validation of a 3D CFD model based on the small-scale PAR.

Chapter 5 presents a ‘modelling chapter’ published as a research article [Kozhukhova, A.E., du Preez, S.P., Malakhov, A.A., & Bessarabov, D.G. (2021). *A thermally conductive Pt/AAO catalyst for hydrogen passive autocatalytic recombination. Catalysts*, 11(4), 491]. This chapter (specifically subsections 5.2.5 and 5.3.4) addresses the application of the CFD model, developed in Chapter 4. The numerical analysis (and experimental evaluation) of an in-house developed Pt/AAO catalyst is presented, in terms of the temperature distribution and hydrogen recombination efficiency, for safety purposes.

Chapter 6 presents another combined ‘experimental and modelling chapter’, recently accepted for publication (08/10/2021) in 19th International Topical Meeting on Nuclear Reactor Thermal Hydraulics (NURETH-19) as a research article [Malakhov, A.A., Avdeenkov, A.V., Du Toit, M.H.

and Bessarabov, D.G., (2021). *Study of the efficiency of a PAR Pt catalyst and CFD verification of detailed mechanism of H₂/O₂ oxidation.*]. It describes the performance of a recombiner section testing station (small-scale PAR discussed in Chapter 4) under a high inlet H₂ concentration (6–7 vol %). This chapter presents an analysis of the catalyst temperature in terms of the hydrogen self-ignition limit, the dynamic/start-up performance, and the steady-state performance of the hydrogen recombiner. Furthermore, a description, and the development and validation of, a detailed 3D CFD model that includes the surface and gas-phase mechanism/s is given.

Chapter 7 presents the conclusions to the work described in this thesis (with reference to the objectives: Chapter 1, as well as recommendations for the future development and application of the CFD models towards a more detailed study of physical-chemical processes in terms of hydrogen energy.

Appendix A presents the development of the hydrogen recombiner numerical model (2D) published as a research article [Avdeenkov, A.V., Sergeev, V.V., Stepanov, A.V., Malakhov, A.A., Koshmanov, D.Y., Soloviev, S.L., Bessarabov, D.G. (2018). *Math hydrogen catalytic recombiner: Engineering model for dynamic full-scale calculations. International Journal of Hydrogen Energy*, 43(52), 23523–23537]. It is included in this thesis as the theoretical background of numerical methods focusing on the hydrogen autocatalytic recombination mechanisms.

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CHAPTER 2: LITERATURE REVIEW

The research described in Chapter 2 represents a literature survey that has been conducted by the author in an attempt to answer the scientific question that was defined in objective I, “To identify the relevant literature and to recognise the gaps in the literature on the experimental and computational investigations into hydrogen mitigation safety technologies: (i) the use of forced/natural ventilation systems for hydrogen removal from underground tunnels and residential garages, and (ii) the use of PARs as the generally accepted hydrogen safety device in nuclear power plants as well as others applications”.

OVERVIEW

The hydrogen industry is playing an increasingly great role towards a clean, renewable and affordable energy future. Great progress has been made with hydrogen fuel cell technology and it is rapidly becoming more advanced, clean, and environmentally friendly to replace the use of traditional fuel. However, similar to any other energy sources, hydrogen presents certain health and safety risks when used on a large scale (industrial, domestic). Hydrogen leaks (detected or undetected) are associated with an increased risk of a hydrogen explosion. This is of particular concern when hydrogen is used in residential or industrial buildings (i.e., a confined environment/space). It is therefore of utmost importance to investigate potential hazards and define mitigation strategies. There are two main approaches to mitigate the consequences of hydrogen leakage and maintain safe conditions in semi-closed and confined spaces. The first approach involves the utilization of ventilation systems that provide sufficient hydrogen mixing with air to lower than the flammable limit, thereby preventing the formation of flammable clouds. A more sophisticated approach involves using a passive autocatalytic recombiner, the working operation of which is maintained by the exothermic H_2/O_2 autocatalytic reaction. Both these technologies can be suitably investigated numerically by utilizing computational fluid dynamics methods.

2.1 Introduction

Climate change is expected to increase sea levels, and changes in the amount and pattern of precipitation. Such changes may increase the frequency and intensity of extreme weather events, such as floods, droughts, heat waves, and hurricanes. These changes themselves subsequently cause changes in agricultural yield, glacier retreat, reduced summer streamflow and can contribute to biological extinctions. Thus, human activity leads to exceeding the ability of ecological systems to ensure living conditions for humanity and the total biosphere on Earth.

Since the 1960s, scientists have recognized that fossil fuels (coal, oil, and natural gas) are decreasing, and will sooner or later become depleted. According to estimates, the production of fluid fossil fuels (oil, coal, and natural gas) will peak around the year 2010 and thereafter will begin to decline (Elliot, 1972; Parent, 1979; Vezirolu and Barbir, 1992; Attanasi and Root, 1994; Kerr, 1998; Cavallo, 2004; Helm, 2011; Dudley, 2016). Eventually, all scientists concluded that current habits of energy production anticipate extremely rapid environmental pollution and worldwide energy demand—endangering our future.

In 2021, fossil fuel sources continue to lead the world's electricity production. The International Energy Agency (IEA, 2021) recently reported trends of electricity generation that included the main fuel sources around the world from 1971 until 2019. Figure 2-1 shows that the coal industry is still dominant in global energy production.

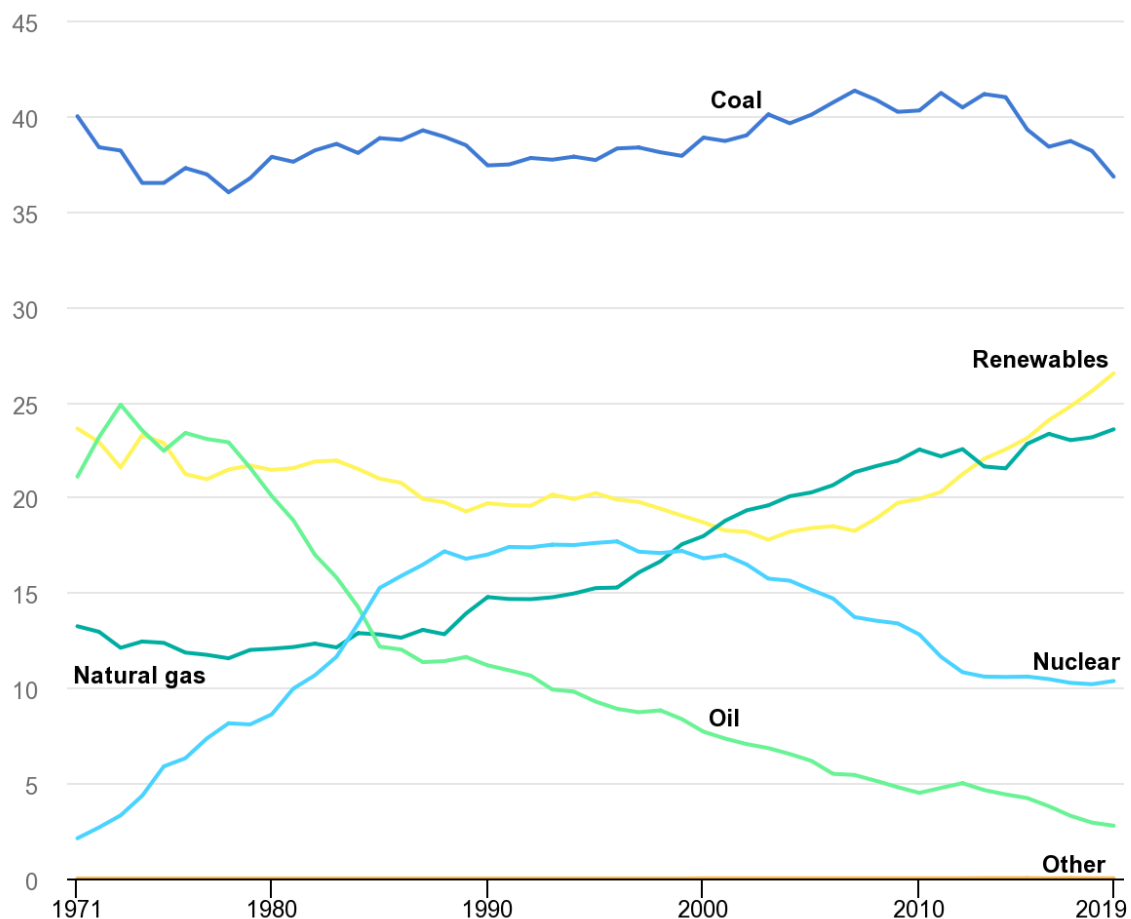


Figure 2-1: World electricity generation by different fuels (IEA, 2021).

However, in recent years, it is evident that renewable energy usage is only 10% behind. In 2019, renewable electricity sources (hydro, solar, wind, biofuel and waste, other renewables) provided almost 27% of the global electricity; this is expected to rise to 45% by 2040. Furthermore, since 2015, the renewable energy sector has begun to grow rapidly, while the domination of coal electricity on global electricity generation is falling (IEA, 2021). This positive renewable energy trend promises a future perspective to completely replace traditional fossil fuels and reduce human environmental impact.

Scientists involved in energy research are now actively engaged in looking into possible sources of energy to replace fossil fuels. Suitable future energy sources should meet the following requirements: suitability as a fuel for transportation, easily convertible to other forms of energy (heat, electricity) up to customer purposes, high utilization efficiency, safety throughout all of the stages of the fuel cycle, compatible with the environment, and inexpensive. There are several primary energy sources available: fission and fusion nuclear energy, geothermal energy, solar energy, wind energy, ocean currents, tides, and waves.

In this regard, if one tries to find the definition of a perfect fuel, hydrogen probably satisfies most of the desirable characteristics of such a fuel. The high energy content per mass unit of clean-burning hydrogen has the potential to be the energy source of the future. According to data received for 2020, roughly 87 Mt of hydrogen was produced worldwide for various purposes. The International Energy Agency predicts that global hydrogen production will grow rapidly to about 445 Mt for energy use plus 75 Mt for process use by 2070 (Biol, 2020). All this points to the fact that the importance of the hydrogen economy is growing, and research projects into the production, storage, transportation and utilization of hydrogen should be strongly supported. Especially, related safety technologies and mitigation strategies need to be investigated and strengthened.

Within the scope of hydrogen energy usage, the safety aspect is well recognized as significantly important. Indeed, many pathways of the hydrogen industry such as production, storage, transportation and utilization are following restricted safety strategies and applying advanced technologies. Ever since the introduction of computational fluid dynamics (CFD) methods in the research community, it has become a promising tool to analyse many physical–chemical phenomena. CFD methods can provide advanced opportunities to simulate, evaluate and consolidate each pathway of hydrogen energy usage from the safety viewpoint. Moreover, advanced three-dimensional CFD models can examine many parameters of process or technology of interest; furthermore, CFD offers an alternative to high-cost experiments.

2.1.1 Hydrogen fuel cells for mining operations

In recent years, the trend in the transportation sector is towards electric cars powered by hydrogen fuel cells (HFCs) (Manoharan *et al.*, 2019). HFC technology is currently being developed as an alternative for use in underground mining machines (Middha and Hansen, 2009; Houf *et al.*, 2012) and can be a very promising technology to reduce the harmful impact of diesel engine pollution on humans health. An HFC is a device that converts chemical energy into electrical energy using the movement of charged hydrogen ions across an electrolyte membrane to generate current. At the electrolyte membrane, hydrogen ions recombine with oxygen to produce energy as the main product and water as a by-product.

According to different estimations, the contribution of the mining industry to global CO₂ emissions is 3–8% (Azadi *et al.*, 2020). To achieve desired global warming reduction by 2050, the mining industry should reduce its CO₂ emissions to zero. Fuel cell (FC) vehicles have the mobility, power and safety of a diesel unit, with the advantage of being environmentally friendly. Lower costs and higher productivity of HFC could make the mining vehicles a cost-competitive technology (Miller *et al.*, 2012). Meanwhile, the real conditions of the operational mine could serve to determine how the hydrogen should be stored, distributed and utilized. Figure 2-2 presents a working HFC vehicle, successfully demonstrated in 2012 at an underground platinum mine in South Africa. This vehicle contained a 17 kW FC. The manufacturer stated an energy capacity for this vehicle at about 48 kWh, which allows for an operation time of about 8 h, without recharging. Moreover, the required time to recharge an FC is < 1 h (refuelling hydrogen vessel) (Miller *et al.*, 2012).



Figure 2-2: Anglo American locomotive prototype, equipped with fuel cell and metal hydride hydrogen storage onboard. Presentation at Khomanani Mine, South Africa, 2012 (Langmi *et al.*, 2022).

In efforts to achieve zero-carbon emission in the mining industry, the search is on for perspective technologies in terms of a clean and environmentally friendly energy carrier. HFC technology has the flexibility to respond to some of the transportation and operational challenges in the mining industry. However, hydrogen usage in underground tunnels must be carefully monitored in terms of unintended leaks, flammable cloud formation, and any emergency scenarios.

2.2 Safety considerations for hydrogen emergency systems

From a safety point of view, the usage of hydrogen is accompanied by a risk of leaks of gaseous fuel inside, for example, residential or industrial buildings (confined environment/spaces). The most important safety consideration associated with any application of hydrogen energy is prevention of the formation of flammable mixtures with air. The range of the flammable volume fraction of hydrogen in air is 4–74 vol % at atmospheric pressure (Du Toit *et al.*, 2018). The self-ignition temperature range is 845–858 K (Du Toit *et al.*, 2018). Table 2-1 summarizes relevant physical properties of hydrogen, compared to methane and propane.

Table 2-1: Combustion properties: Hydrogen, methane, propane.

Property	Units	Hydrogen	Methane	Propane
Molecular weight	g/mol	2.016	16.04	44.097
Density at NTP	kg/m ³	0.0838	0.6512	1.87
Self-ignition temperature	K	845–858	813–905	760–766
Minimum ignition energy	mJ	0.02	0.29–0.33	0.26–0.305
Flammability range in air	vol %	4–74	5–15	2.1–10
Adiabatic flame temperature	K	2318–2400	2158–2226	2198–2267
Energy per unit of mass	MJ/kg	120.1	55.6	46.35

It is therefore important that hydrogen safety systems be installed to maintain accidentally released hydrogen below the flammability limit (< 4 vol %), moreover a minimum ventilation rate (if FV has been deployed to mitigate hydrogen release) has to be sufficient to mix up a potential hydrogen leak up to 25% of the LFL (< 1 vol % H₂). Commonly, the hydrogen storage facility must be equipped with pressure relief device (PRD) valves (European Commission, 2010), which are fitted to the fuel tank and serve by releasing the gas in the event of high temperatures, for instance in conditions when hydrogen leakage leads to a hydrogen jet fire. A PRD can provide rapid hydrogen release from a fuel tank, thereby avoiding or minimizing the possibility of an explosion of the tank itself. However, for indoor application, a high mass flow rate from the hydrogen storage throughout a PRD, in an emergency case, is unacceptable.

The potential risk of ignition and explosion may be caused by the failure of hydrogen infrastructure components or by human error. In this regard, hydrogen safety relies on the following key considerations (Barilo, 2015):

- Identification of hazards and defining risk mitigation strategies
- Provision of proper ventilation to prevent accumulation of hydrogen
- Ensuring that hydrogen leaks are detected and isolated
- Securing system integrity
- Providing personnel training.

Hydrogen is flavourless, colourless and tasteless—it cannot easily be detected by human senses (unless in very close proximity to the flame). Thus, the immediate/soonest detection of any hydrogen leakage is very important to define the best strategy to mitigate an unintended release

of this highly flammable gas. The leakage identification system should consist of a sensitive gas sensor that is able to detect low hydrogen amounts in the air (± 0.25 vol % of hydrogen in air). Another method is by monitoring the pressure of the hydrogen inside the system piping for changes that would suggest a leak has emerged. The design of the leak identification system must ensure that leaking hydrogen would pass by the gas sensor to activate visual and audible warnings. Simultaneously, an automatic shutdown of the hydrogen source must be provided, and transition to a safe regime, with activation of an adequate air ventilation flow. Lastly, the system integrity and sustainability must be checked to ensure safety performance targets.

Depending on the origin of the hydrogen leak, it can be classified into two categories. According to Schefer *et al.* (2006) the first category is the leakage of hydrogen through holes, breaks, cracks, or any physical damages of/in material or vessel that contain/store hydrogen. This type of leak can be described from a thermodynamic point of view as a continuum flow regime (collision between gas atoms are involved) and can be characterized in terms of various sizes of orifice (hydrogen leak point) and pressure (or mass flow rate) release. In turn, 'convective leak' can be either low-pressure subsonic laminar or turbulent flows, and if a gas release is from a high-pressure source it is a sonic flow. A low-pressure release involves low-momentum leakage mode when hydrogen mixes in an insufficiently uniform manner with surrounding gas and reaches the ceiling of the building/facility with stratification concentrations (Hoyes and Iivings, 2016). Whereas a high-pressure release can be characterized by a high-initial-momentum leakage mode, it means the gas is fully mixed with surrounding gas upon reaching the ceiling (Han *et al.*, 2014).

When hydrogen leaks through an orifice into ambient air, the leak begins as a hydrogen jet. According to the pressure ratio between a hydrogen source and the surrounding atmosphere, hydrogen jet behaviour will be dominated by three types of hydrogen jets: a) only buoyancy, b) initial momentum and buoyancy, c) initial momentum. Figure 2-3 represents these three types of hydrogen jets.

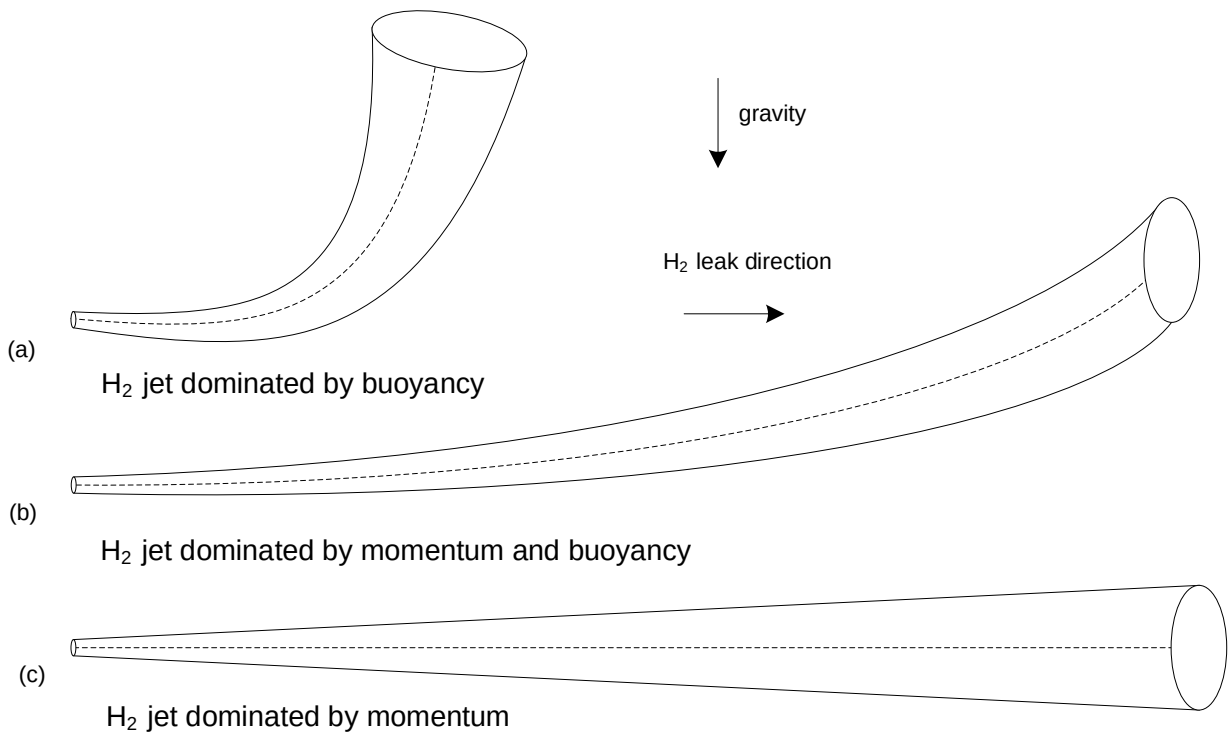


Figure 2-3: Schematic representation of different hydrogen jets behaviour.

Since the initial momentum of hydrogen release dominates (Figure 2-3 c), the jet will be expanded in a narrow straight direction away from the leak point; it will be not depending on the gravity force. However, if hydrogen release is initiated by low pressure, the buoyancy effect will dominate for hydrogen jet formation and stratification concentrations (Figure 2-3 a). Figure 2-3 b illustrates an intermediate type of hydrogen jet, the propagation of which is dominated by initial momentum and buoyancy effects. The critical pressure of the conversion from the subsonic jet to the under-expanded sonic jet is about 0.2 MPa (NTP) for hydrogen (Yang *et al.*, 2021). Nevertheless, hydrogen storage, pipelines, refuelling stations, and FC vehicle infrastructure pressure is generally > 0.2 MPa. This means that leakage occurring from the main hydrogen sources will, in most cases, lead to the formation of an under-expanded sonic jet dominated by initial momentum.

The second leak category is the permeation of hydrogen through the surface of a hydrogen storage vessel (Schefer *et al.*, 2006). This case is reflected in the molecular flow regime (collision between gas atoms and vessel surface are involved) and can be observed in a storage vessel that has a large surface area and a long storing time. This hydrogen leakage category will not be considered in this thesis.

Regarding safety considerations, hydrogen leakage, dispersion, and accumulation in confined spaces with complicated geometric configurations poses a great danger—this concern must be predicted and prevented. There are two major methods accepted to mitigate the risk of a hydrogen leak, ignition, and detonation: catalytic recombination conducted in passive autocatalytic recombiners (PARs) and fresh air forced ventilation (FV). The space geometry plays a role in the selection of the use of natural ventilation or FV. The location of the recombiner is also very important. Recently, very important steps have been proposed for mitigation strategies in hydrogen safety. However, to provide detailed step-by-step safety measures, the chosen technologies require in-dept investigations in terms of experimental performance and development of innovative CFD models.

2.2.1 Natural and forced ventilation to mitigate hydrogen leak accident

Insofar as there is the possibility of failure of hydrogen valves, pipelines, and other infrastructure components due to manufacturing defects, transportation damage, or human error, it is vital to investigate and create safety requirements for mitigation strategies. The formation and evolution of a hydrogen–air mixture becomes an important issue, principally when hydrogen is leaking into a confined space. Convective leakage and dispersion accidents from a storage/utilization vessel into a semi-open space or confined space (garage, tunnel), as well as HFC vehicle hydrogen release, have been studied in many experimental and numerical research works (e.g., Barley and Gawlik, 2009; Ekoto *et al.*, 2011; Bie and Hao, 2017; Gye *et al.*, 2019).

Tsunemi *et al.* carried out a quantitative risk assessment of human life during the operation of a hydrogen refueling station (Tsunemi *et al.*, 2019). There, the authors included the calculation of three accident scenarios: a hydrogen leak from an external pipeline, a leak from a high-pressure accumulator connection pipeline, and a leak from a high-pressure compressor. Results indicated that there was no leakage risk from external piping for hydrogen refueling station workers. However, the fatal risk for hydrogen leakage in a high-pressure accumulator and compressor is significantly increased in the area < 10 m from an ignition source. In this regard, the authors proposed that a fire barrier be installed around any suspected hydrogen leakage/ignition source.

Fire barrier walls can serve to interrupt the blast wave, thus averting the fatal injury of workers and damage to buildings. Meanwhile, the ventilation system (natural or FV) can offer a strong effect on a released hydrogen cloud, and even prevent an explosion. For instance, Swain and Swain studied a leakage of hydrogen at different release rates (up to 100 L/min) into a confined chamber with various rates of ventilation flow (up to 7.5 L/s m²) (Swain and Swain, 1996). They numerically determined that the upper ventilation position (closer to the ceiling) had a stronger effect on flammable gas cloud formation than a lower ventilation position. Moreover, their study

revealed that steady-state hydrogen concentration decreased linearly with increased forced fresh air ventilation rates. The results of their earlier work are interesting to note here; specifically, a comparison of flammable gas leakage into a plexiglass chamber that represented a kitchen (Swain and Swain, 1992). They concluded (experimentally and numerically) that in the event of gas leakages such as that of propane, methane, and hydrogen at flow rates great enough to produce appreciable fuel gas concentration gradients, it is propane that produces larger combustible fuel clouds, and more quickly than methane and even hydrogen.

Hydrogen leakage in a confined space was investigated in several works by Matsuura *et al.* (Matsuura *et al.*, 2008; Matsuura, 2009; Matsuura *et al.*, 2010), where the natural and FV contribution to the formation of flammable hydrogen clouds was observed numerically and demonstrated experimentally. Apparently, only the upper positions of ventilation apertures (for either natural ventilation or FV) affect hydrogen cloud formation. In terms of natural ventilation, they concluded that small-area distributed vent apertures are more effective than large-area distributed vent apertures. In turn, FV may cause global circulation and transport hydrogen clouds to the lower part of the enclosure. Therefore, if FV creates circulation, a ventilation aperture at the lower part of the enclosure will begin to play an important role. Moreover, it is necessary to design the shape and position of the ventilation apertures with regards to maintaining the global circulation and constant removal of released hydrogen. However, the configuration and distribution of vent apertures considered in their studies seem complicated, and not appropriate to the real facilities where hydrogen technologies are operational.

Significant numerical validation work in terms of ignited hydrogen release from on-board storage inside a residential garage through PRD was carried out by Hussein *et al.* within the scope of the HyIndoor project (Hussein *et al.*, 2018). The numerical study was based on a series of laboratory and real-scale experiments that were carried out at different facilities equipped with a single ventilation aperture with various configurations. Several release rates, as well as PRD diameters, were chosen to represent emergency scenarios. In that research, the authors stated that the radiative heat transfer mechanism should be taken into consideration to correctly simulate ignited hydrogen pressure release. Among four different turbulence models that were applied to simulate the experimental results, the authors reported that the realizable k-epsilon model provided a good agreement. The simulation approach demonstrated that a reduction of the PRD diameter leads to a decreased duration of the hydrogen release. Thereby, an adequate ventilation system (e.g., with respect to possible release pressure) can reduce consequences of ignited release and it is strongly recommended that such a system be installed to address hydrogen safety considerations.

CFD simulations is a powerful approach for research of hydrogen safety. Certain release scenarios from a HFC inside an operating facility (garage, tunnel) have been investigated experimentally and validated through CFD (Houf *et al.*, 2012; Choi *et al.*, 2013; Liu and Christopher, 2015). Insofar as an HFC vehicles is becoming generalized around the world, it is vital to study hazardous accidents of hydrogen release, dispersion and potential ignition from HFC. The importance of FV on the mitigation of a hydrogen leak from HFC vehicle into residential parking garage was studied numerically by Tamura *et al.* (2014). In that case, hydrogen was released upwards from a nozzle with an internal diameter 4 mm at 2000 NL/min flow rate under the car. The ventilation air was delivered to a test vehicle by means of a blower with attached duct. Tamura *et al.* study certainly confirmed that, the FV can dilute unintended HFC leakage to below 4 vol % at air velocity of 10 m/s. Hydrogen concentrations in both underfloor section and cabin decreased after the delivery of ventilation air from a duct, whereas in another study (Tamura *et al.*, 2012) they reported that FV at flow rate of 2 m/s is even enlarged at the region of hydrogen concentrations that is exceeding the lower flammable limit (4 vol %). Thereby, it was suggested that the velocity of FV needs to be increased to dilute released hydrogen to safe level.

There are many pathways causes of hydrogen release into confined spaces: pipeline damage, valve failure, storage vessel accident, or the release of hydrogen inside a FC. Such cases have been studied over the past twenty years. Several research groups have introduced numerical methods and simulation models to investigate the hydrogen leak phenomenon as well as the contribution of FV on the formation of flammable hydrogen clouds. However there are only few numerical studies of real-scale horizontal hydrogen leakage coupled with proper FV system.

2.2.2 PAR: an advanced hydrogen safety technology

During the hypothetical case of a severe accident in an NPP, the cooling water in contact with zirconium-based cladding in the reactor core can generate large amounts of hydrogen into the containment. (IAEA, 2011; Gardner, *et al.*, 2019). Subsequently, the local concentration of hydrogen may become significantly high and may exceed the low flammability limit. To prevent this potential hazard, one has to limit the hydrogen concentration in the confined space to levels lower than the flammability limit (Markert *et al.*, 2007; Paladino *et al.*, 2012). Generally accepted global practice to remove hydrogen from containments of nuclear power plants is currently based on the chemical principle of passive autocatalytic hydrogen recombination, specifically on a passive autocatalytic recombiner (Blanchat and Malliakos, 1999; Bachellerie *et al.*, 2003). A PAR operates at temperatures much lower than those required for gas-phase ignition and reduces the accumulation of hydrogen and detonation risk after any case of hydrogen release. A PAR consists of a rectangular vertical flow channel to allow incoming hydrogen to pass through catalytic

sections and thus maintain natural convection during normal operation. The lower part of the channel includes a number of elements covered by a catalyst material. The upper part of the channel includes a chimney outlet to release chemical reaction products—water vapour and heat.

That catalytic elements play a key role in the recombiner during normal operation. Initially, gaseous hydrogen arrives at the catalytic surface, where the chemical recombination reaction with oxygen (in atmospheric air) takes place, with the release of heat and water vapour as products. Manufacturers have proposed two main geometric shapes for the catalytic elements: SS plates (sheets) covered by platinum (Reinecke *et al.*, 2004) or aluminium ceramic cylinders covered by a platinum washcoat (Anpilov *et al.*, 2013). The operation of a PAR is maintained by means of the natural convection that is initiated when hydrogen passes through the recombiner channel. Thus, an exothermic surface chemical reaction leads to the heating of the catalyst units and then activates natural convection that moves the gases upward inside a PAR. The recombiner channel can be of various dimensions (still retains rectangular) depending on the number of included catalyst elements, and the length of the chimney section (Reinecke *et al.*, 2013). A PAR containing a plate-type catalyst (manufactured by AREVA, France) is shown in Figure 2-4.

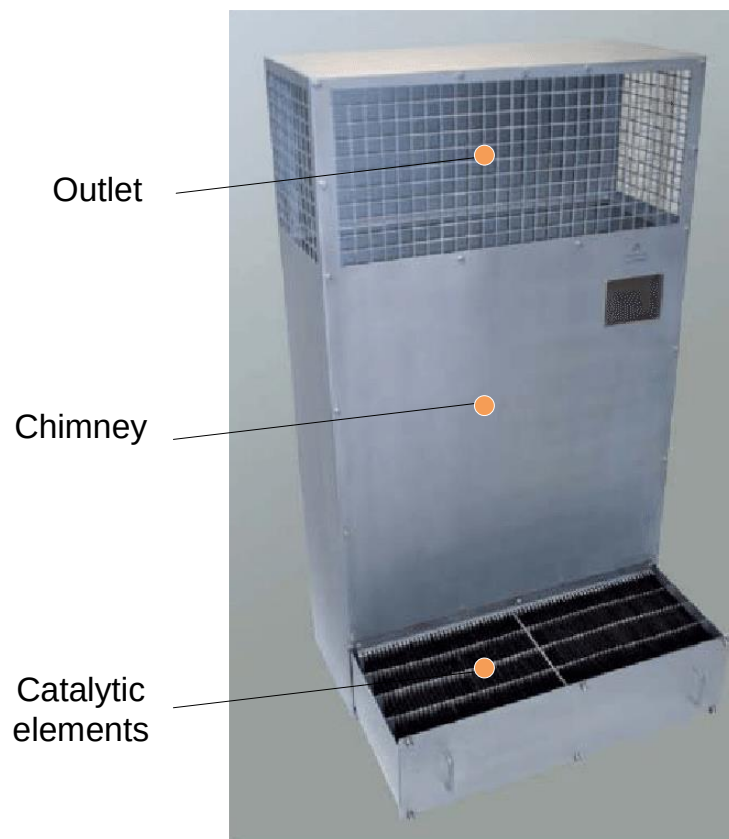


Figure 2-4: Passive autocatalytic recombiner containing plate-type catalytic elements (AREVA, France) (AREVA, 2011).

The thermal energy that is released during the multi-step chemical reaction of hydrogen/oxygen recombination can lead to heating of both the catalyst and gas inside the PAR. As a result, this heat will maintain natural upward convection in the PAR channel. The moment of onset of hydrogen recombination might present a potential risk for the recombiner. If the mixing process of the reaction components is not optimized in terms of timing, the gas mixture of hydrogen and air could self-ignite and damage the PAR (Paladino *et al.*, 2012; Rożeń, 2015). Hence, the geometry of the PAR should make provision for a sufficient level of gas mixing.

Furthermore, the recombiner should begin to operate as soon as gaseous hydrogen enters the catalyst area, even at low ingoing hydrogen concentrations. Thereby, the catalytic elements, as well as catalyst material, need to respond quickly within the different inlet and environment conditions. There are several important conditions that must be considered before a PAR is accepted for operation in safety application, including working in high humidity, lowest inlet hydrogen content to initiate an autocatalytic reaction, initial catalyst temperature (pre-heating of the catalyst is not required) and oxygen starvation (Du Toit *et al.*, 2018).

In efforts to research and define the characteristics of a PAR, as well as to develop and validate detailed numerical models, numerous experimental programs have been conducted in small- and full-scale recombiner facilities around the world. Braillard *et al.* (1997) published a report describing a test programme that supported the introduction of PAR technology as a safety device to control and remove combustible hydrogen–air mixtures from the containment of NPP. Experimental investigations of the temperature distribution on the catalyst surface of a small PAR, designed as a cut-out of a commercial recombiner section, were performed during a test series at the REKO-3 test facility (Jülich, Germany) (Reinecke *et al.*, 2004). Within the scope of that project, the RECO-DIREKT numerical code was developed to describe the chemical reaction processes inside a PAR (Reinecke *et al.*, 2005). A two-dimensional CFD model of the catalytic hydrogen recombiner has been presented by Rożeń (2015). A single-step reaction model of hydrogen recombination at the catalyst surface was utilized to simulate chemical surface reactions in Ansys Fluent software. The developed model can well predict the catalyst thermal profile, gas temperature, and gas composition along a single recombiner channel. The application and efficiency of a PAR for the removal of hydrogen inside a car garage has been reported in work by Baggemann *et al.* (2017). In that study, the sensitivity of a PAR for changing boundary conditions, scenarios of hydrogen release, and PAR positions were investigated utilizing CFD simulations.

Among other parameters of numerical validation of a PAR in terms of safety performance is the estimation of the Soret effect (the thermal diffusion) influence. The Soret effect is the mass

diffusion due to the presence of a temperature gradient and can be an important phenomenon, evident in hydrogen hotspots with concentrations beyond the ignition limit. The Soret effect was recognized Rozeń (2015) and partly investigated Meynet *et al.*, (2014) through numerical simulations of plate-type recombiner catalysts (but not for cylindrical-type catalytic elements). CFD calculations revealed that, at some point, hydrogen can exceed its inlet concentration. The PAR SS wall is exposed to heat radiation that comes from the overheated catalyst surface. As a consequence, the temperature gradient between the recombiner wall and adjacent gas increases, resulting in the diffusion of light hydrogen towards the side walls, not covered by the platinum catalyst. Such behaviour of a PAR could be rather dangerous in terms of overrunning the hydrogen flammability limit. It is largely dependent on the geometry of catalyst elements.

2.3 Diffusion kinetics theory and numerical solution method in hydrogen catalytic recombination

The main purpose of macroscopic kinetics is to study the effect of physical processes on chemical reactions. The most important of the physical processes are the diffusion of the reactants and products, and the evaluation of heat transfer of heterogeneous chemical reactions (Frank-Kamenetskii, 1987). Hydrodynamic conditions affect both, the diffusion and the heat transfer of these processes. For instance, gas motions affect convective heat transfer. Accordingly, the higher the rate of supply of the reacting material to the surface, due to convective diffusion, the higher will be the rate of the heterogeneous reaction.

In general, the diffusion flux depends on the concentration gradient of all components of the mixture as well as on the temperature gradient. In the approximation of the independent diffusion theory, it is assumed that the flow of each component depends only on the gradient of its concentration (Kirpichev, *et al.*, 1940; Kafarov, 1962). Diffusion in an immobile medium can be observed in a pure form only in a solid environment; in liquids and gases are unavoidably accompanied by a motion in a natural or forced convection. If the motion of the liquid or gas is caused by the temperature gradient or concentrations that determine the transfer of heat (or reactant and products), the convection is referred to as natural. In the presence of convection, the heat transfer law must be supplemented by additional terms expressing the transfer of heat or a substance by the mass flow. The most general description of the transfer processes is achieved if the molecular diffusion is not separated from the convective transfer and if the average velocities of the individual components are used. The average velocities of the individual components are included in molecular diffusion as well as convection transfer.

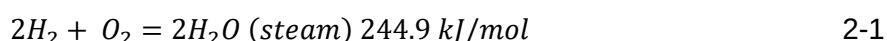
The type of motion of the gas or liquid influences the character of the convective transfer of heat or substance. In laminar flow, the mechanism of heat and substance convection is essentially the same as in a solid medium. In the case of turbulent flow, the transfer mechanism takes place through turbulent pulsations, i.e., disordered motions of small volumes of gas or liquid. Motions of the flow through a layer composed of material particles (such as a catalyst layer) depend on several factors: the shape of the particles forming the layer, the packing density of the particles in the layer (catalyst layer or other reactant material), and uneven of particle sizes. All these factors are difficult to quantify. Nonetheless, several investigations into the influence of the packing density of particles in the layer and their shape on convection in a layer of particles have been carried out (Taskin *et al.*, 2008; Karthik and Buwa, 2019). This factor is named layer porosity. The effect of layer porosity on convection in a layer of particles was studied by Bernshtin (1948). In their work, airflow was supplied through a layer that contains an ideal spherical particle. They concluded that, with an increase in the layer porosity, the free surface of the particles increases, but the true reaction rate decreases.

It is widely known that the kinetics of heterogeneous reactions on a surface is determined not only by the concentrations of substances but also by an important parameter, the fractional site coverage. The fractional site coverage is the ratio of the number of active catalyst sites occupied by a species to the total number of sites available for adsorption on the catalyst surface. The reaction course is always determined in one of two ways, either by an absorption reaction on a surface or by a 'direct blow' of the species at the surface. In terms of an absorption reaction, the absorption rate or reaction rate is proportional to the fractional site coverage, whereas in a 'direct blow' reaction it is proportional to the concentrations of the species.

As it is known, chemical reactions are either homogeneous or heterogeneous. Homogeneous reactions take place in a single phase (in a gas volume), while heterogeneous reactions take place at an interface (on a surface). Generally, the rate of a heterogeneous chemical reaction is determined by detailed surface chemical kinetics and by the speed of the supply of the reactants to the surface through convective diffusion. A great accomplishment in investigations into the course of chemical processes using the methods of similitude theory and modelling of heat and mass transfer was the introduction of CFD (Kee and Miller, 1989; Reinecke *et al.*, 2013; Orszulik *et al.*, 2015). The recombination reaction commences with the arrival of molecular hydrogen and oxygen at the surface of a catalyst; this is followed by their dissociation. Studies of a detailed chemical reaction mechanism of hydrogen oxidation on a Pt catalyst surface have progressed significantly over the past few years, especially with the help of CFD methods.

CFD methods are advantageous in that provide detailed analysis of experimental results and, furthermore, extend the capacity of an investigation to parameters that cannot be included in the experimental scheme. The various comprehensive problems involving the flow of fluids or solids, homogeneous and heterogeneous chemical reaction kinetics, heat transfer, radiation, electrochemistry, solid stress, laminar, and turbulent flow motion can be successfully verified and solved using CFD methods.

Two modelling approaches are involved to simulate hydrogen recombination reactions. The single-step approximation is based on the transformation of stable reactants into stable products of the chemical reaction. This approach does not consider any of the intermediate reactions and their products that affect the course of the chemical reaction. The single-step reaction is as follows:



As it is generally known, the rate equation of a single-step reaction is obtained from a detailed study of mechanism and kinetics, with reasonable simplifications. Schefer introduced a kinetic model that describes the reaction rate as follows (Schefer *et al.*, 1980; Schefer, 1982):

$$k = 14 \times \exp\left(-\frac{16.1 \times 10^6}{R_u \times T}\right) \times C[H_2] \quad 2-2$$

Equation (2) is an Arrhenius equation with empirical parameters, determined by Schefer from experiments performed with hydrogen concentrations varying from 7% to 20% and at temperatures ranging from 450 K to 1200 K, at atmospheric pressure. The pre-exponential factor here is proportional to the hydrogen concentration.

In practice, the autocatalytic hydrogen recombination process is a multi-stage process. The detailed chemical mechanism may contain different numbers of reactions, depending on the purpose of the study. As mentioned earlier, the rate of a heterogeneous chemical reaction is determined by two processes: by the real kinetics of chemical reaction on a surface and by convective diffusion. The regions of the chemical reactions that correspond to these two processes are the so-called kinetic and diffusion regions, respectively. Equation (2) is obtained in the statement of a recombination reaction that takes place in the diffusion region—where the speed of supply of the reactants to the surface determines the rate of the entire heterogeneous chemical process. However, Schefer's reaction rate equation (2) does not determine the speed of supply of the reactants to the catalyst surface, it only determines the possible rate of recombination reaction at given concentrations of reacting components and temperature.

In the detailed study of the hydrogen recombination processes, it is necessary to take into account physicochemical processes occurring both on the surface of the catalyst (a surface chemical mechanism) and in the gas volume (a gas-phase chemical mechanism) (Appel *et al.*, 2002). A model of a detailed chemical kinetic mechanism, which includes surface and gas-phase chemistry, was introduced by several authors (Ljungström *et al.*, 1989; Deutschmann *et al.*, 1996; Rinnemo *et al.*, 1997; Mueller *et al.*, 1999). The results that the authors obtained for temperature evaluation and reaction species transport were in good agreement with experimental results. The surface chemical mechanism is summarized in Table 2-2.

Table 2-2: Mechanism of surface chemistry.

	Reaction	pre-exponential factor, A (cm ³ mol s)	activation energy, E _A (J/kmol)	sticking coefficient (s)
1	$H_2 + 2Pt^{(s)} \rightarrow 2H^{(s)}$	4.4579×10^{10}	0.0	0.046
2	$2H^{(s)} \rightarrow H_2 + 2Pt^{(s)}$	3.7000×10^{21}	6.740×10^7	0.0
3	$O_2 + 2Pt^{(s)} \rightarrow 2O^{(s)}$	1.8000×10^{21}	0.0	0.023
4	$O_2 + 2Pt^{(s)} \rightarrow 2O^{(s)}$	0.023	0.0	0.070
5	$2O^{(s)} \rightarrow O_2 + 2Pt^{(s)}$	3.7000×10^{21}	2.132×10^8	0.0
6	$H_2O + Pt^{(s)} \rightarrow H_2O^{(s)}$	0.750	0.0	0.750
7	$H_2O^{(s)} \rightarrow H_2O + Pt^{(s)}$	1.0000×10^{13}	4.030×10^7	0.0
8	$OH + Pt^{(s)} \rightarrow OH^{(s)}$	1.0	0.0	1.0
9	$OH^{(s)} \rightarrow OH + Pt^{(s)}$	1.0000×10^{13}	1.928×10^8	0.0
10	$H^{(s)} + O^{(s)} = OH^{(s)} + Pt^{(s)}$	3.7000×10^{21}	1.150×10^7	0.0
11	$H^{(s)} + OH^{(s)} = H_2O^{(s)} + Pt^{(s)}$	3.7000×10^{21}	1.750×10^7	0.0
12	$OH^{(s)} + OH^{(s)} \rightarrow H_2O^{(s)} + O^{(s)}$	3.7000×10^{21}	4.820×10^7	0.0

The surface chemical mechanism described in Table 2-2 consists of 12 reactions, providing the absorption–desorption reactions of the gas species on the catalyst surface and various surface reactions. The surface reactions in Table 2-2 include the so-called intermediate reactions and their products that influence the course of a chemical reaction, as mentioned earlier. The rate of adsorption of gas species through the catalyst surface is determined by the probability of collisions

of the gas molecules with a particle on a surface. This probability is generally referred to as the sticking coefficient. The sticking coefficient is a function of surface temperature, the fractional site coverage and the structural details of a surface (Zhang *et al.*, 2020). There is yet another important parameter that must be noted, the surface site density. The site density represents the number of available sites per unit area of the catalyst material. The supported catalyst is simulated by a platinum layer with the surface site density taken as $S_0 = 2.7 \times 10^{-8} \text{ kmol/m}^2$. This value was estimated from the density of platinum (Deutschmann *et al.*, 1994; West, 1987).

Table 2-3: Mechanism of gas-phase chemistry.

	Reaction	pre-exponential factor, A (cm ³ mol s)	activation energy, E _A (J/kmol)	temperature coefficient (β)
1	$H + O_2 = O + OH$	1.915×10^{14}	6.8784960×10^7	0.0–0.39
2	$O + H_2 = H + OH$	5.080×10^4	2.6325728×10^7	2.67–2.65
3	$OH + H_2 = H + H_2O$	2.160×10^8	1.4351120×10^7	1.51–1.40
4	$O + H_2O = OH + OH$	2.970×10^6	5.606560×10^7	2.02–2.11
5	$H_2 + M = H + H + M$	4.577×10^{19}	4.368096×10^8	-1.40–(-1.68)
6	$O_2 + M = O + O + M$	4.515×10^{17}	4.974776×10^8	-0.64–(-0.50)
7	$OH + M = O + H + M$	9.880×10^{17}	4.271864×10^8	-0.74–(-1.00)
8	$H_2O + M = H + OH + M$	1.912×10^{23}	4.958040×10^8	-1.83–(-2.00)
9	$H + O_2 (+M) = HO_2 + M$	3.482×10^{16}	-4.665160×10^6	-0.411
10	$HO_2 + H = H_2 + O_2$	1.660×10^{13}	3.443432×10^6	0.0–0.35
11	$HO_2 + H = OH + OH$	7.079×10^{13}	1.234280×10^6	0.0–0.72
12	$HO_2 + O = OH + O_2$	3.250×10^{13}	0.0	0.0–0.33
13	$HO_2 + OH = H_2O + O_2$	2.890×10^{13}	-2.079448×10^6	0.0–0.24
14	$H_2O_2 + O_2 = HO_2 + HO_2$	4.634×10^{16}	2.1200328×10^8	-0.35–0.0
15	$H_2O_2 + O_2 = HO_2 + HO_2$ (2)	1.434×10^{13}	1.5505904×10^8	-0.35–0.0
16	$H_2O_2 + M = OH + OH (+M)$	1.202×10^{17}	1.9037200×10^8	0.0
17	$H_2O_2 + H = H_2O + OH$	2.410×10^{13}	1.6610480×10^7	0.0
18	$H_2O_2 + H = H_2 + HO_2$	6.025×10^{13}	3.3262800×10^7	0.0–0.70
19	$H_2O_2 + O = OH + HO_2$	9.550×10^6	1.6610480×10^7	2.00–2.68
20	$H_2O_2 + OH = H_2O + HO_2$	1.000×10^{12}	0.0	0.0–0.59
21	$H_2O_2 + OH = H_2O + HO_2$ (2)	5.800×10^{14}	3.9986488×10^7	0.0–0.59

Third body efficiency coeff. (M) for R₅: H₂=2.5; H₂O=12.0.

Third body efficiency coeff. (M) for R₆: H₂=2.5; H₂O=12.0.

Third body efficiency coeff. (M) for R₇: H₂=2.5; H₂O=12.0.

Third body efficiency coeff. (M) for R₈: H₂=0.73; H₂O=12.0.

Third body efficiency coeff. (M) for R₉: H₂=1.3; H₂O=14.0.

Third body efficiency coeff. (M) for R₁₆: H₂=2.5; H₂O=12.0.

Appel *et al.* carried out computations using a two-dimensional numerical model that included a conjugated approach with gas-phase reactions (homogeneous) and surface chemical reaction (heterogeneous) mechanisms (Appel *et al.*, 2002). The authors also tested four homogeneous and three heterogeneous reaction mechanisms in the model against experimental homogeneous ignition characteristics; they reported better agreement to the experimental measurements for the surface mechanism of Deutschmann *et al.*, (1996) and the gas-phase mechanism of Warnatz *et al.*, (1990). Table 2-3 summarizes the gas-phase chemical mechanism.

This mechanism of gas-phase chemical kinetics has been compared against a wide range of experiments and validated using several numerical codes, such as SENKIN (Lutz *et al.*, 1987), PREMIX (Kee *et al.*, 1985), CHEMKIN (Kee, *et al.*, 1986) and SPARK (Meynet, 2012). Based on previous studies, the reaction rate coefficient can be calculated by the following equation:

$$k = A \exp\left(\frac{-E_A}{R_u T}\right) = A' T^\beta \exp\left(\frac{-E_A}{R_u T}\right) \quad 2-3$$

where, A is the pre-exponential factor and E_a is the activation energy. The pre-exponential factor, for some of the reactions (see Table 2-3), depends on temperature, leading to an additional factor in Equation (3); this factor is denoted as temperature exponent β .

The gas-phase mechanism described in Table 2-3 consists of 21 reversible elementary reactions among 9 species. Reverse reaction rates are determined from thermochemistry. Thermochemical properties were taken from the CHEMKIN thermodynamic database (Lutz *et al.*, 1988). The thermodynamic properties are fitted with a seven-coefficient polynomial (Gordon and McBride, 1971).

2.4 Conclusions

The literature review clearly reveals that the importance of the hydrogen industry has grown significantly over the past twenty years. HFC technology has been identified as one of the most prospective technologies—it will surely go a long way to reducing carbon emissions. However, from the available literature, several gaps were identified in terms of mitigation strategies for hydrogen safety. Considering the potential risk of unintended hydrogen release, the literature identifies two acceptable safety technologies that can be employed to prevent the dispersion of leaking hydrogen, and the formation of flammable mixtures of hydrogen with air: FV systems and PARs.

The ventilation system can promote flow circulation, thus mixing the hydrogen with air to below the flammability limit and hence avoiding the formation of stratification concentrations. An

adequate ventilation system is able to provide safety conditions and significantly reduce severe consequences of the hydrogen release. It has been identified that a minimum ventilation rate has to be sufficient to mix up a potential hydrogen leak up to 25% of the LFL ($< 1 \text{ vol } \% \text{ H}_2$) for all possible accident scenarios. However, the detailed behavior of horizontally directed hydrogen leaks at low- and high pressures requires further investigation. Also, not much attention has been given to investigate the dilution effect of ventilation systems in terms of horizontally directed hydrogen release into a confined environment.

Another technology, based on the autocatalytic recombination reaction, is widely recognized in the nuclear industry to mitigate unintended hydrogen releases. The catalytic element plays a significant role in a PAR operation. Revised relevant literature is identified that the plate-type catalyst has been broadly investigated in terms of various initial parameters. In this concern, to fulfil the scientific database of PAR research, the cylindrical-type PAR Pt catalyst needs to be investigated in terms of the temperature distribution, hydrogen recombination/conversion efficiency, and any other effects of mass and energy transport during PAR operation.

In efforts to elaborate these two technologies, the CFD simulations can offer a number of advantages in terms of examining the parameters of a simulated phenomenon by assessing variables that cannot be accurately measured experimentally. The STAR-CCM+ software package, utilizing the CFD approach, can be extremely useful to investigate technologies for hydrogen safety. Many benefits of the numerical approach have been identified in the literature. Early literature indicates that only one- and two-dimensional numerical models have been utilized to simulate the chemical mechanism of hydrogen autocatalytic recombination. Furthermore, the multi-step mechanism of hydrogen recombination on a Pt catalyst still remains to be validated, especially in terms of three-dimension simulations.

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CHAPTER 3: CFD SIMULATION AND EXPERIMENTAL STUDY OF A HYDROGEN LEAK IN A SEMI-CLOSED SPACE WITH THE PURPOSE OF RISK MITIGATION

The research described in Chapter 3 has been conducted by the author in an attempt to answer the scientific question that was defined in objective II, “To analyse the hydrogen distribution under a leakage accident in a confined space, with regards to the size of the leaking orifice and the hydrogen release pressure, and then to characterize the efficiency of forced and natural ventilation on hydrogen mitigation by performing full-scale tests in the experimental facility and validate results through the CFD simulations”.

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OVERVIEW

Computational fluid dynamics (CFD) methods were used to analyze hydrogen leakage in a semi-closed ventilation facility. The goal of the research was to apply numerical simulations to verify hydrogen distribution in the semi-closed space using the commercial STAR-CCM+ code and to compare the simulation results with experimental results. Experiments were conducted in a container with the dimensions 12.11 m × 2.39 m × 2.34 m. The experimental facility represents part of an underground mining tunnel. In the study, different combinations of hydrogen release pressure and leak orifice size were considered. The efficiency of forced ventilation (FV) in semi-closed spaces was also investigated. The hydrogen distribution in the ventilation facility was studied through experimental investigation and confirmed by CFD simulation. Our numerical results could be useful in the analysis of safety issues in semi-closed ventilation facilities, such as in mining tunnels.

3.1 Introduction

Safety is widely recognized as one of the most important issues facing the furtherance of hydrogen use. The importance of developing mitigation strategies for hydrogen safety has increased significantly in recent years (Molkov, 2007).

Hydrogen is considered as one of the leading fuels for a future renewable and environment friendly energy carrier (Züttel *et al.*, 2010; Bentaib, Meynet and Bleyer, 2015; Petrosyan *et al.*, 2018). However, the high-pressure storage and use of hydrogen pose unique challenges due to its ease of leakage, low-energy ignition, high buoyancy and diffusion rate in air, and a wide range of combustible fuel–air mixtures (Markert *et al.*, 2007). The ignition volume fraction range for hydrogen is 4–74% in air at atmospheric pressure (Alcock, *et al.*, 2001; Cengel and Boles, 2015). The explosion volume fraction range is 18–59% and the minimum ignition energy is 0.02mJ (Isuru, *et al.*, 2009). The risks associated with hydrogen leakage in partially enclosed spaces depends on both the total volume of the released hydrogen and the pressure at which hydrogen is being released. Hence, the performance of an emergency hydrogen removal systems has to be accurately predicted in order to ensure that the hydrogen concentration remains below the lower flammability limit of hydrogen in air.

The release and accumulation of hydrogen in semi-closed spaces is potentially dangerous. Hydrogen dispersion in a semi-closed space with one open boundary, with uniform or nonuniform concentration distribution of the hydrogen, depends on the conditions of release, such as the hydrogen pressure, leak size, direction of release, and the enclosure parameters such as its volume and vent sizes. After release, the hydrogen moves rapidly upwards, i.e., to above the leakage point. This is due to the large difference between the density of hydrogen and air.

Research into leaking hydrogen is important for preventing accidental ignition and setting safety requirements for any leakage due to incomplete sealing, system degradation, or human error. Therefore, in efforts to ensure the safe use of hydrogen, the development of risk management strategies for hydrogen leakage and dispersion is essential (Middha and Hansen, 2009). There is a wealth of research that has focused on understanding the process of leakage, dispersion, and subsequent deflagration of hydrogen. This includes research into transient dispersion in a vertical cylinder (Vudumu and Koylu, 2009); hydrogen leakage into complex-shaped spaces, such as around the hydrogen tank of a fuel cell (FC) electric vehicle (Matsumoto and Shimizu, 2011); and dispersion and ventilation in a garage (Barley and Gawlik, 2009; Papanikolaou *et al.*, 2010), or a household room (Lowesmith *et al.*, 2009). The ability to predict all the physical phenomena that may occur following an accidental hydrogen release is mandatory for future safety studies on an industrial or urban scale (Jakel, *et al.*, 2014). The use of hydrogen as a fuel inevitably results in risks to the public, as is the case for the use of any combustible materials. Generic accident scenarios in semi-closed spaces, such as in underground private garages, were investigated in the works Gupta *et al.* (Gupta *et al.*, 2009) and Choi *et al.* (Choi *et al.*, 2013).

The mining sector is an energy-intensive industry. In its efforts to control costs, one of the priorities of mining companies is energy reduction. Another important priority is, of course, to reduce employees' risk in underground mines. Machines that are used by the mining industry run on diesel fuel. The World Health Organization classifies diesel engine exhaust as “carcinogenic to humans”, based on sufficient evidence to suggest that it is associated with an increased risk of lung cancer and related diseases (Iordache, 2016).

Fuel cells, using hydrogen, offer significant advantages in reducing carbon emissions generated by transportation systems and they have higher efficiency compared with traditional fossil fuels (St-pierre, Wilkinson and Systems, 2001; Momirlan and Veziroglu, 2005). However, the safety requirements for hydrogen systems are different to the requirements for traditional fuel. The hydrogen–air mixture is rather explosive. Safe handling requires exclusion of detonation and deflagration, which may occur at very low hydrogen concentrations, at ~4%. The gradual replacement of diesel vehicles with hydrogen FC vehicles will not only help to make the mining industry cleaner, but could also reduce the cost of diesel fuel.

Some work has been carried out to analyze hydrogen release in tunnels (Molkov, *et al.*, 2008; Bie and Hao, 2017). However, there is currently insufficient guidelines to mitigate the risk of such scenarios for underground tunnels. One key component of the emergency hydrogen removal system is a FV system (Matsuura, *et al.*, 2010). Nuclear power plants (NPPs) with pressurized water reactors are fitted with an emergency hydrogen removal system, which is a passive autocatalytic hydrogen recombiner (PAR) (Reinecke *et al.*, 2013; Agrawal, *et al.*, 2017). Similar principals that apply to modelling hydrogen removal in NPPs can be used to mitigate hydrogen safety in ventilation tunnels in the mining environment and the ventilation for hydrogen FC vehicles in residential garages (Baggemann *et al.*, 2017). FV can promote the removal of hydrogen from a room and PARs can prevent the formation of explosive mixtures in the accident localization zone.

Hence, related to this, there is an urgent need to construct and study numerical models of hydrogen distribution processes in enclosed and semi-closed spaces. Hydrogen release and subsequent dispersion can be investigated using commercially available computational fluid dynamics (CFD) software (Papanikolaou *et al.*, 2011; Dieguez *et al.*, 2013; He *et al.*, 2016). A simulation using CFD techniques can provide detailed data such as the concentration of hydrogen, the flammable region, the spatial dispersion, etc. CFD is increasingly used to perform safety analyses of potential accident scenarios related to the production, storage, and distribution of hydrogen and its use in FCs.

3.2 Experimental facility

The experimental facility used in this study represents a part of an underground mining tunnel. Large-scale experiments on hydrogen–air distribution were performed in a standard sized container: length 12.11 m, height 2.39 m, width 2.34 m; total inside volume $\sim 67.7 \text{ m}^3$. See Fig. 3-1.



Figure 3-1: Experimental facility, showing the open boundary, including the fan and ventilation tube (HySA Mining Platform Test Facility for Green Mining).

The geometry of the facility has one completely open side, i.e., it is open to the atmosphere. Hydrogen escapes the enclosure at this open boundary. The inner diameter of the ventilation tube is 0.6 m. The cross-sectional area of the ventilation tube is 1.13 m^2 . The axis of the ventilation tube is shifted toward the side wall by 0.71 m relative to the middle of the container. The axis of the ventilation tube is located at a height of 2.17 m above the floor, leave 0.22 m space between the upper part of the ventilation tube and the ceiling. The ducting is constructed of high strength material, able to withstand stresses caused by high flow rates that the ventilation fan produces. Fig. 3-2 shows a schematic diagram of the ventilation facility.

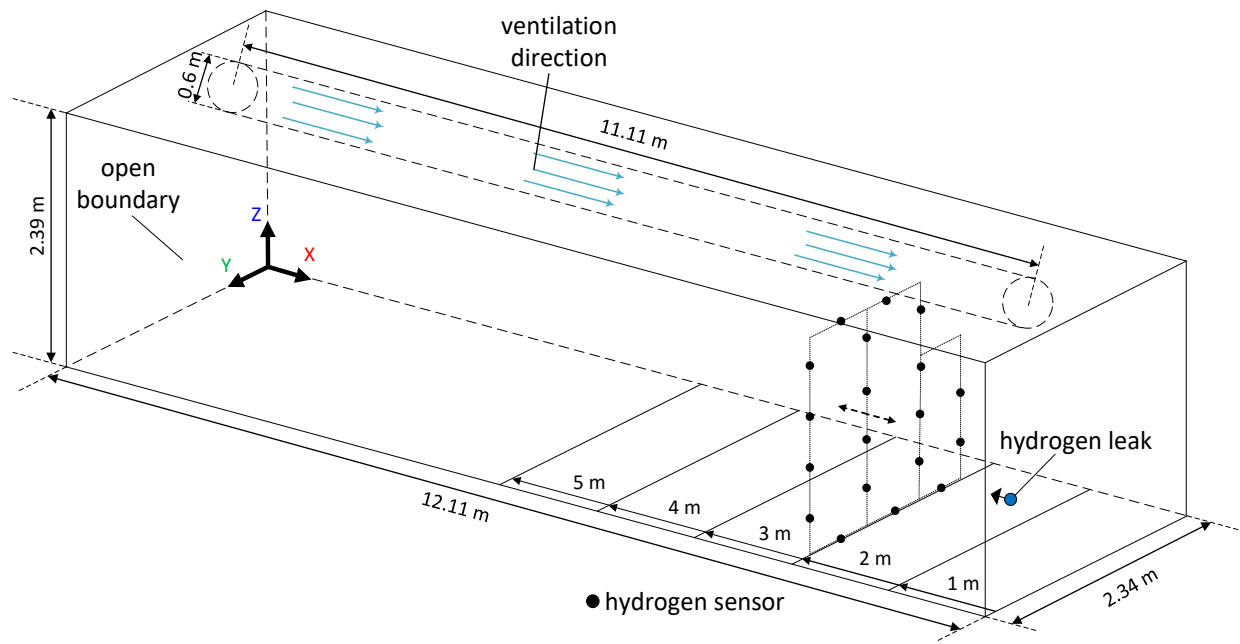


Figure 3-2: Schematic diagram of ventilation facility with the matrix of hydrogen sensors and position of hydrogen leakage.

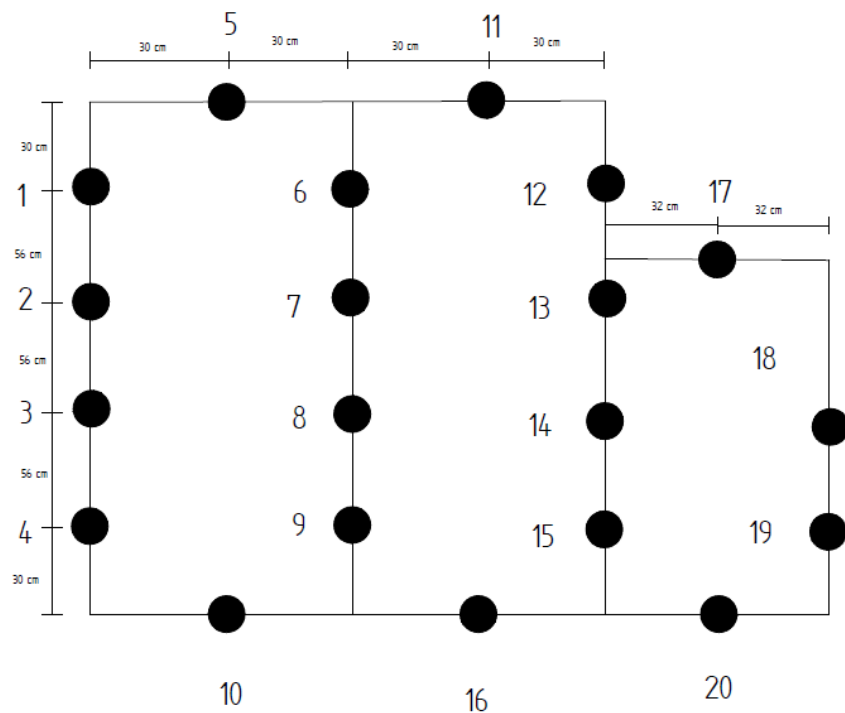


Figure 3-3: Positions of sensors: layout and numbering.

The fan blows air into the facility. The air–hydrogen mixture leaves the facility through the open boundary. An air fan is used to maintain a constant ventilation flow rate inside the container. LabVIEW software was used to collect and measure the experiments data. A National Instruments (NI) cRIO-9024 controller is used to control all the equipment used in experiments. The NI cRIO-9024 uses two NI-9205 voltage modules to read the Neodym ProtiSen hydrogen sensors. The Hanbay valve, which is used to open the hydrogen gas line, is controlled with the NI-9265 voltage module. The RPM value of the WEG CFW-11 frequency inverter, which is used to control the fan, is controlled by the NI-9203 current module. The design of the blade is an aerofoil section. The aerofoil section blade and hub design of the fan are constructed from a composite material, glass reinforced plastic. The ventilation fan is rated at 55 kW and can operate over a wide range of flow rates due to the implementation of a variable speed drive up to 1450 rpm. In this study, a drive speed of 500 rpm was used; it corresponds to 6.5 m/s ventilation flow rate at the outlet of the tube. The ventilation flow rate was estimated by the vane anemometer. All of the above components are integrated into a system used to simulate underground mining conditions.

The source of pure hydrogen is located in the front wall of the container at a distance of 1.02 m from the floor and 0.33 m from the side wall. The test parameters are shown in Table 3-1.

Table 3-1: Test parameters for different experiments.

H ₂ source orifice size, mm		Inlet H ₂ pressure, bar
Ventilation flow rate 6.5 m/s		
Run no.		
1	0.8	20
2	4.572	2
3	4.572	5
No ventilation		
4	0.8	20
5	4.572	2

The hydrogen supply consists of 10 cylinders, each pressurized to 200 bar. Each experiment was conducted for at least 300 s to reach a steady state of the distribution of hydrogen inside the facility. To determine the hydrogen concentration inside the ventilation facility, we used a matrix of sensors.

The sensors were fixed on a special frame (Fig. 3-2 and 3-3). The width of the sensors matrix is 184 cm, which leaves 25 cm to each wall (Fig. 3-3). Concentration measurements were carried out by moving the frame with the sensors (Fig. 3-3) to different distances from the point of

hydrogen leakage: 1, 2, 3, and 4 m away. The sensors matrix is centered between walls and is 15 cm above the floor. Respectively, the sensor number 3 is located at a distance of 101 cm from the floor and 0.25 m from the side wall. The hydrogen leak is located in the front wall of the container at a distance of 1.02 m from the floor and 0.33 m from the side wall. In each test, the sensor matrix moved in such a way that the hydrogen jet was approximately in the same position.

3.3 CFD modelling

The CFD code STAR-CCM+ (CD-adapco, 2017) was used as the numerical tool for the simulations. STAR-CCM+ provides an engineering process for solving problems involving flow (of fluids and solids), heat transfer, and stress. It has been validated that such codes are quite applicable to hydrogen safety issues in the cases where leakage and dispersion, or hydrogen erosion of stratified layers by a buoyant jet, are involved (Choi *et al.*, 2013). The simulations were performed using a workstation HP Z840 containing 20 Intel Xeon 2.4 GHz 64-bit CPUs.

A brief outline of the main areas of concern associated with this test setup is now presented, as well as some CFD calculations that serve as a guideline on what hydrogen concentrations can be expected at certain distances when conducting the tests.

3.3.1 Conversation equations

The mathematical models that describe the physics of continua are derived from fundamental laws that express conservation principles. The fundamental laws that govern the mechanics of fluids and solids are the conservation of mass, angular momentum, linear momentum and energy (CD-adapco, 2017).

Equation 1 presents the conservation of mass

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \quad 3-1$$

where ρ is the density (the mass per unit volume), and $\mathbf{v}$ is the continuum velocity.

Equation 2 presents the conservation of momentum

$$\frac{\partial (\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) = \nabla \cdot \boldsymbol{\sigma} + \mathbf{f}_b, \quad 3-2$$

where $\otimes$ denotes the Kronecker product, $\mathbf{f}_b$ is the resultant of the body forces (such as gravity and centrifugal forces) per unit volume acting on the continuum, and $\boldsymbol{\sigma}$ is the stress tensor.

Equation 3 presents the conservation of energy

$$\frac{\partial(\rho E)}{\partial t} + \nabla \cdot (\rho E \mathbf{v}) = f_b \cdot \mathbf{v} + \nabla \cdot (\mathbf{v} \cdot \boldsymbol{\sigma}) - \nabla \cdot \mathbf{q} + S_E, \quad 3-3$$

where E is the total energy per unit mass, q is the heat flux, and S_E is an energy source per unit volume.

3.3.2 Turbulence model

The turbulence model is used to predict the turbulence in the flow. The turbulence model is a two-equation model that solves transport equations for the turbulent kinetic energy and the turbulent dissipation rate in order to determine the turbulent eddy viscosity. Various forms of the model have been used for a number of decades and it has become the most widely used model for industrial applications (Shih *et al.*, 1995; Giannissi *et al.*, 2015; Zhang *et al.*, 2015). In this paper, use is made of one of the forms of the k- ϵ (k-epsilon) model, a realizable k-epsilon model with a two-layer approach (Rodi, 1991). The coefficients in the models are identical, but the model gains the added flexibility of an all $-Y^+$ wall treatment.

3.3.3 Numerical details and validation of the model

The geometry was created by means of the 3D-CAD tool integrated in STAR-CCM+. The computational domain has the same size as the actual experiment facility (12.11 m $\times$ 2.34 m, height 2.39 m), including the ventilation tube (Fig. 3-2). The governing equations are the continuity equation, the compressible Navier–Stokes equations with gravitational force, the energy equation, and the transport equation for the mass fraction of hydrogen. The perfect gas equation is used here. The flow is nonreacting and has only two gas components: hydrogen and air. Gas properties for air and hydrogen were taken from the STAR-CCM+ database. The inlet of hydrogen at the leak point is a stagnation inlet boundary and the outlet of the air–hydrogen mixture from the facility through the open boundary is the pressure outlet. To simulate a constant air flow through the ventilation tube, this boundary was defined as a velocity inlet. It was assumed that the walls have a high heat capacity and thus remain at an initial temperature of 300 K. The initial environmental pressure is the standard atmospheric pressure. The hydrogen release pressure is identical to the experimentally analyzed cases (see Table 3-1). A tetrahedral mesh with a cell base size of 0.06 m was used for calculations of the facility (total number of cells $\sim$ 3 million). See Fig. 3-4.

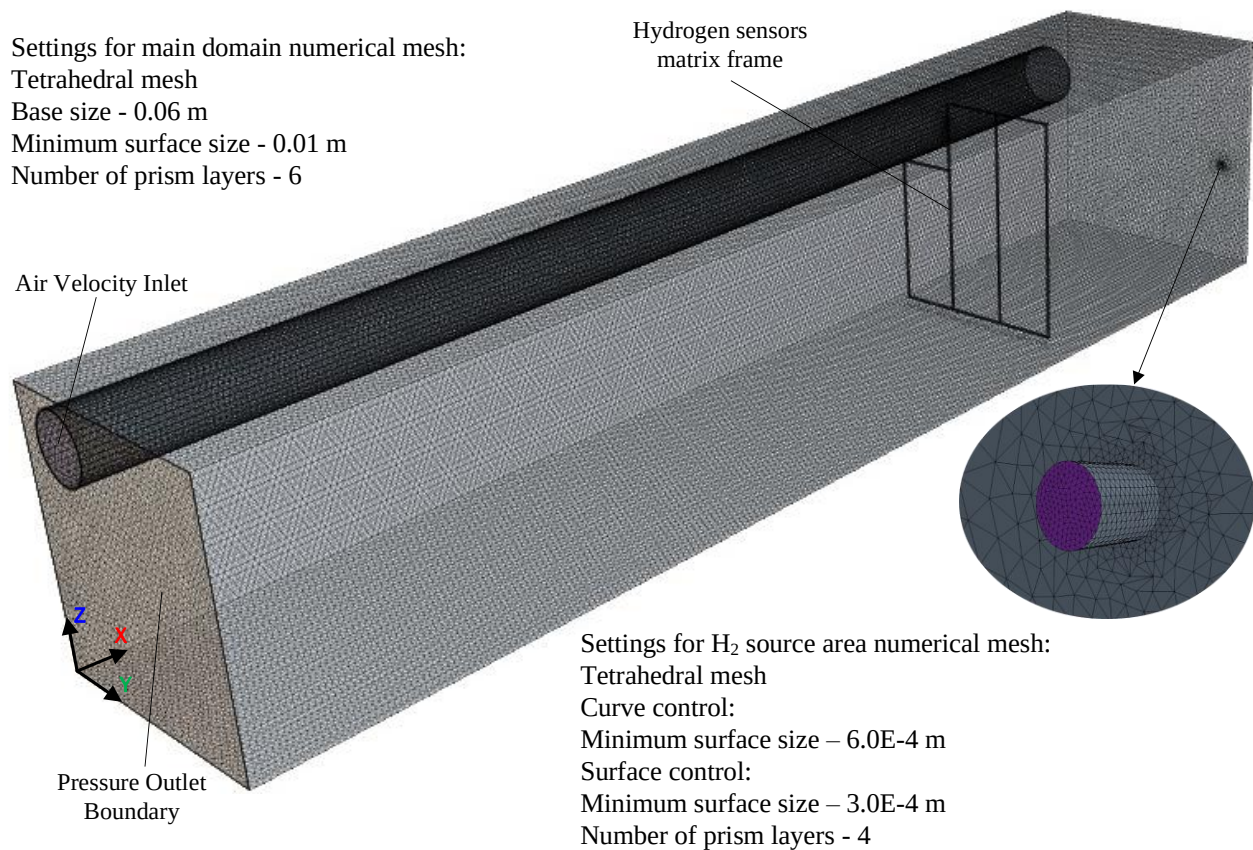


Figure 3-4: General view of numerical mesh and refinement of hydrogen source area with settings.

The numerical grid verification procedure has been done for the developed CFD model. Two grid settings were designed to improve simulations accuracy. The numerical domain contains tetrahedral cells with a base size of 0.05 m and 0.06 m (total amount of cells ~ 3,7 million and ~ 3 million respectively) were designed to estimate the accuracy and CPU time cost. Moreover, the latest numerical domain included grid refinement around the hydrogen leak position. Taking into account the small size of the hydrogen source compared to the main domain volume, in an effort to preserve the cylindrical shape of the source the numerical mesh in this area was refined by surface control and curve control. This means that the cell size in the hydrogen source area was set to 0.5% of the base cell size for the surface control and 1% for the curve control. For a more accurate solution, six near-wall flow prism layers were also generated in the numerical mesh. During the grid independence verification, it was observed that the later designed numerical domain with a grid base size of 0.06 m and applied refinements shows appropriate accuracy. Meanwhile, a smaller base size grid without refinements did not have enough simulation accuracy and convergence, even the CPU time was increased. Calculations were done for the sets of parameters as denoted in Table 3-1. The steady-state model is used for all calculations in this

study. When the residual value tends to be stable and $<1 \times 10^{-5}$, the result is considered to be converged.

3.4 Results and discussion

A comparison of the experimental and computational results is now presented. The main idea was to compare the distribution of hydrogen from a small leakage in the container both with and without ventilation. We used only one small hole as a source of hydrogen in order to verify our numerical procedure on rather sensitive experimental data.

After the leakage occurs, a quite intense buoyancy jet is formed, where the hydrogen concentration decreases as the distance from the leakage point increases. The jet mostly has direction to the sensor number 3 and is rather far from sensor number 8. The volume concentration distributions of hydrogen along the length of the container are shown in Figs 3-5–3-12.

Figs 3-5 and 3-6 show a comparison of the experimental and numerical results for the case with a small-size orifice of 0.8 mm and a rather large inlet pressure to release hydrogen (20 bar), for both with and without air ventilation. The experimental and numerical results agree within 20% at a maximum discrepancy and demonstrate that the hydrogen leakage is already quite harmless after 2 m from the wall, as the highest concentration (~4%) is shown by sensor number 3. Another interesting feature is that at such a high inlet pressure the ventilation does not play any role in the overall hydrogen distribution; the dangerous flammable locations are near the orifice only (see Fig. 3-6), around the narrow hydrogen jet up to 2 m from the wall. Both experiments and calculations show that hydrogen at such a low concentration diffuses more or less homogeneously at least up to a distance of 3 m from the wall. It is rather difficult to see the stratification, but it occurs beyond 3 m. This will be checked in future work.

On the other hand, the behavior of the hydrogen distribution for a larger orifice and a smaller inlet pressure (see Figs 3-8 and 3-9) is quite different. With a working ventilation, there still is a narrow hydrogen jet close to sensor number 3, while the distribution is quite homogenous beyond this sensor. Moving away from the leak the jet is dispersed and therefore the concentration peak at sensor number 3 begins to decrease. This is caused by the mixing due to ventilation.

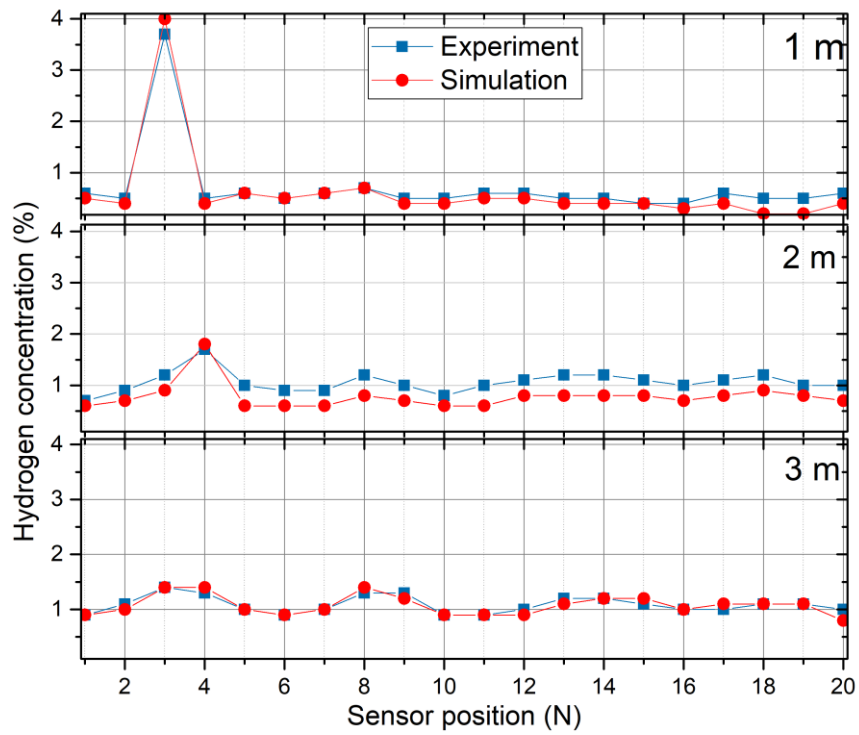


Figure 3-5: The hydrogen concentration for each of the 20 sensors along the length of the container from the leakage at (1, 2, and 3 m, respectively) for run no. 1 (see Table 3-1).

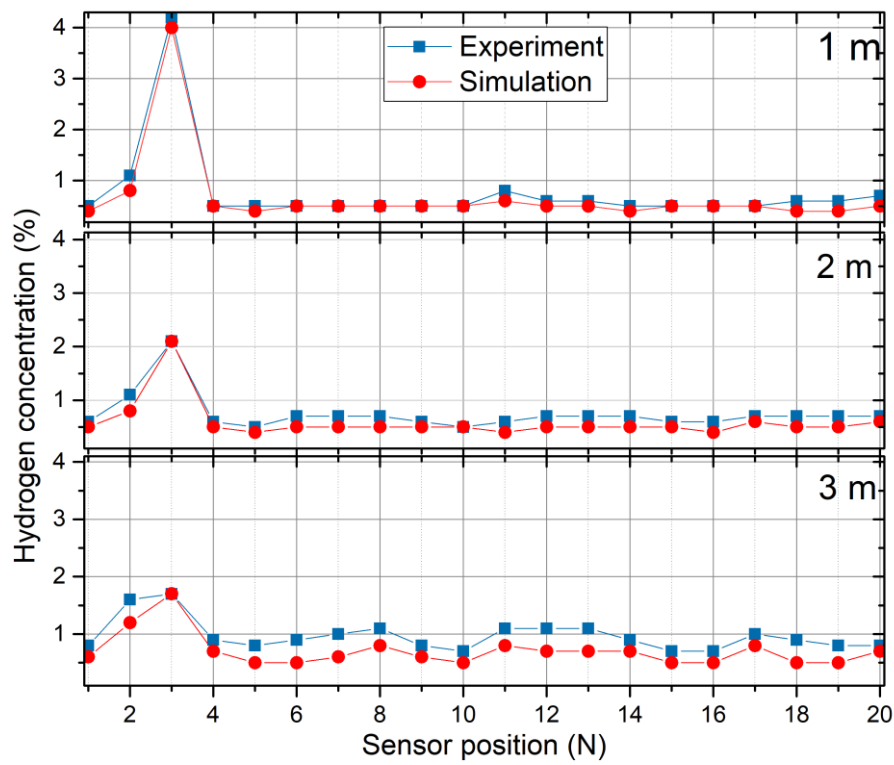


Figure 3-6: The hydrogen concentration for each of the 20 sensors along the length of the container from the leakage at (1, 2, and 3 m, respectively) for run no. 4 (see Table 3-1).

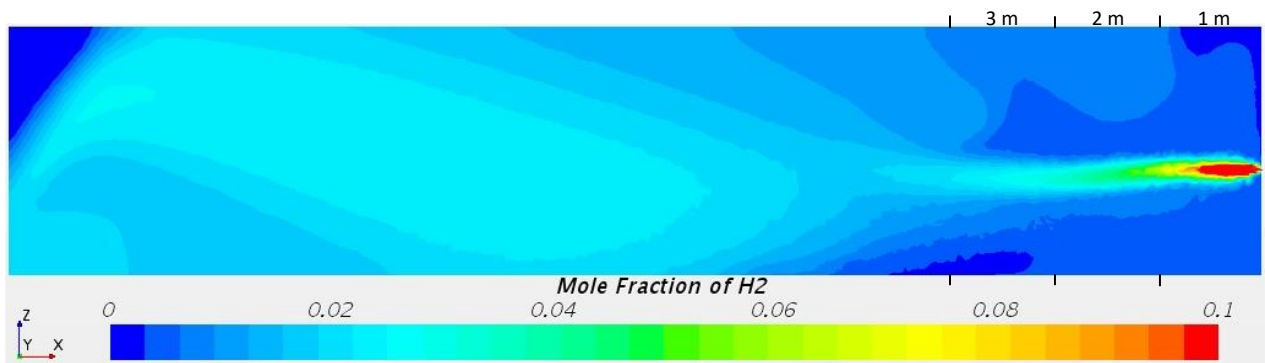


Figure 3-7: The cross-section of the hydrogen distribution for run no. 1 (see Table 3-1) at a leak point in the Y direction.

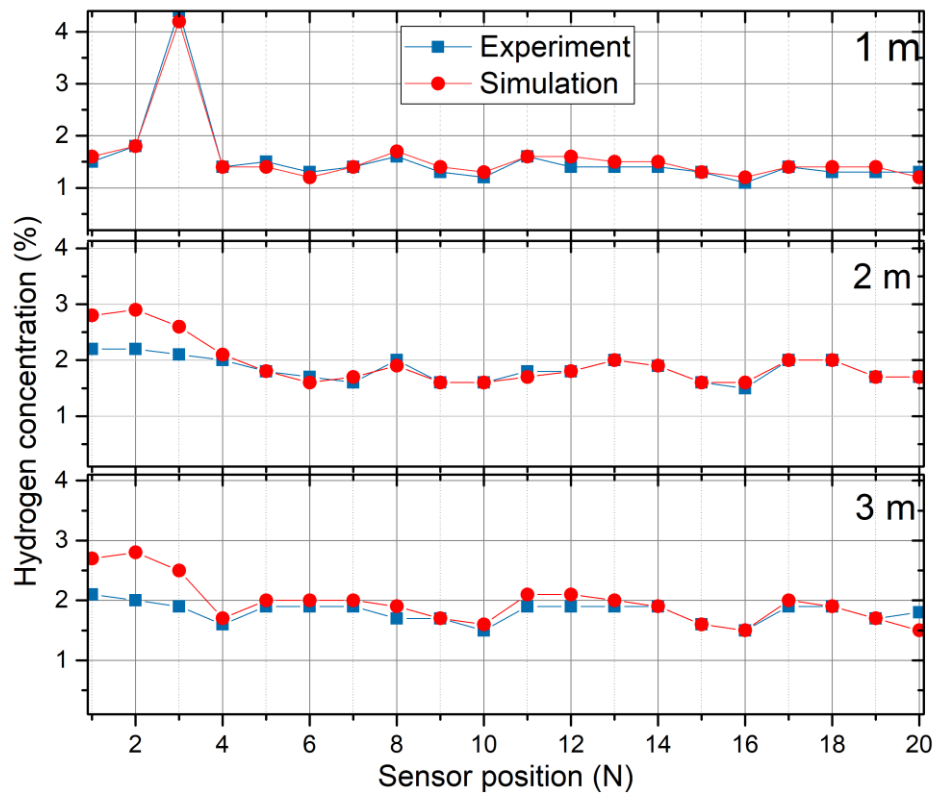


Figure 3-8: The hydrogen concentration for each of the 20 sensors along the length of the container from the leakage at (1, 2, and 3 m, respectively) for run no. 2 (see Table 3-1).

Without ventilation, the hydrogen jet flows upwards (Fig. 3-11) and is stratified, as the upper sensors (P5, 6, 11, 12, 17) show a higher hydrogen concentration compared to in the case of ventilation (Fig. 3-10). Comparing hydrogen distribution for runs no 2 and no 5 one can see the quite expectable result that ventilation is working and provides less hydrogen concentration in the container. Furthermore, the average hydrogen concentration is slightly lower with the working ventilation at least up to 4 m from the wall with the hydrogen source. The flammable concentrations appear within a narrow range along the hydrogen jet, extending up to 5 m (almost half of the container) in the case of no ventilation (Fig. 3-11). It is almost twice as long as in the case of the working ventilation. The concentration in the middle of the jet is also higher for the case with no ventilation.

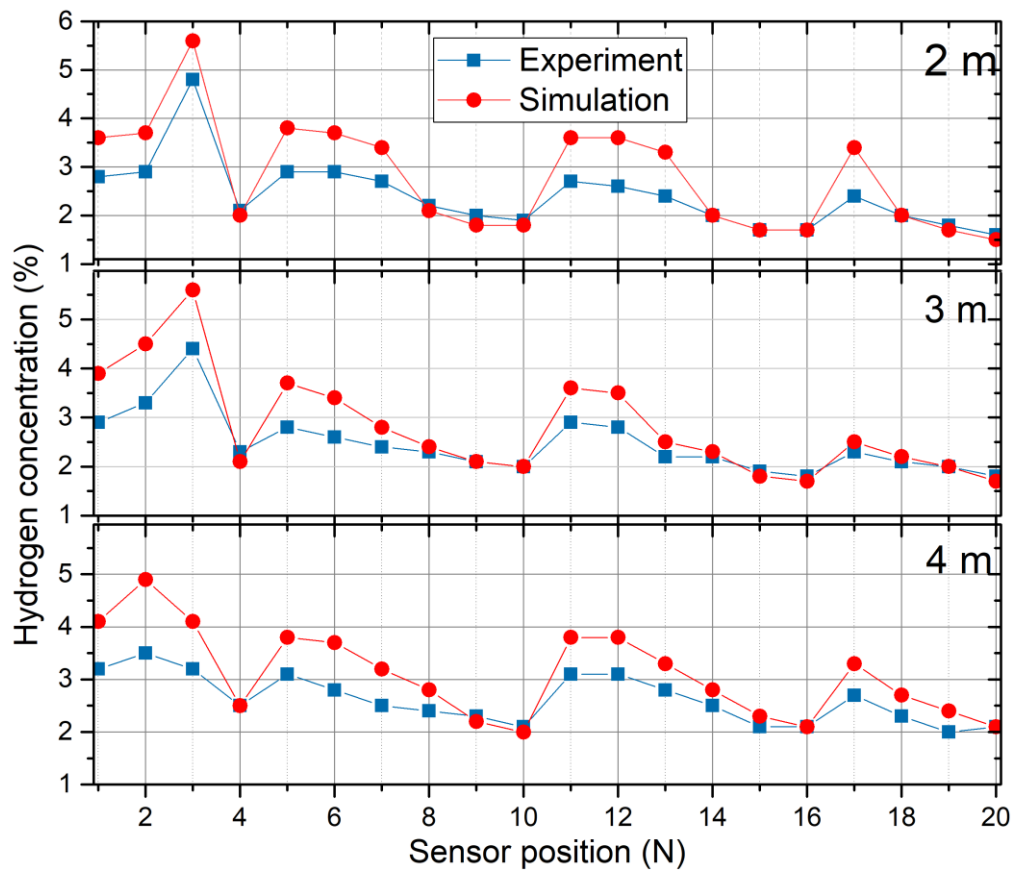


Figure 3-9: The hydrogen concentration for each of the 20 sensors along the length of the container from the leakage at (2, 3, and 4 m, respectively) for run no. 5 (see Table 3-1).

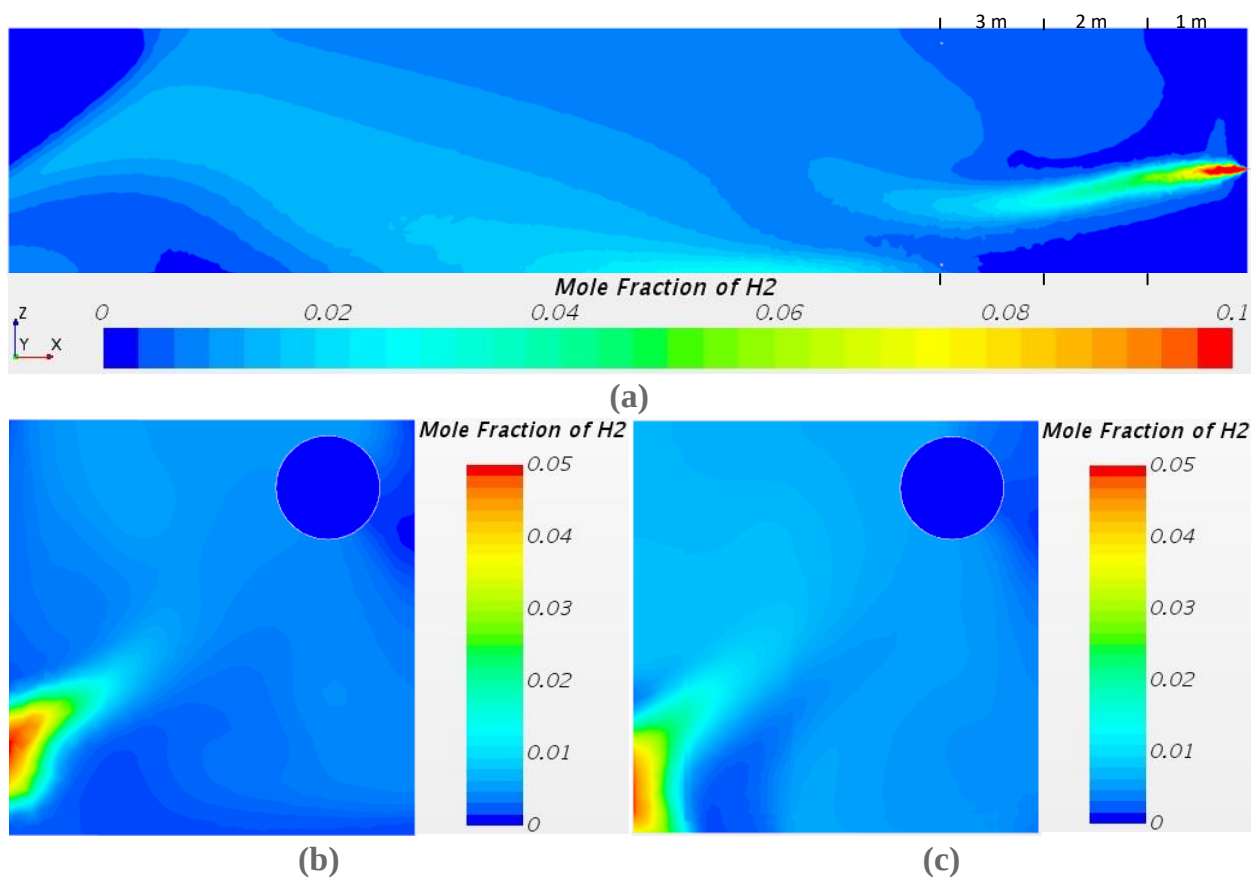


Figure 3-10: The hydrogen concentration distribution for run no 2 (see Table 3-1): (a) cross-section of the hydrogen distribution at X = 2 m from the leak point; (b) cross-section of the hydrogen distribution at X = 3 m from the leak point; (c) cross-section of the hydrogen distribution at the leak point in the Y cross-section.

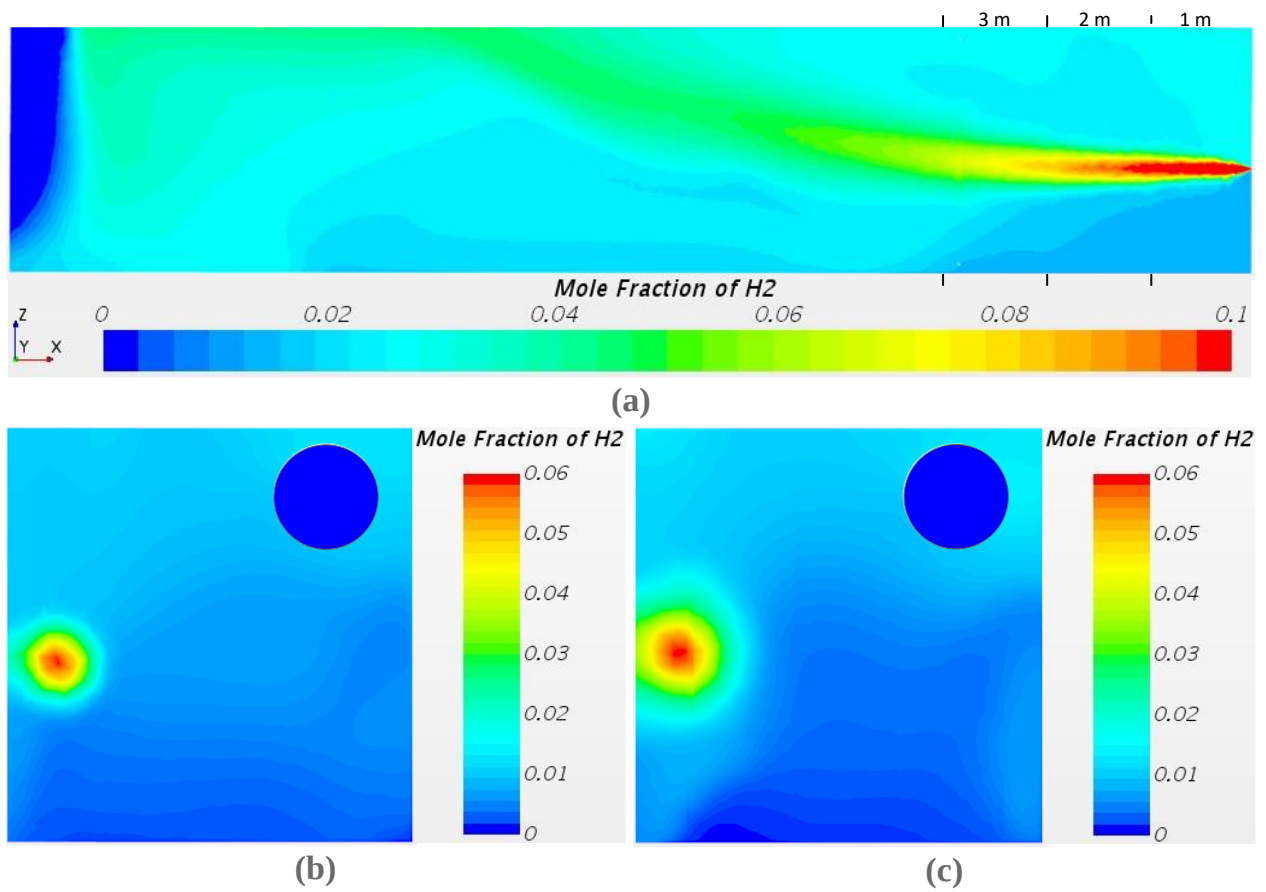


Figure 3-11: The hydrogen concentration distribution for run no 5 (see Table 3-1): (a) the cross-section of the hydrogen distribution at $X = 2$ m from the leak point; (b) cross-section of the hydrogen distribution at $X = 3$ m from the leak point; (c) cross-section of the hydrogen distribution at the leak point in the Y cross-section.

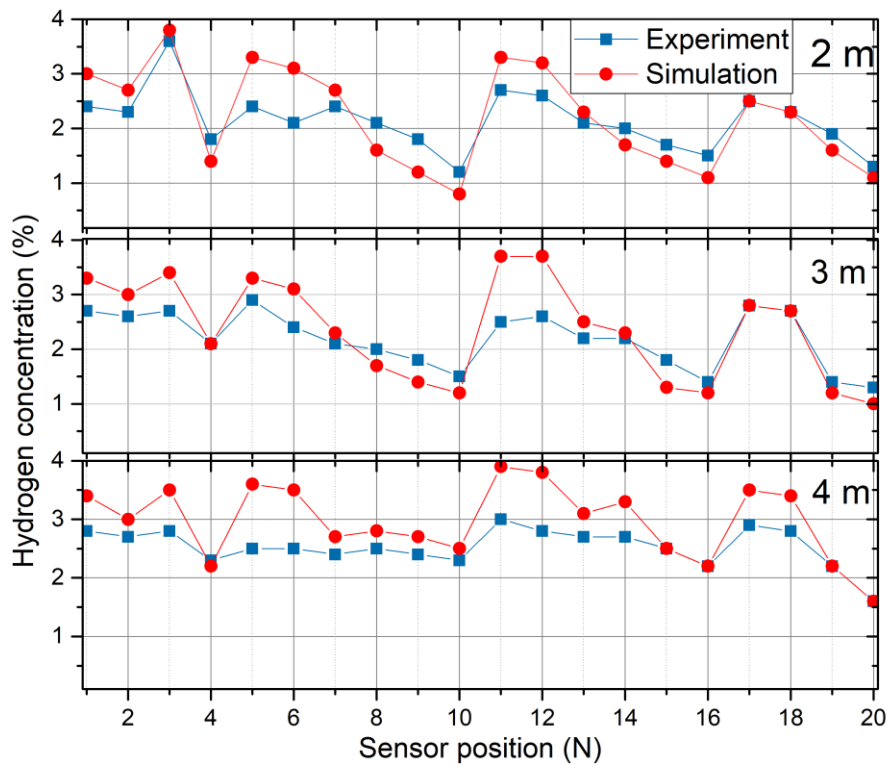


Figure 3-12: The hydrogen concentration for each of the 20 sensors along the length of the container from the leakage at (2, 3, and 4 m, respectively) for run no. 3 (see Table 3-1).

In the case of a higher input pressure (set of parameters №3) but with the same orifice (set of parameters №2), the distribution and the motion of hydrogen is rather complex; although it does retain some visible stratification up to 4 m from the wall (Fig. 3-12), it is rather homogeneous after that distance (>4 m). For this particular case, there are quite large deviations between the experimental data and the calculations, which may reach 45% in several cases.

It should be noted that the numerical results may be quite sensitive to some parameters at a large orifice and input pressure (such as an unknown orifice angle), the surrounding nonuniform temperature of the container's surface, the geometry of the sensors itself, and some others. Such conditions are yet to be studied, to verify our calculations and to define model errors.

3.5 Conclusions

The hydrogen distribution in semi-closed facility under a leakage accident was studied experimentally and verified numerically. The results are shown a nonuniform concentration distribution based on the conditions of the hydrogen release and the ventilation flow rates.

Hydrogen release scenarios have been conducted to understand a hydrogen jet behavior in order to different initial parameters. Simulation results demonstrated that release hydrogen is forming a rather intense buoyancy jet even at very low release pressure. The hydrogen concentration is slightly decreasing as far as the distance from the leakage point increases. Results revealed a difference in behaviour of hydrogen distribution for a small orifice (0.8 mm) and at high pressure (20 bar) compared with a large orifice (4.572) and at low pressure (2 bar). A large orifice during a low-pressure releases a greater amount of hydrogen into the facility. Nevertheless, the case with a small orifice and high-pressure demonstrated a relatively lower amount of released hydrogen. Alternatively, the experimentally and numerically obtained results demonstrated the significant importance of forced ventilation in case of hydrogen release into semi-closed space. According to obtained data, the ventilation flow velocity of 6.5 m/s is sufficient to dilute unintended hydrogen leak to below 4 vol %. The effect of FV, causes potentially flammable hydrogen cloud to mix with air and move away from the leak point much faster in contrast with the absence of ventilation. Thereby, forced ventilation is strongly recommended to be deployed to the facility which is using hydrogen.

The experimental and numerical results agree within 20% at a maximum discrepancy. The numerical reproduction of the experiments is in fair agreement, however, simulations data is adequate to describe experimental results. The scenarios described in this study can serve as valuable information in order to address hydrogen safety.

3.6 Acknowledgments

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CHAPTER 4: TEMPERATURE PROFILE MAPPING OVER A CATALYTIC UNIT OF A HYDROGEN PASSIVE AUTOCATALYTIC RECOMBINER: AN EXPERIMENTAL AND COMPUTATIONAL FLUID DYNAMICS STUDY

The research described in Chapter 4 has been conducted in an attempt to answer the scientific question that was defined in objective III, “To develop and validate a 3D CFD model of a small-scale PAR by experimental evaluation of a PAR’s cylindrical-type catalyst section in terms of temperature distribution and hydrogen recombination efficiency under low hydrogen inlet concentrations of 2–5 vol %”.

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OVERVIEW

Passive autocatalytic recombiners (PARs) are used for the removal of accidentally released hydrogen inside confined spaces. The high catalyst surface temperature is an important safety issue to be considered in the use of a PAR. The ability to predict the catalyst surface temperature could be very useful in preventing the self-ignition and explosion of hydrogen inside the PAR. This study seeks to investigate the changes in temperature profiles of the PAR catalytic section upon variation of the inlet hydrogen concentration. Experiments were conducted on a small-scale test setup. The catalytic section comprised cylindrical ceramic elements arranged in parallel and held upright by a stainless-steel frame. The temperature profiles were measured with a high-resolution infrared camera. The commercial computational fluid dynamics (CFD) code STAR-CCM+ was used as a numerical tool for modelling the gas mixture flow inside the experimental setup and the chemical reaction kinetics. The results of numerical studies are presented and compared with experimental results. The presented CFD-based approach and software offer an appropriate numerical tool for the investigation of hydrogen safety issues. Finally, the catalyst was subjected to a prolonged high-temperature combustion fatigue procedure to determine its stability. The surface of the fatigued catalyst was evaluated by scanning electron microscopy and energy-dispersive X-ray spectroscopy. It was found that decomposition of the protective surface layer occurred at elevated temperatures; the catalytic activity was unaffected by this. In addition, a relatively uniform reactive metal particle size was maintained over the entire temperature range, suggesting that no aggregation occurred.

4.1 Introduction

Hydrogen is an advanced fuel for wider future use as an energy carrier in various applications. Hydrogen fuel cell (HFC) vehicles are being developed as an alternative for powering underground mining machines (Arnold and Miller, 2000; Miller *et al.*, 2012; Valicek and Fourie, 2014). HFCs and vehicles based on fuel cells offer significant advantages in terms of reducing carbon emissions. However, the use of hydrogen in confined spaces is accompanied by the risk of emergency releases because of leaks, component failures, or human error. The most important safety consideration in any hydrogen application is to prevent the formation of flammable mixtures of hydrogen with air. The ignition volume fraction range for hydrogen is 4–74% in air at atmospheric pressure (Alcock, *et al.*, 2001). The self-ignition temperature range is 845–858 K (Du Toit, *et al.*, 2018). It is therefore important that emergency hydrogen removal systems be in place to keep the hydrogen concentration below the flammability limit of ~4% vol.

Several methods are used to mitigate the risk of hydrogen deflagration or detonation, for example, catalytic recombination conducted in passive autocatalytic recombiners (PARs) and forced ventilation (FV). The consequences of leakage and then the dispersion and accumulation of hydrogen in terms of the geometric configuration of a confined space have been reported by Matsuura (Matsuura, 2009). The space geometry plays a role in the selection of the natural or FV used. Analysis of the efficiency of natural ventilation has been carried out (Matsuura, *et al.*, 2009), and FV in semi-closed spaces and tunnels has been studied (Molkov, Verbecke and Makarov, 2008; Bie and Hao, 2017). In previous work, we investigated the ventilation efficiency in a full-scale facility, representing a part of an underground mining tunnel, during hydrogen leakage occurrence (Malakhov, *et al.*, 2020).

The properties of hydrogen, such as its wide flammability range, low density, and low ignition energy, increase the probability of a fire/explosion hazard in any spaces where hydrogen is present (Du Toit, *et al.*, 2018). The catalyst sections in a PAR mainly uses platinum (Pt). In the event of a severe accident in a light water reactor, high temperatures inside the reactor will result in the zirconium alloys therein being oxidized by steam to form hydrogen, in an exothermic reaction. The generally accepted global practice to remove hydrogen from containments of nuclear power plants is currently based on the principle of passive catalytic hydrogen recombination in the presence of catalysts such as Pt (IAEA, 2011; Della, 1992; Ferroni, *et al.*, 1994; Agrawal, *et al.*, 2017). PARs are used to mitigate the effects of hydrogen release. A PAR operates at temperatures much lower than those required for gas-phase ignition and reduces the accumulation of hydrogen and detonation risk after any hydrogen release. A key component of a

passive catalytic hydrogen recombiner is the catalyst, on the surface of which a hydrogen recombination reaction with oxygen takes place.

PARs are available in various sizes depending on the dimensions, the number of catalytic sections, and the length of the chimney section (Blanchat and Malliakos, 1999). Catalytic elements can be of various geometric shapes, including sheets made of stainless steel and coated with a Pt catalyst material (Reinecke, *et al.*, 2004; Reinecke *et al.*, 2010), and cylindrical catalytic elements made of ceramic with a Pt coating (Grigoriev *et al.*, 2009; Avdeenkov *et al.*, 2018). A typical PAR is shown in Figure 4-1.

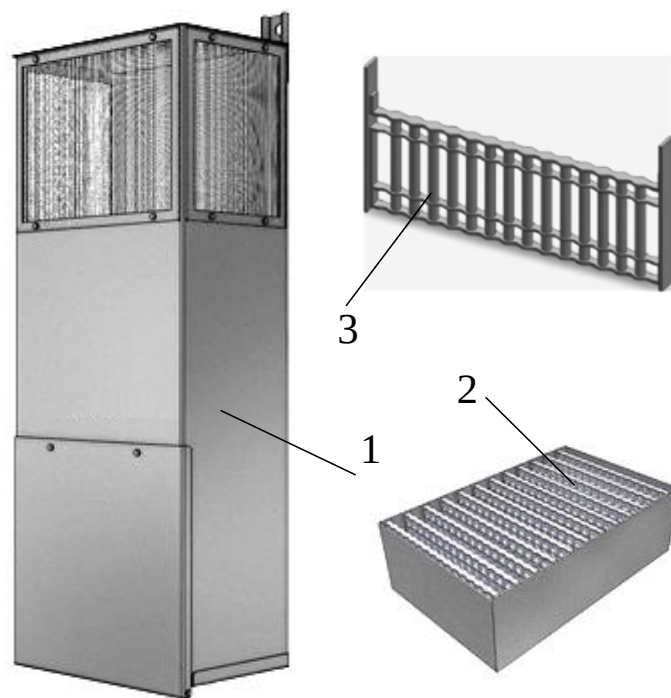


Figure 4-1: Schematic of a typical PAR: (1) PAR framework, (2) catalyst unit consisting of a set of catalytic frames, and (3) catalyst rods combined in frames.

The recombination reaction begins with the arrival of molecular hydrogen and oxygen at the catalyst's surface; this is followed by their dissociation. An exothermic chemical reaction occurs between hydrogen and oxygen. The heat released during the chemical reaction heats both the catalyst and the gas, which may create a natural convection in the PAR framework. It should be noted that the moment of onset of hydrogen recombination might present a potential risk for the PAR. If mixing the reaction components is not optimized in terms of timing, the gas mixture of hydrogen and air could self-ignite and damage the PAR (Du Toit, *et al.*, 2018). Hence, the

geometry of the PAR should make a provision for sufficient level of gas mixing. The main product of hydrogen recombination (water vapor) passes through the outlet of the PAR and into the atmosphere. Generally, the recombination occurs both at the boundary of the catalyst surface and in the gaseous medium.

In our study, we consider only low-concentration hydrogen mixtures with 2–5 vol % hydrogen. The experiments were performed at low hydrogen concentrations in air due to safety considerations. At such low concentrations, only surface catalysis may afford the recombination of hydrogen and oxygen while the temperature of the gaseous medium is too low to ignite. It is for this reason that we considered it adequate to only take the surface chemistry into account.

In this study, chemical kinetics of the catalytic recombination of hydrogen was analyzed using the CHEMKIN software package (Kee and Miller, 1989; Orszulik, *et al.*, 2015), the database of which is part of STAR CCM+ software (Reinecke *et al.*, 2013; Klauck *et al.*, 2014; Rozeń, 2015; Baggemann *et al.*, 2017) (CD-adapco, 2017). The self-consistent problem of thermohydraulics, by means of computational fluid dynamics (CFD) methods and chemical kinetics, can be successfully verified, and solved using this software. In a similar manner, the application and efficiency of a PAR for the removal of hydrogen inside a car garage have been reported in works by Reinecke *et al.* and Baggemann *et al.* (Reinecke *et al.*, 2013; Baggemann *et al.*, 2017). In those study, the sensitivity of a PAR for different boundary conditions, scenarios of hydrogen release, and PAR positions were investigated by means of CFD simulations.

CFD is increasingly used to perform safety analysis of accident scenarios with hydrogen release (Dieguez *et al.*, 2013). Numerical simulation tools are widely used in current research to gain a good theoretical understanding of the experiment, and CFD software is extensively used in this respect. CFD is a detailed numerical tool in 3D modelling.

The aim of this study was to determine the effects of different inlet hydrogen concentrations on heating the catalyst by comparing experimental data with numerical calculations.

4.2 Experimental section

4.2.1 Experimental setup: description and instrumentation

Efforts are underway at DST HySA Infrastructure Center of Competence (HySA), North-West University Potchefstroom (South Africa), to investigate on and to create an innovative technology in the field of hydrogen—detailed experiments are currently being performed. The experiments described in this study were carried out using a small-scale test setup at HySA to study the behavior of a commercially available PAR section under defined conditions (Figure 4-2).

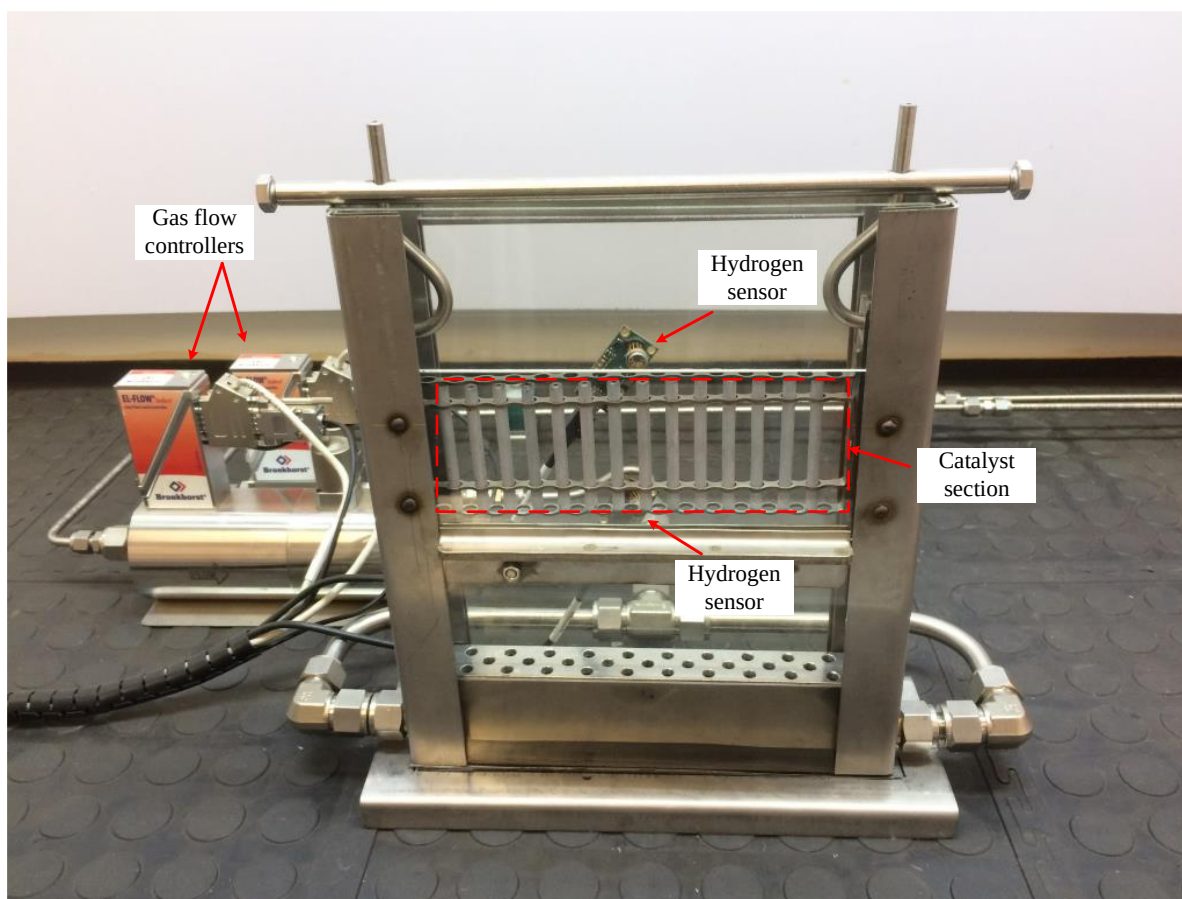


Figure 4-2: Experimental setup—including a catalyst section, hydrogen sensors, and gas flow controllers.

The flow channel is constructed as a vertical rectangular box (cross-sectional area: 45.5 mm × 242 mm). The experimental setup allows one to investigate catalyst samples inside a vertical flow channel under well-defined conditions such as the flow rate and the inlet concentration of hydrogen and air. The catalysts are cylindrical ceramic rods (height: 64 mm; diameter: 5 mm). The 14 catalyst cylinders, coated with a Pt catalyst, are arranged in parallel; they are held upright by a stainless-steel frame. The catalytic section was taken from a nondisclosed commercial PAR manufacturer.

In order to calculate the hydrogen concentration, sensors were fixed in two places. The first sensor is installed in the center, at the bottom of the catalyst, to determine the inlet hydrogen concentration. The second sensor is installed above the catalyst section to determine the outlet hydrogen concentration after the catalytic reaction. The hydrogen concentration is measured using a commercial sensor Xensor Integration XEN-5320. The XEN-5320 is an intelligent gas sensor for the measurement of gas composition. The sensor is based on the measurement of the

thermal conductivity of an ambient gas, using the proven thermal conductivity sensor XEN-TCG3880 (Integration, 2020).

To eliminate any errors due to the difference between room temperature and operating conditions and to minimize the inaccuracies in measuring concentrations, the sensors were calibrated under conditions as close as possible to the eventual operating conditions (e.g., temperature, humidity, and so on). The accuracy of the sensors, in terms of the measured values, was a maximum error of 150 ppm (Integration, 2020). The signal response and recovery time were virtually immediate. LabVIEW software was used for the logging of the hydrogen sensors, and the concentration data were logged every 1 s. Mass flow controllers ensured the supply of defined concentrations of gas mixture components. A uniform flow distribution was achieved by means of velocity and turbulence smoothing element by varying the number of holes on the pipe, hole sizes, and inlet gas velocity. Figure 4-3 shows a schematic diagram of the experimental setup used and the constituent parts.

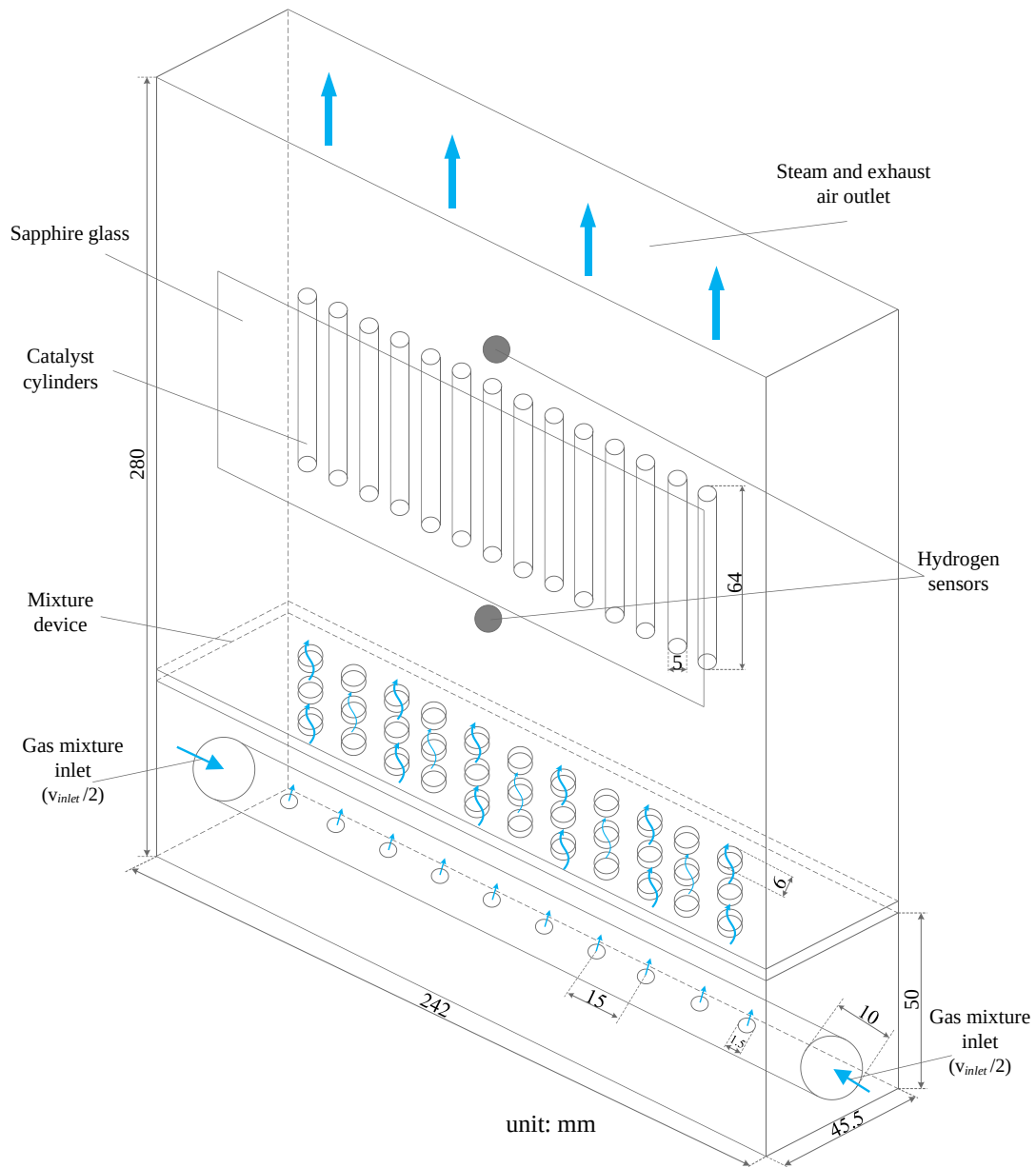


Figure 4-3: Schematic diagram of the experimental setup with boundary conditions and sapphire glass.

4.2.2 Infrared camera description and temperature measurements

One of the most important features of the setup is the opportunity to measure the temperature with an infrared (IR) camera. IR can be used to identify objects and scenes by detecting radiation in the thermal IR range. IR uses detectors to image objects of interest as single pictures or videos (Richards and D'souza, 2009). A Telops Midwave HD Series (M100hd) high-resolution IR camera was used to capture thermal data generated during the recombiner experiment. The IR camera is suitable for use in the 3–5 μm IR spectral range. It was calibrated for four filter wheels, which

allow the camera to capture electromagnetic intensities corresponding to up to 2500 °C. In this work, the camera was fitted with a lens suitable for capturing thermal images in the temperature range 0–325 °C. The manufacturer specified a lens emissivity of >93%. Calibration of the lens resulted in a 0.06 °C median error in the radiometric temperature. The IR camera was operated using the HypIR software package (V4.5.0). A frame rate of 1 Hz (similar time interval to the CFD model) was used to capture thermal images. HypIR software was used on an HP Z4 workstation with an Intel Xeon CPU (W-2125 4.0 GHz), 64 GB DDR4 memory, and a NVIDIA Quadro P4000 GFX graphics card (8 GB).

The glass used in the setup was made of synthetic sapphire for optical and thermal visibility, as well as for containing the gases inside the setup. Sapphire is widely used for optical applications because of its ability to transmit from the ultraviolet (UV) wavelengths into the mid-IR wavelengths. Sapphire is an anisotropic uniaxial crystal. Being a dielectric and thermally stable material up to 1600 °C, synthetic sapphire also has excellent optical properties—transparency in the range of 0.17–5.5 μm (Rogalin, *et al.*, 2018). The above-listed qualities of sapphire allow it to retain all the optical properties and make it an indispensable material for working at high temperatures. Considering the spectral range of the IR camera lens and the steady transmittance of sapphire at wavelengths in the range of 3–5 μm , the level of transmission is 85% (Sova *et al.*, 1998; Niu *et al.*, 2016).

4.2.3 Set of input parameters

The test series to be presented in this paper is summarized in Table 4-1.

Table 4-1: Overview of Test Series.

Computational cases, no.	H ₂ inlet concentration C[H ₂], vol %	Mass flow rate $\dot{m}$, g/s	Volume flow rate $\dot{V}$, m ³ /h
1,2,3,4	2.0/ 3.0/ 4.0/ 5.0	0.92 ± 0.1	2.82 ± 0.1

High-purity electrolytic hydrogen (>99.999 vol %) from a renewable hydrogen storage facility at HySA Center and compressed air were used for the gas supply. A mixture of hydrogen and air, with hydrogen concentrations (C[H₂]) up to 5.0 vol %, is fed into the flow channel at an inlet velocity of 10.0 m/s. The flow rate of the inlet gas mixture volume for each case is $\dot{V} \sim 2.8 \text{ m}^3/\text{h}$, at a gas temperature of 25 °C. The flow rate was calculated based on the area. Air properties were used. In the cases considered in this paper, the apparent experimental inlet mass flow rate allowed to be slightly lower (taking into account a small decrease in the density of gas mixture in the

presence of hydrogen under the given test conditions). However, because of the complexity of the geometry, it is reasonably assumed that it has little effect on the velocity distribution near the catalyst elements.

The same assumption was applied to the dynamic viscosity of the mixture, as it is rather close to the viscosity of air. As the hydrogen concentration is relatively small, the inlet viscosity of the mixture is also close to the air viscosity.

In the test cases, the hydrogen concentration is increased from 2.0 to 5.0 vol %. After each increase, the following variables were measured: the inlet hydrogen concentration and new steady-state values such as outlet hydrogen concentrations and catalyst temperatures.

4.2.4 Catalyst fatigue testing

The catalyst was subjected to a fatigue procedure to evaluate the stability and catalytic activity of the catalyst as a function of continuous high-temperature catalytic hydrogen combustion. The fatigue testing was performed by exposing a vertically placed section of a catalyst to a flow of air with a high hydrogen content at a flow rate slightly below a flow rate that would facilitate autoignition of the hydrogen-containing steam. For this procedure, hydrogen was supplied using an in-house-developed electrolytic hydrogen generator (HySA), and a flow rate of 75 mL/min hydrogen was used. The nozzle of the hydrogen source was placed 3 mm below the catalyst, allowing premixing of hydrogen and air prior to the gas mixture reaching the reactive catalyst surface. The hydrogen concentration prior to reaching the catalyst was approximately 63 vol %. The total sample length was 70 mm. The catalyst surface temperature was measured at the top, center, and bottom; a measurement was taken every second. The fatigue procedure was performed for 250 h. The average temperature values and standard deviations presented were based on at least 60,000 measurements. The hydrogen content in the exhaust steam was measured to be <1 vol %, suggesting the near-complete combustion of hydrogen by the catalyst for this experimental setup and parameters.

Postfatigue characterizations of the catalyst surface morphology and chemical composition were performed by scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy, respectively. A FEI Quanta 2000 scanning electron microscope integrated with an Oxford Instruments INCA 200 EDX spectroscope microanalysis system was used. All micrographs were prepared in the secondary electron mode. Platinum particle diameters of the investigated areas of the catalyst (top, center, and bottom) were determined with high-resolution transmission electron microscopy (TEM) using a Tecnai F20 high-resolution transmission electron microscope. Samples were prepared by mechanically separating the surficial layer of the catalyst

at the top, center, and bottom, followed by extensive ultrasonication in ethanol. Directly after ultrasonication, droplets were placed on a carbon grid and allowed to dry. Particle size analysis was done on TEM images using ImageJ software.

4.2.5 Safety considerations

Taking into account ignition and detonation potential risks, safety measures were applied to the experiment. The setup is installed inside a ventilated fume hood to remove hydrogen out of the performance area. In addition, the mass flow controllers have a built-in safety to start the flow of the air first when the setup is started and gradually adds hydrogen. The same rule is applied when it is shut down. The hydrogen concentration decreases gradually and then the air supply continues for some time to make sure the system is purged. Finally, hydrogen concentrations were controlled by sensors.

4.2.6 Experimental results

Tests were carried out consistently, in which the inlet hydrogen concentration ($C[H_2]$) was increased from case to case. The time interval between the tests was around 2 h in order to allow the establishment of steady-state conditions of the catalyst temperatures.

The catalyst temperature increased due to the exothermal reaction taking place on the catalyst surface, where the extent of increase depends on the hydrogen concentration. Each steady-state measurement was reached ~40 min after commencement of the experiment.

The experimental (IR camera) steady-state distribution for the temperature profiles on the rod surfaces measured by the IR camera for each case of the inlet hydrogen concentration is presented in Figures 4-4–4-7. The surface temperature along the vertical axis of the rods was extracted from the IR camera software package and plotted. For the purpose of the following calculations and analysis, the distance along a catalyst cylinder was divided into 30 equal points. The vertical axis for each rod was taken in the middle of the surface facing the IR camera. The measured numerical values for each case, over 30 points (from the top to the bottom), are plotted in Figures 4-4–4-7 to illustrate the temperature distribution along the middle vertical axis for each rod. The measured numerical values for each case, over 30 points going from 64.0 mm to 0 mm (from the top to bottom).

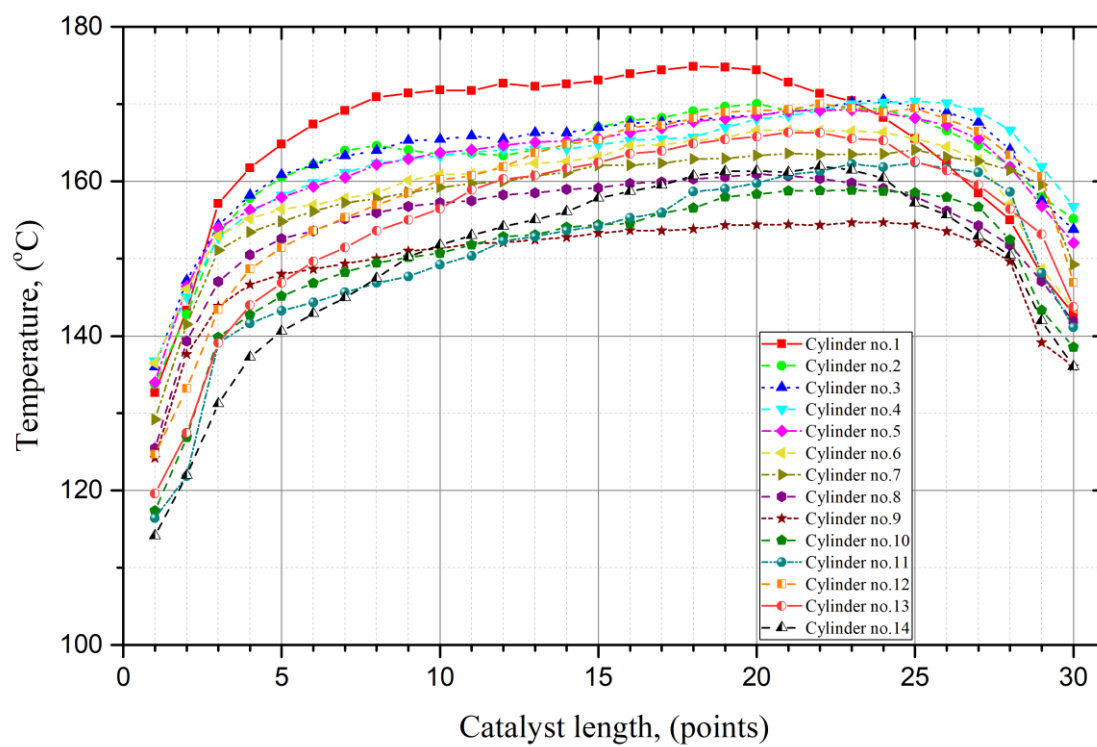


Figure 4-4: Experimental temperature distribution for each catalyst cylinder for case no. 1, $C[H_2] = 2$ vol %.

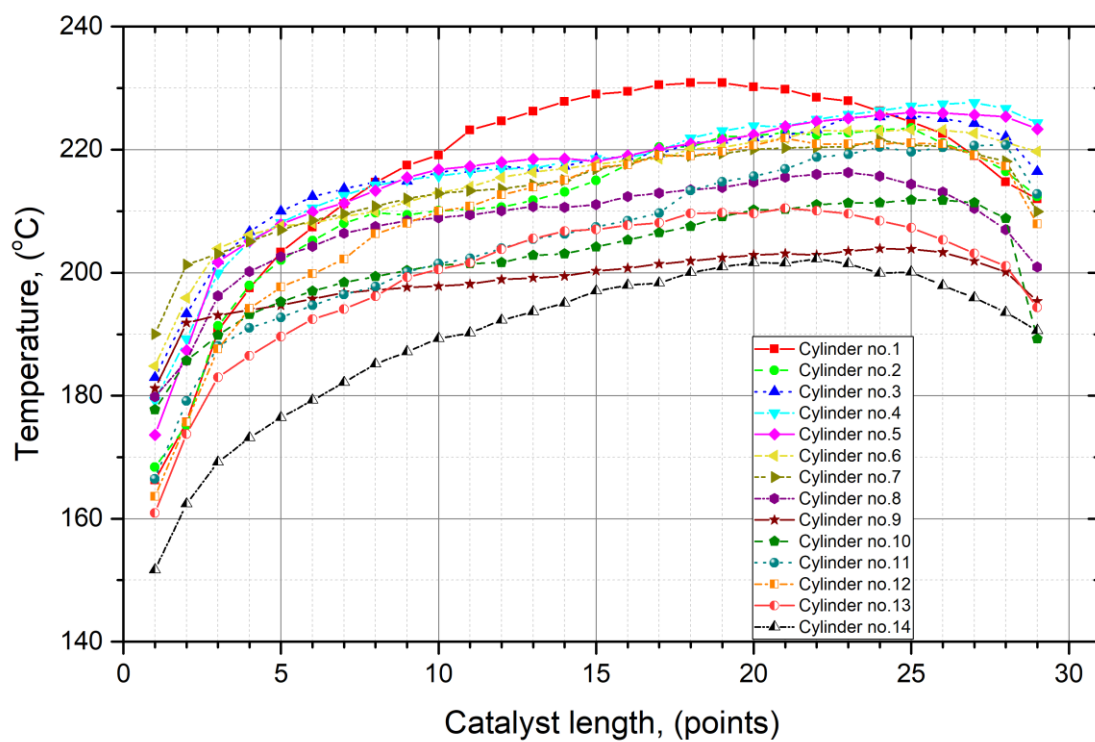


Figure 4-5: Experimental temperature distribution for each catalyst cylinder for case no. 2, $C[H_2] = 3$ vol %.

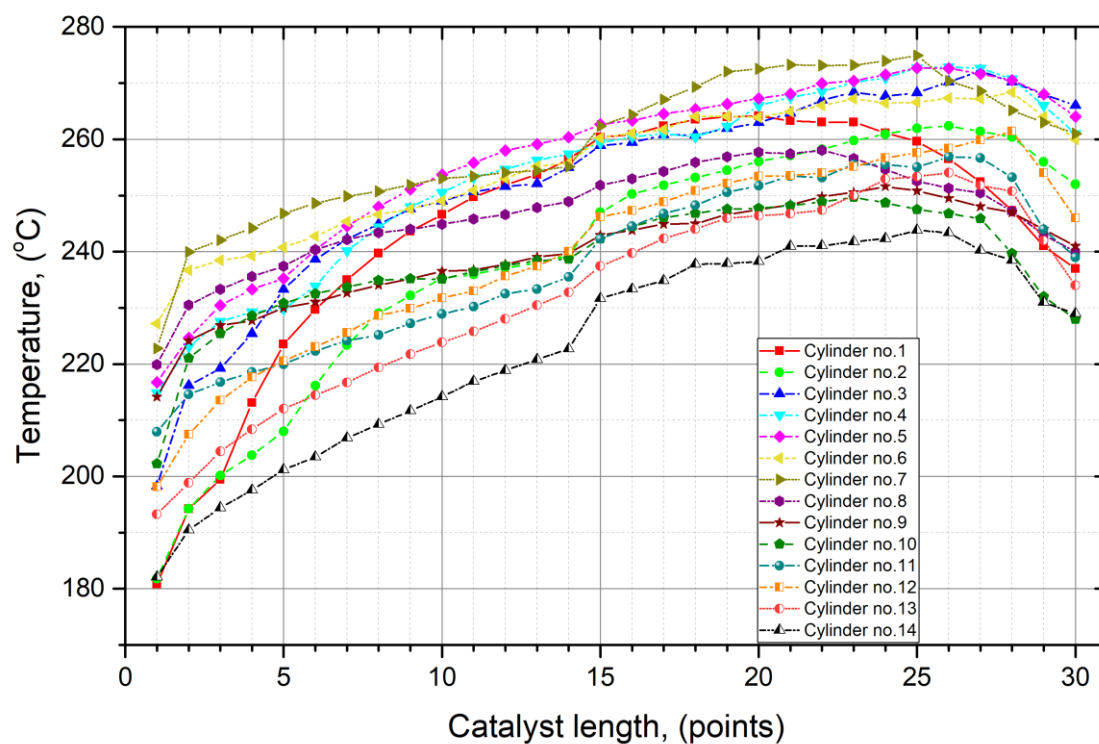


Figure 4-6: Experimental temperature distribution for each catalyst cylinder for case no. 3, $C[H_2] = 4$ vol %.

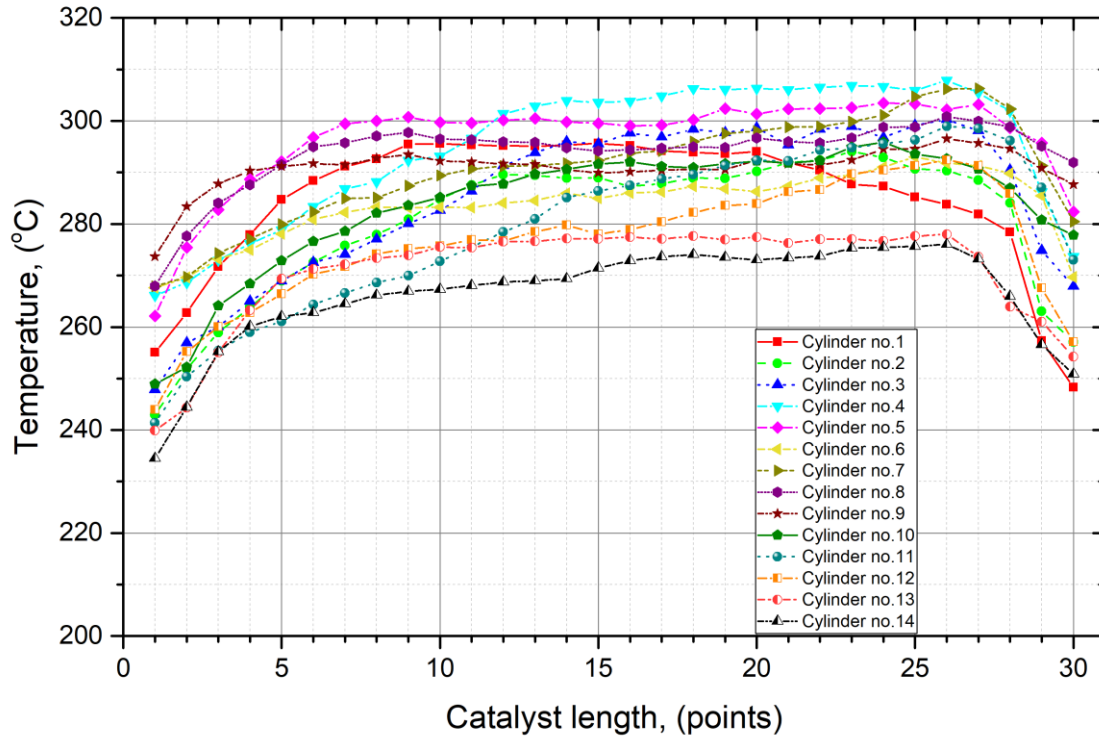


Figure 4-7: Experimental temperature distribution for each catalyst cylinder for case no. 4, $C[H_2] = 5$ vol %.

Figure 4-4 demonstrates a rather homogeneous distribution from rod 1 (right) to rod 14 (left) for the lowest inlet hydrogen concentration (2 vol %). Figures 4-4–4-6 show the temperature profile for case nos. 1, 2, and 3; the maximum temperature in those cases is 174, 232, and 273 °C, respectively. We observed some shift in the temperature peak region toward rod 1 (right) as the hydrogen inlet concentration decreases from 5 to 2 vol %. The reason for this is the amplification of turbulent vortices after the gas mixture passes through the mixing device.

We can see the points of the lowest temperatures on the top and on the bottom of the rods. In Figure 4-7, one can see that a gas mixture of 5 vol % (case no. 4) hydrogen in air leads to a maximum temperature of ~ 310 °C at point 26 in rod 4 (right). For case no. 4, the temperature difference from rods 1 to 14 is approximately 65 °C.

The main part of the hydrogen oxidation reaction takes place centrally (between the bottom and the top of the catalyst cylinders). Accordingly, regions of higher temperatures are approximately between points 15 and 25 for all cases considered.

The results present a rather “linear” profile of temperatures for each catalyst cylinder. The following points on the catalyst length have lower temperatures due to heat dissipating into the surrounding air on the sides: points 1 and 30. Another reason why the temperature at points 1 and 30 is lower is related to the position of the stainless-steel frame.

The IR camera images with temperature distribution for all cases are presented in Section 3.3 “Comparing Experimental and Numerical Results”.

4.2.7 Fatigued catalyst characteristics

During the fatigue procedure, a rather significant temperature gradient was observed. The catalyst bottom, which was exposed to the highest concentration of hydrogen, had a surface temperature of 509 ± 21 °C. The catalyst middle and top had temperatures of 281 ± 12 and 168 ± 12 °C, respectively. The large temperature gradient could be ascribed to the low thermal conductivity of the ceramic support and partially to a decrease in the hydrogen content as the hydrogen feed progresses upward over the catalyst surface. Nevertheless, insufficient thermal conductivity from the hot to cold zones of the catalyst may result in autoignition of the hydrogen-rich feed if the energy required for ignition is achieved (du Preez *et al.*, 2019, 2020). In addition to the significant temperature gradient, a distinctive change in catalyst color was also observed. The color change correlated with the surface temperature zones—the top, middle, and bottom of the catalyst had different colors. The surface morphology and chemical composition of the top, middle, and bottom of the catalyst were investigated using SEM (Figure 4-18) and EDX (Table 4-4).

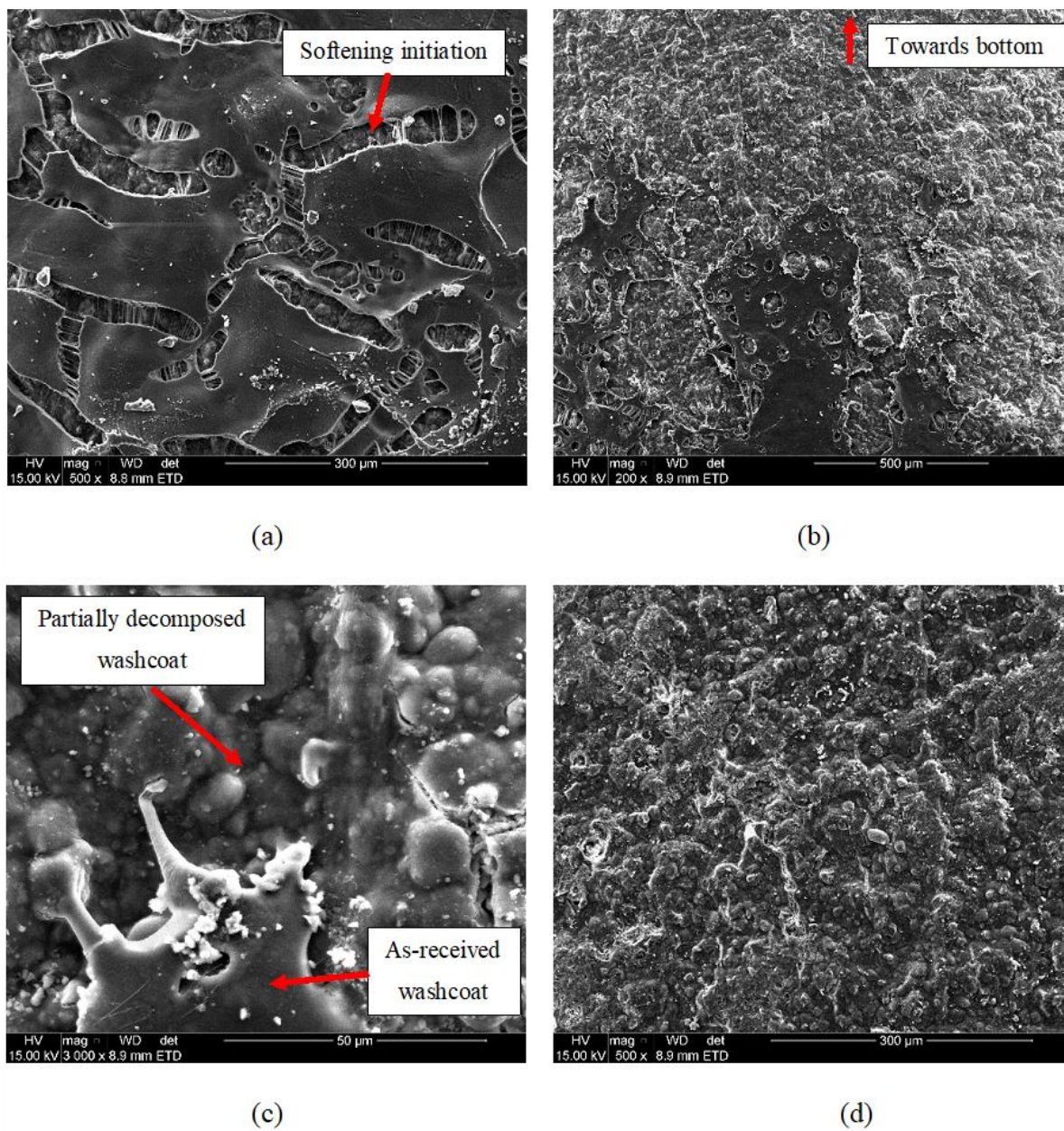


Figure 4-8: SEM micrographs: (a) catalyst top, (b) transition zone between the catalyst top and middle, (c) similar area as shown in (b) at greater magnification, and (d) catalyst bottom of a 250 h fatigued catalyst.

Table 4-2: SEM–EDX (at. %) of the Surface of a 250 h Fatigued Catalyst^a.

Sample area (temperature, °C)	Detected element (at %)				
	O	F	Al	Si	Pt
Top (168.20)	4.76 ± 0.14	90.01 ± 0.73	5.24 ± 0.56	-	-
Middle (281.16)	61.25 ± 0.39	-	38.20 ± 0.45	0.93 ± 0.06	-
Bottom (509.43)	59.37 ± 2.78	-	40.16 ± 2.31	-	0.47 ± 0.50

* Minimum of three 600 × 600 μm areas were considered; averages and standard deviations indicated.

- Below detection limit of instrument.

Figure 4-19 shows a change in the catalyst surface morphology as a function of position—this is directly correlated with the surface temperature. This observed change may be ascribed to thermal decomposition of the F-rich layer, as is evident from the total removal of fluorine content from the surface at temperatures >168 °C (Table 4). The surface presented in Figure 18 (a) shows the initiation of softening of the catalyst-protecting layer (identified by cracking and inter-crack wire formation), whereas Figures 18 (b) and (c) show the transition phase from the as-received to a partially decomposed layer. Figure 18 (d) shows the support surface after complete layer decomposition, revealing the underlying Al-rich oxide support. The change in morphology may be ascribed to F-containing species evaporation, which is the case for fluorocarbon-based polymers. For example, polytetrafluoroethylene (PTFE) undergoes slow decomposition at >260 °C, whereas rapid decomposition occurs at 400 °C (Simon and Kaminsky, 1998). According to Lewis and Maylor (1947), PTFE undergoes degradation during continuous exposure to temperatures >360 °C (Naylor, *et al.*, 1947). According to Madorsky (1953) (Madorsky, *et al.*, 1953), and Wall and Michaelson (1956) (Wall and Michaelson, 1956), PTFE decomposition occurs by a first- and zero-order rate law at >510 and <480 °C, respectively. Thus, it is likely that the catalyst-protecting layer at the catalyst bottom (Figure 4-18 d) was totally decomposed and, as a result, the Pt detected by EDX (Table 4-4) was subsequently deposited directly onto the support. EDX mapping of the catalyst bottom was performed in an effort to determine the extent of Pt aggregation (Figure 4-19). The observed EDX mapping for Pt was ascribed to the complete (or at least near-complete) degradation of the catalyst-protecting layer.

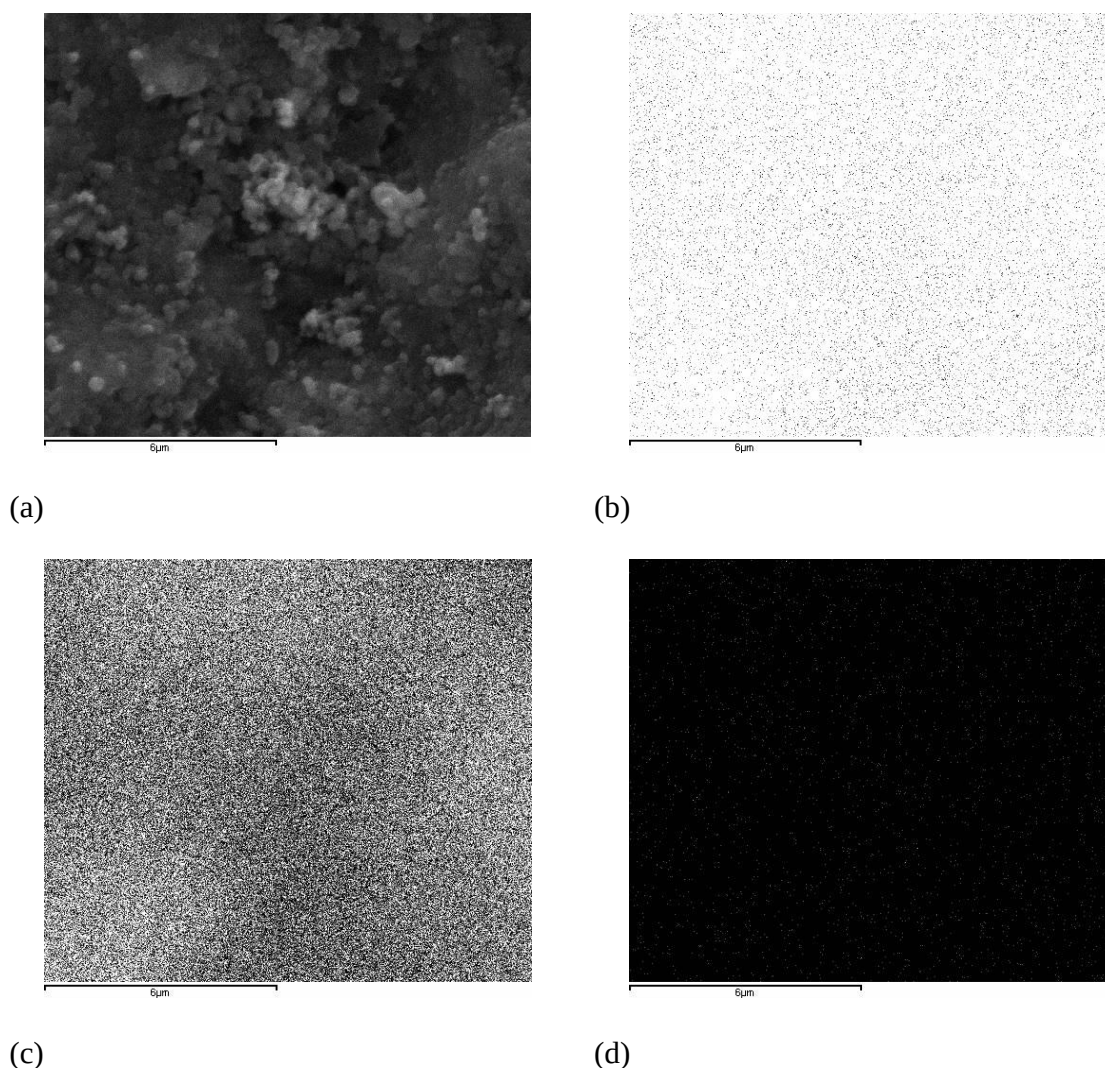


Figure 4-9: SEM micrograph of the surface of the bottom of a 250 h fatigued catalyst (a), and its corresponding EDX mappings for Al (b), O (c), and Pt (d).

Reactive metal aggregation is a critical aspect of any catalyst. Typically, Pt aggregation (sintering) occurs relatively slowly; it may be accelerated at elevated temperatures (<500 °C) and in the presence of water vapor (Bartholomew, 2001). However, this aggregation may be limited/prevented if a suitable catalyst support is used (du Preez *et al.*, 2019). To determine the occurrence/extent of Pt aggregation, the Pt particle sizes present in the three different areas of the catalyst here were investigated. A representative TEM image of Pt particles present at the bottom of the catalyst is shown in Figure B1 (Appendix B). The Pt particle size at the top was calculated to be 5.61 ± 1.07 nm (based on 244 particles), whereas particles present at the middle and the bottom were 5.49 ± 1.01 nm (based on 266 particles) and 5.58 ± 1.10 nm (based on 194

particles), respectively. Considering the relatively consistent particle size, it is evident that Pt aggregation did not occur over a wide temperature range, 168.2–509.4 °C.

In summary, the following can be deduced from our investigations into the characteristics of fatigued catalysts: i) a large temperature difference occurred between the catalyst top (168 °C) and bottom (509 °C), ii) degradation of the catalyst-protecting layer occurred at high temperatures and it did not affect catalytic activity, iii) it is concluded that the PAR would be able to safely remove large quantities of hydrogen, and iv) in extreme and unlikely cases, autoignition of hydrogen may occur due to the low thermal conductivity of the ceramic support.

4.3 CFD calculations and numerical analysis

CFD simulation is a well-recognized tool that provides an in-depth understanding of the thermohydraulics of complex objects and, in combination with the chemistry tools of CHEMKIN, offers a very powerful tool to predict the quite complex physical and chemical behavior of a PAR. In this work, the CFD code STAR-CCM+ was used as the numerical tool for the simulations (CD-adapco, 2017). The STAR-CCM+ simulation environment offers all stages required for carrying out the numerical analyses: creation of 3D geometries, generation of the numerical mesh, solution of the governing equations, and analysis of the results.

The numerical model is based on the full 3D experimental setup. The model includes the following: a horizontally positioned pipe with holes, a mixing device, a vertical rectangular flow channel, and a cylindrical catalyst area with a stainless-steel frame (Figure 4-3).

4.3.1 Numerical approach and computational domain solution

The numerical domain here is the same size as in the experimental setup (242 mm × 280 mm × 45.5 mm). The governing equations are the continuity equation, Navier–Stokes equations with gravitational force, the energy equation, and the transport equation for the mass fraction of gas-mixture components. The modelling assumes a turbulent flow, which is implemented by the k-epsilon (k-ε) turbulence model (Rodi, 1991). A realizable k-epsilon model with a two-layer approach was used for simulation turbulent flow. For the inlet mass flow used here, the velocity along the pipes is <0.2 m/s, at best, for the selected hydrogen concentration (Figure 4-8), and the flow is rather laminar, $Re \sim 250$. The Reynolds number was calculated for the empty rectangular box. However, at other positions in the experimental setup, the flow is turbulent. Generally, we further applied the selected turbulence model. The Star-CCM+ package used in this study utilized the Reynolds averaging model to predict density fluctuations, and other options, such as Favre averaging, were deemed to be unnecessary. Figure 4-8 shows a typical vector field of the calculated velocity distribution inside the experimental box.

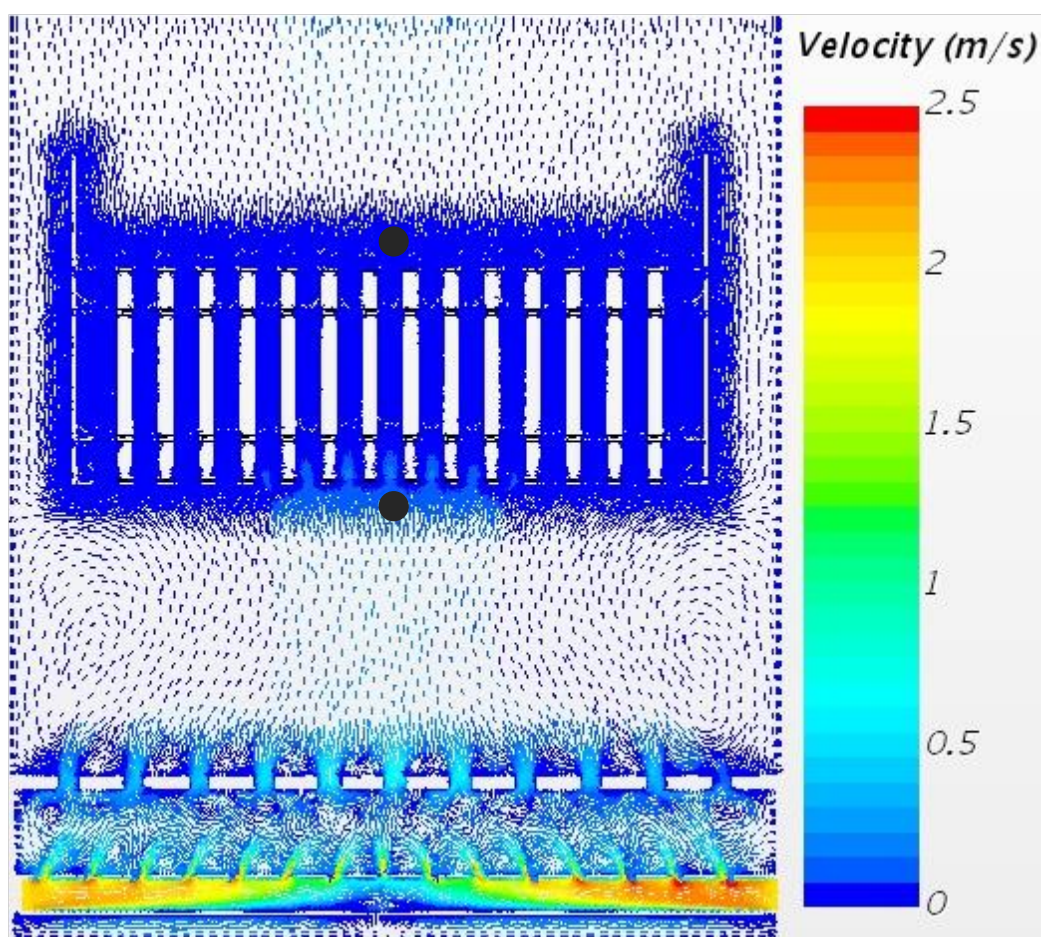


Figure 4-10: Typical vector field of the calculated velocity distribution inside the experimental box.

The flow has three gas components: nitrogen, oxygen, and hydrogen. We made the assumption that the mixture of hydrogen with air is an ideal gas. All properties of gases used in the calculations were applied from the STAR-CCM+ database. The inlet of hydrogen is a velocity inlet boundary and the steam outlet is a pressure outlet. The walls are adiabatic, and their initial temperature is 300 K. The initial environmental pressure is 1 atm. The supported Pt catalyst is simulated by a Pt layer with the surface site density taken as $S_0 = 2.7 \times 10^{-8} \text{ kmol/m}^2$ (Schefer, 1982; Rinnemo *et al.*, 1997; Appel *et al.*, 2002) (Warnatz, *et al.*, 1990). Pt was present on a relatively small percentage of the catalyst surface, and it was considered that the catalyst surface was flat. The catalytic activity was restricted to the surface of finely distributed Pt.

As polyhedral cells generally have a low skewness, we can calculate a more accurate face flux than in tetrahedral cells (CD-adapco, 2017). Polyhedral cells also provide a smooth volumetric growth, which is important for capturing complex geometry effectively, such as the catalyst

cylinder combined in the frame. The fluid domain is discretized by means of a polyhedral grid with a base cell size of 4.0 mm, and the total number of cells is $\sim 1,200,000$. The mesh resolution is nearly homogeneous except for a refinement within the pipe and mixing device areas, as well as in the catalyst zone. The denser mesh showed only small improvements in the calculated parameters. Figure 4-9 shows computational domain properties, such as boundary conditions and numerical mesh settings.

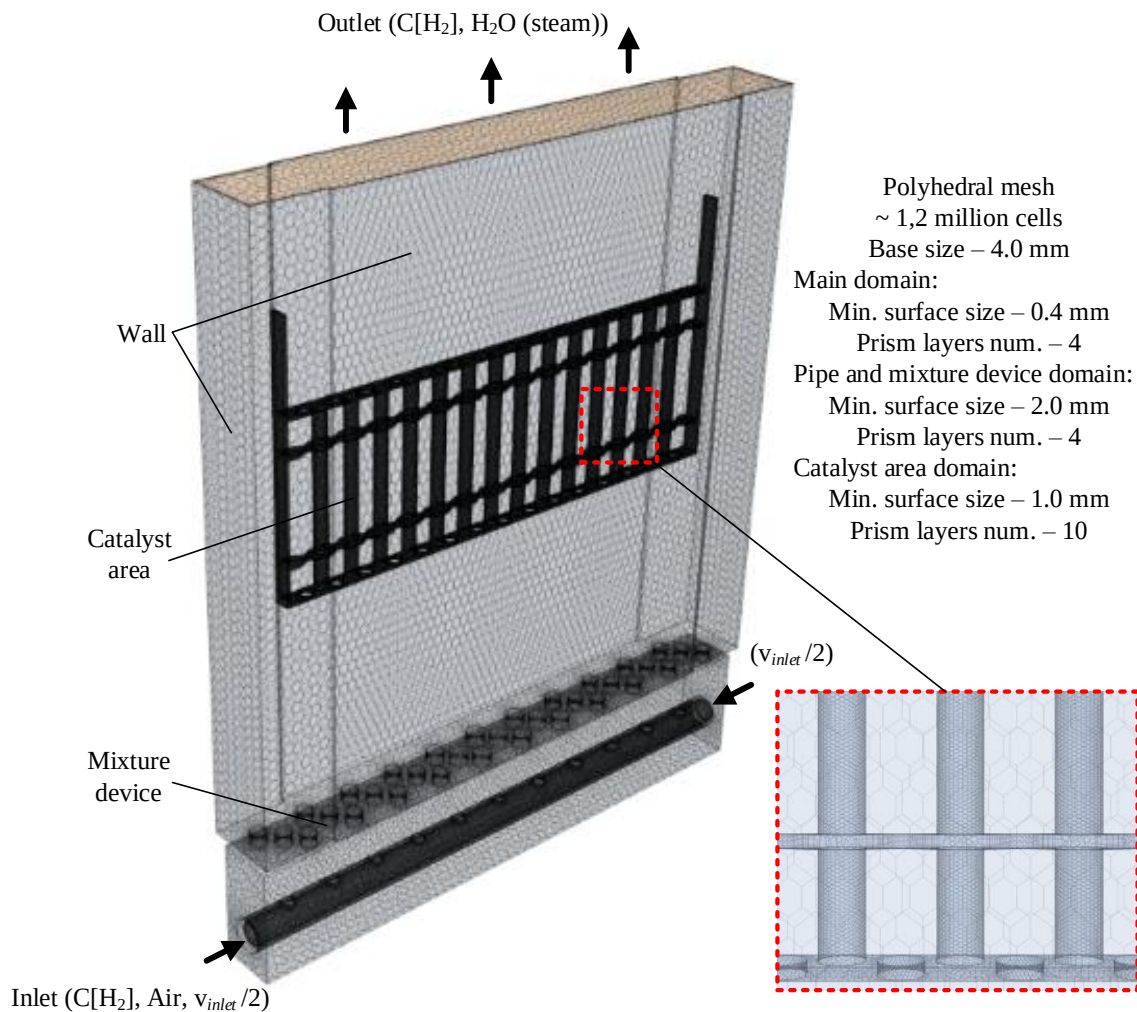


Figure 4-11: General view of the numerical mesh for the computational domain.

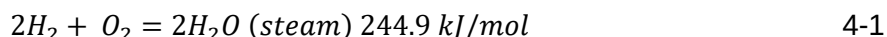
The mesh in the calculation zones here was refined by surface control and volumetric control. The cell size in the specific areas here was changed to 25% of the base cell size for the catalyst and 50% for the pipe and mixing device zones.

A denser mesh with a minimum surface size of 0.2 mm was also created to validate our calculations. This mesh consisted of ~ 3.1 million cells. The target surface size was 50% smaller,

while the number of cells was doubled. In this case, twice the amount of time was required for the same calculation. For a more accurate solution of the chemical process, 10 near-wall prism layers were generated near the catalyst zone. Calculations were performed for the set of parameters, as defined in Table 4-1. The steady-state model was used for all calculations in this model.

4.3.2 Reaction kinetics

The hydrogen oxidation (recombination) reaction is exothermic—energy is released.



There are two approaches to obtaining an estimate of the reaction rate: either obtaining a single-step reaction rate expression or a detailed chemical reaction mechanism. In reality, the hydrogen recombination is a multistep process (Rinnemo *et al.*, 1997; Appel *et al.*, 2002; Warnatz, *et al.*, 1990; Smith, *et al.*, 1999; Miller and Bowman, 1989; Mueller *et al.*, 1999). However, for some applications, it is really unnecessary to use the detailed mechanism of this reaction—the single-step overall reaction provides a reasonable explanation of some data. The single-step reaction (1) does not consider any of the intermediate reactions. The single-step reaction rate expression (2) was empirically derived by Schefer (Schefer, 1982).

$$K = 14 \times \exp\left(-\frac{16.1 \times 10^6}{R_u \times T}\right) \times C[H_2] \quad 4-2$$

Equation (2) is an Arrhenius-type equation with empirical parameters, where the pre-exponential factor is proportional to the hydrogen concentration.

The detailed chemical reaction mechanism includes at least 12 steps (Rinnemo *et al.*, 1997; Appel *et al.*, 2002; Warnatz, *et al.*, 1990; Smith, *et al.*, 1999; Miller and Bowman, 1989; Mueller *et al.*, 1999). It has been suggested (Prabhudharwadkar, *et al.*, 2011), and derived, that at low hydrogen concentration the detailed mechanism can be reduced to the single-step reaction with the following rate equation:

$$K = 4,695 \times T^{\frac{1}{2}} \left(\frac{C[H_2]^2}{C[O_2]} \right) \quad 4-3$$

where $C[H_2]$ is the molar concentration of hydrogen and $C[O_2]$ is the molar concentration of oxygen.

Analysis in (Prabhudharwadkar, *et al.*, 2011) compared empirical and single-step reaction mechanism and showed rather different numerical results for the recombination rate, even at low

inlet hydrogen concentration. In general, the recombination rate is defined by two factors: the reaction's kinetics and the diffusivity of components to the surface. The first is defined by the surface chemistry while the second is defined by the thermohydraulics of the whole environment. From this point of view then, it is more or less clear that the empirical expression (2) takes into account both of these processes. However, it is applicable only for the particular conditions for which this expression was derived. For example, it is known that the recombination rate is quite sensitive to the velocity of the inlet hydrogen–air mixture (Reinecke *et al.*, 2005). Thus, the applicability of this expression has to be verified for our particular case which means that numerical constants in this expression should be corrected.

On the other hand, the expression (3) is derived with the use of the multistep nature of the hydrogen recombination on the surface. But the environmental thermohydraulics is not taken into account which numerically means that the gas components appear immediately on the catalytic surface. Such an approach is not justified as the kinetic rates here are greater than the rates of hydrogen delivery to the catalytic surface and thus the last factor defines the recombination rate on the whole.

Based on the above, we found that only the multistep reaction model allows us to reproduce our experimental data with a minimum of errors. This comparison of single step against multi-step model has been conducted in (Prabhudharwadkar, *et al.*, 2011; Klauck *et al.*, 2014; Rozeń, 2015). The surface kinetic model and associated rate expressions are largely based on previous work on oxidation reactions over Pt. Table 4-2 (Appel *et al.*, 2002) summarizes the mechanism which was implemented in the present work model.

Table 4-3: Surface reaction mechanism of hydrogen oxidation on Pt.

	Reaction	pre-exponent, A (cm ³ mol s)	activation energy, E _A (J/kmol)	sticking coefficient, s
1	$\text{H}_2 + 2\text{Pt}^{(s)} \rightarrow 2\text{H}^{(s)}$	4.4579×10^{10}	-	0.046
2	$2\text{H}^{(s)} \rightarrow 2\text{H}^{(s)} + 2\text{Pt}^{(s)}$	3.7×10^{21}	6.74×10^7	-
3	$\text{O}_2 + 2\text{Pt}^{(s)} \rightarrow 2\text{O}^{(s)}$	1.8×10^{21}	-	0.023
4	$\text{O}_2 + 2\text{Pt}^{(s)} \rightarrow 2\text{O}^{(s)}$	0.023	-	0.070
5	$2\text{O}^{(s)} \rightarrow \text{O}_2 + 2\text{Pt}^{(s)}$	3.7×10^{21}	2.132×10^8	-
6	$\text{H}_2\text{O} + \text{Pt}^{(s)} \rightarrow \text{H}_2\text{O}^{(s)}$	0.750	-	0.750
7	$\text{H}_2\text{O}^{(s)} \rightarrow \text{H}_2\text{O} + \text{Pt}^{(s)}$	1.0×10^{13}	4.03×10^7	-
8	$\text{OH} + \text{Pt}^{(s)} \rightarrow \text{OH}^{(s)}$	1.0	-	1.0
9	$\text{OH}^{(s)} \rightarrow \text{OH} + \text{Pt}^{(s)}$	1.0×10^{13}	1.928×10^8	-
10	$\text{H}^{(s)} + \text{O}^{(s)} = \text{OH}^{(s)} + \text{Pt}^{(s)}$	3.7×10^{21}	1.15×10^7	-
11	$\text{H}^{(s)} + \text{OH}^{(s)} = \text{H}_2\text{O}^{(s)} + \text{Pt}^{(s)}$	3.7×10^{21}	1.75×10^7	-
12	$\text{OH}^{(s)} + \text{OH}^{(s)} \rightarrow \text{H}_2\text{O}^{(s)} + \text{O}^{(s)}$	3.7×10^{21}	4.82×10^7	-

4.3.3 Comparing experimental and numerical results

The most important characteristic of a PAR is its efficiency, that is, the possibility to recombine inlet hydrogen. Experimental and numerical results for outlet hydrogen concentration are given in Table 4-3. The outlet concentration is taken in the location of the upper sensor (see Figure 4-3). One can see that the experimental and numerical values are in good agreement. A maximum deviation of ~10% was observed for case no. 1. In this work, we did not estimate the experimental and numerical errors—it will be addressed in another study. The efficiency of recombination in this study is between 45 and 55% for the tested inlet hydrogen concentration.

Table 4-4: Experimental and numerical results for outlet hydrogen concentration.

Computational cases, no.	H ₂ inlet (bottom sensor) concentration C[H ₂], vol %	H ₂ outlet (top sensor) experimental concentration C[H ₂], vol %	H ₂ outlet (top sensor) computed concentration C[H ₂], vol %
1	2.0	1.01	0.92
2	3.0	1.42	1.35
3	4.0	1.82	1.82
4	5.0	2.14	2.24

The effectivity of recombination can be increased by increasing the mass flow of the hydrogen (Rinnemo *et al.*, 1997). In our case, the velocity in between the rods is quite low and we expect that, at higher velocity, the rate of recombination might be higher. It occurs if the regime of the

recombination is the diffusion one. In such a regime, the rates of chemical reactions are much higher than the rate of hydrogen delivery to the catalytic surface and characterised by a slow decrease in the hydrogen concentration from the interior to the surface (Frank-Kamenetskii, 1969). Figure 4-10 (a) shows such a distribution of the hydrogen concentration between two rods for three different heights from the bottom of the rods.

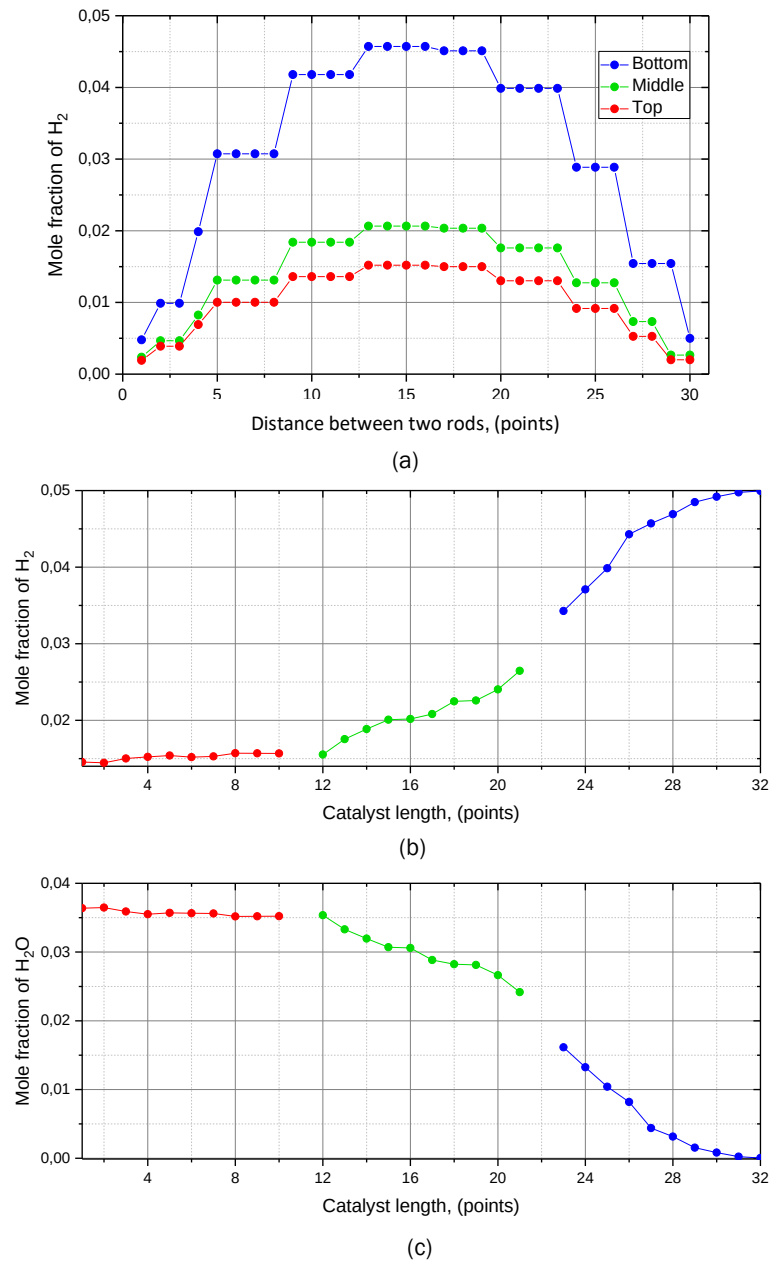


Figure 4-12: Calculated hydrogen distribution at 5 vol % of inlet hydrogen concentration: (a) between two central rods for three different heights along the horizontal axis; (b) along two central rods in the center; (c) calculated water distribution along two central rods in the center between them.

It is easy to conclude that the regime of recombination is deeply in a diffusion mode as the concentration slowly decreases from the center to the surface, which means that the hydrogen diffusion is rather ‘slow’. The other consequence is that the rod is not long enough to recombine all the incoming hydrogen. Figures 4-10 (b) and (c) show that the catalyst removes about two-thirds of the incoming hydrogen.

Figure 4-11 shows the calculated temperatures of the gaseous environment along the rods in between two central rods at 5 vol % of inlet hydrogen concentration. Numerical results shown in Figures 4-10 and 4-11 show that the recombination is more intensive on the lower half of the rods, due to more drastic temperature increase. The two local peaks identify closeness of the lower and upper metallic frames holding the rods together (Fig. 4-2).

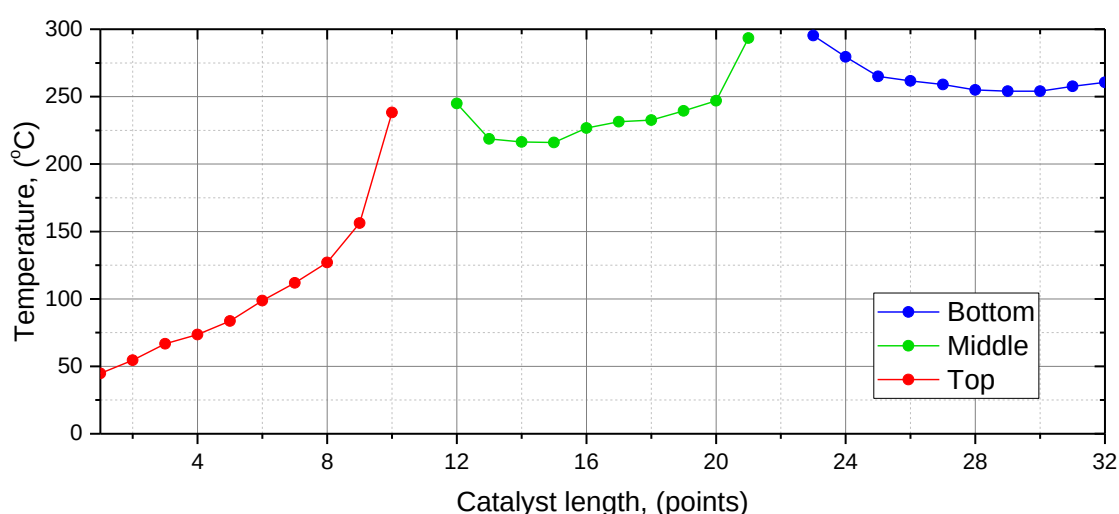


Figure 4-13: Calculated temperatures of the gaseous environment along rods in between two central rods at 5 vol% of inlet hydrogen concentration.

As we have only two hydrogen sensors in the experimental setup, another way in which we can verify our model, in support of such a hydrogen distribution and temperature distribution, is to compare experimental and numerical results for the temperatures of the rods. A comparison of these results is presented in Figures 4-12–4-17.

Figures 4-12–4-15 demonstrate the calculated temperature distribution (left panels) and photographs of IR images of the rods (right panels). Furthermore, Figure 4-14 shows a calculated distribution of hydrogen and water vapor. The largest difference between the temperatures is at the lower part of the rods; it decreases to about 45 °C, while the average temperature is about 170 °C. The highest temperature appears around the central part of the rods—it is about 275 °C

(the average from 5 to 10 rods). In addition, one can see that the central rods are slightly cooler than the edge rods. This may be related to the local velocity distribution (see Figure 4-8); the velocity in the central part is higher.

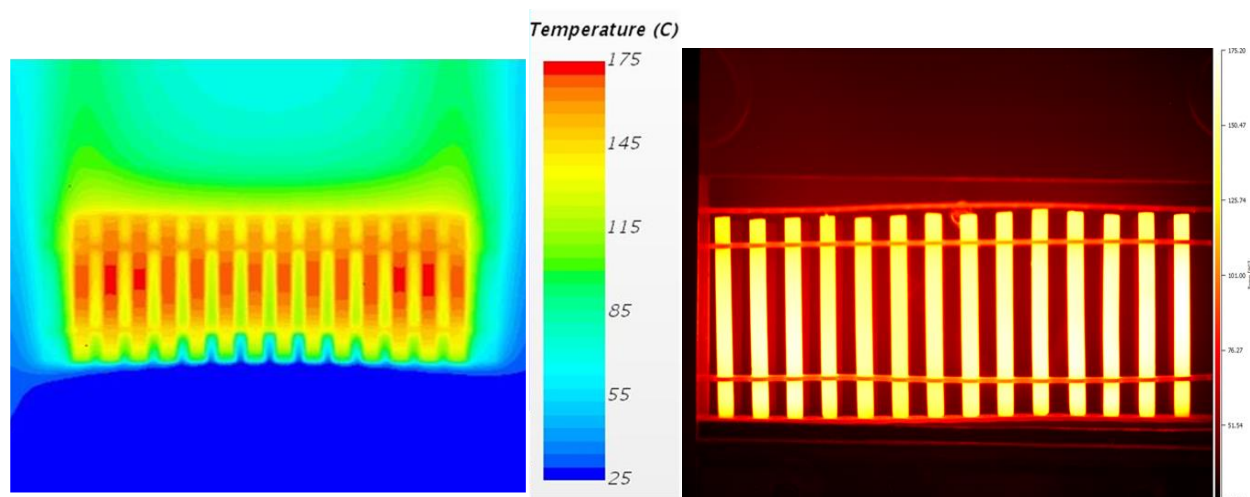


Figure 4-14: Comparison of catalyst temperature profile for case no. 1, $C[H_2] = 2$ vol %: calculated (STAR-CCM+) and experimentally measured (IR camera).

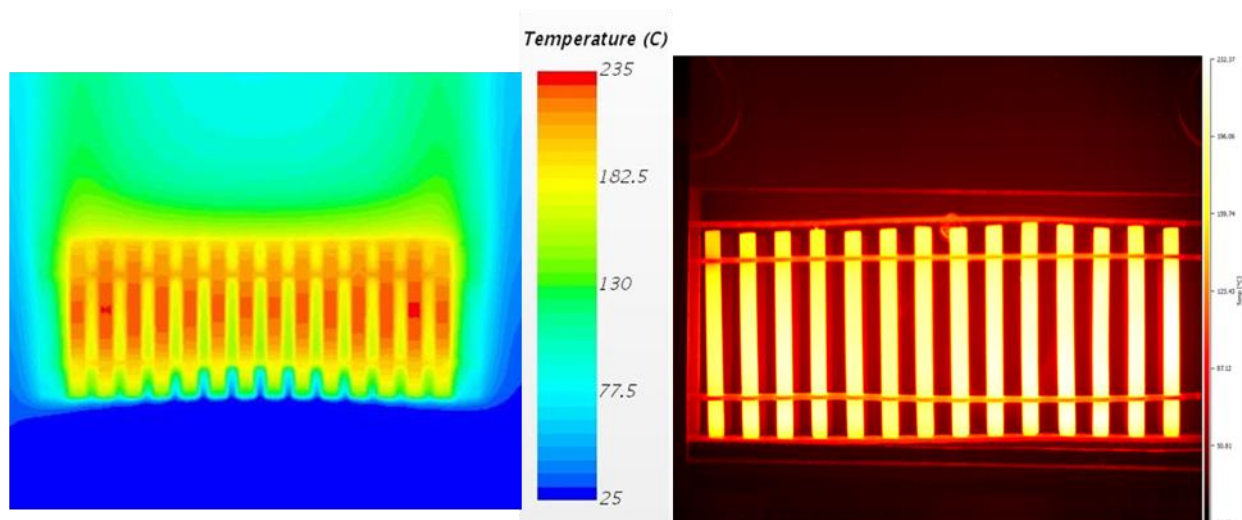


Figure 4-15: Comparison of catalyst temperature profile for case no. 2, $C[H_2] = 3$ vol %: calculated (STAR-CCM+) and experimentally measured (IR camera).

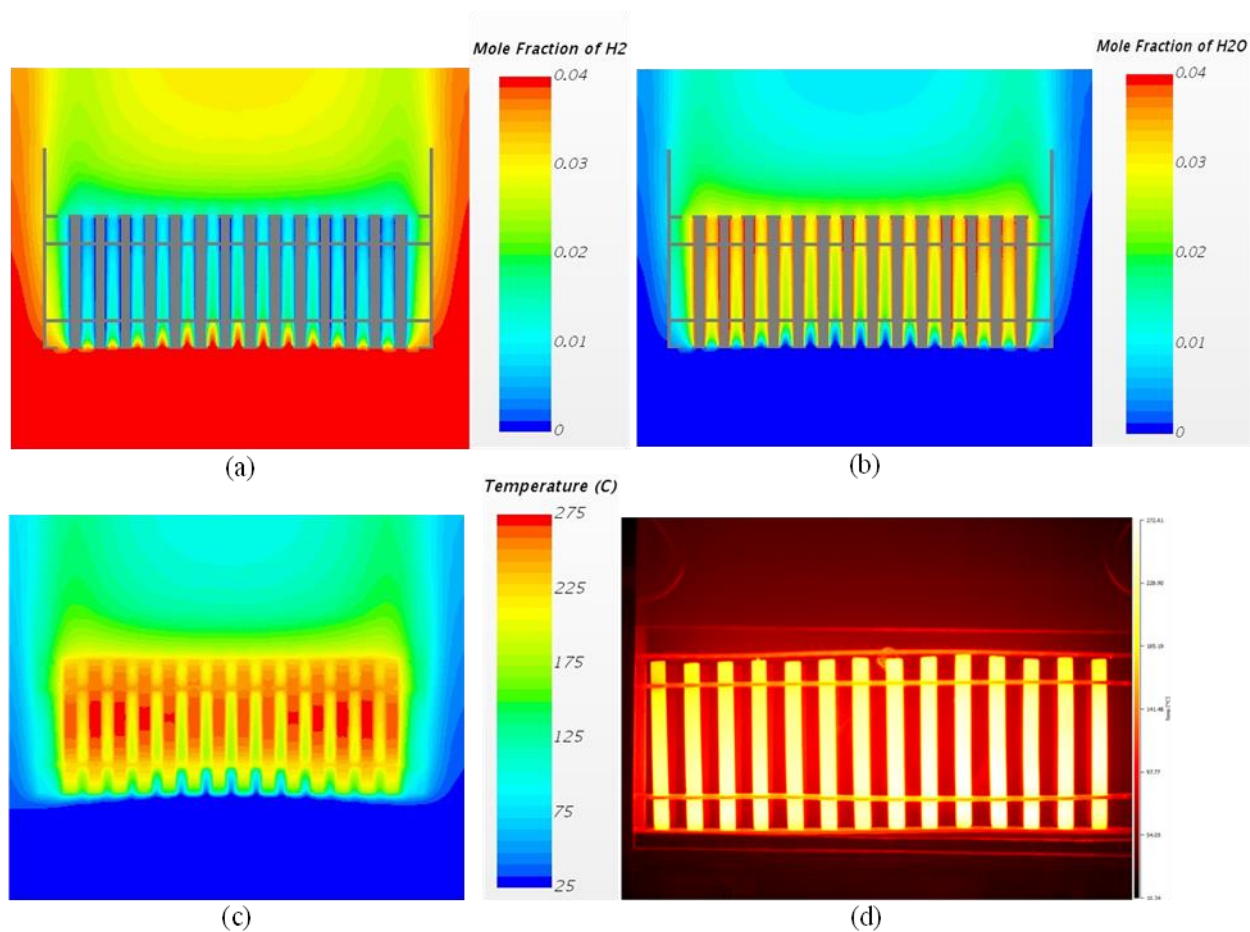


Figure 4-16: Calculated results for reactant and product concentrations (a, b) and comparison between calculated and experimental temperature profiles (c, d) for case no. 3, $C[H_2] = 4$ vol %.

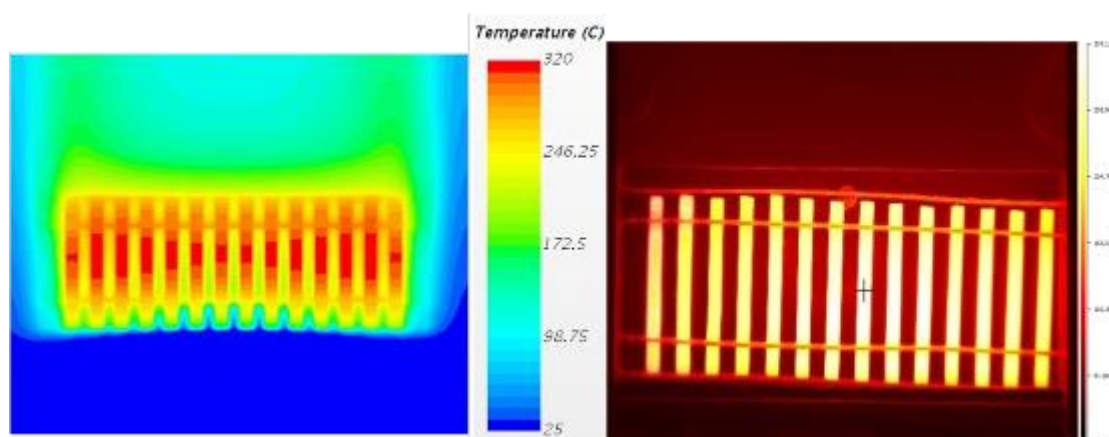


Figure 4-17: Comparison of catalyst temperature profile for case no. 4, $C[H_2] = 5$ vol %: calculated (STAR-CCM+) and experimentally measured (IR camera).

The case no. 3 ($C[H_2] = 4$ vol %) was selected for the presentation of numerical results for investigation of the catalytic section of the PAR with regards to the minimum ignition limit volume concentration of hydrogen in air. Figure 4-16 shows the numerical temperature distribution results for each of the 14 rods for case no. 3.

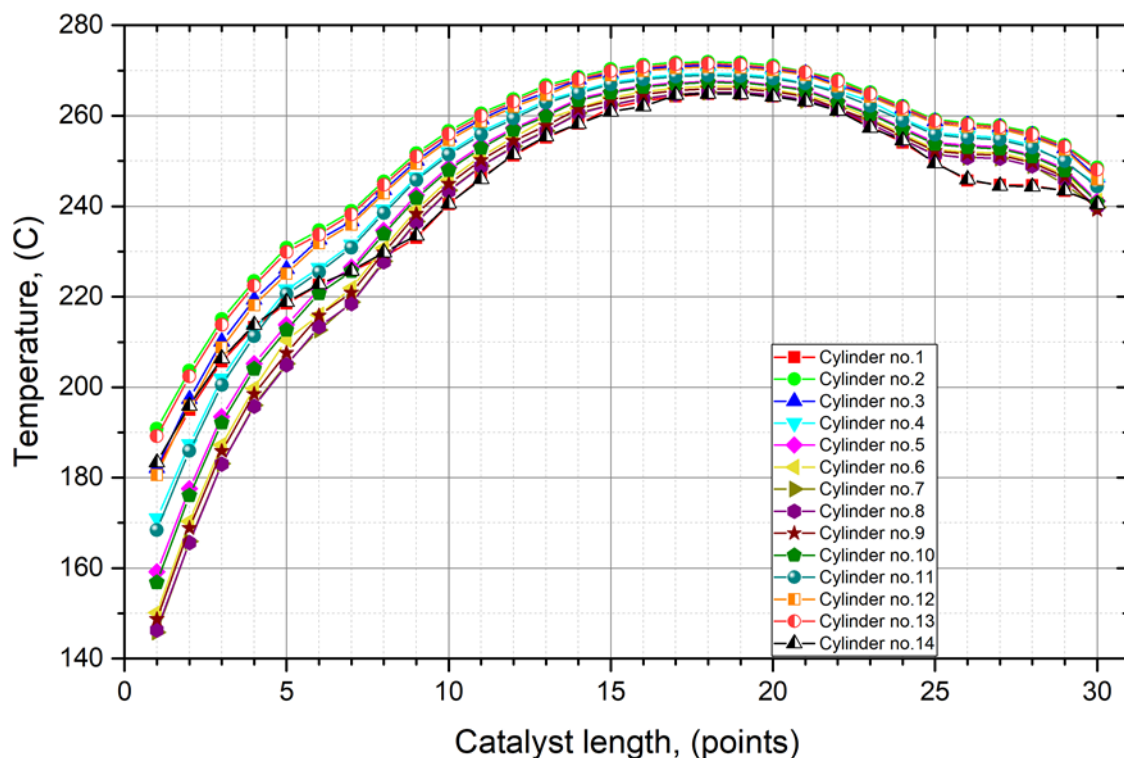


Figure 4-18: Calculated temperature distribution for each catalyst cylinder for case no. 3, $C[H_2] = 4$ vol %.

Figure 4-17 shows the average of numerical results (CFD) and experimentally measured (IR camera) rod temperature profiles for all cases. Deviation of the calculated temperatures from those experimentally measured did not exceed 10%. Such good agreement indicates that the calculated hydrogen distributions are quite close to reality.

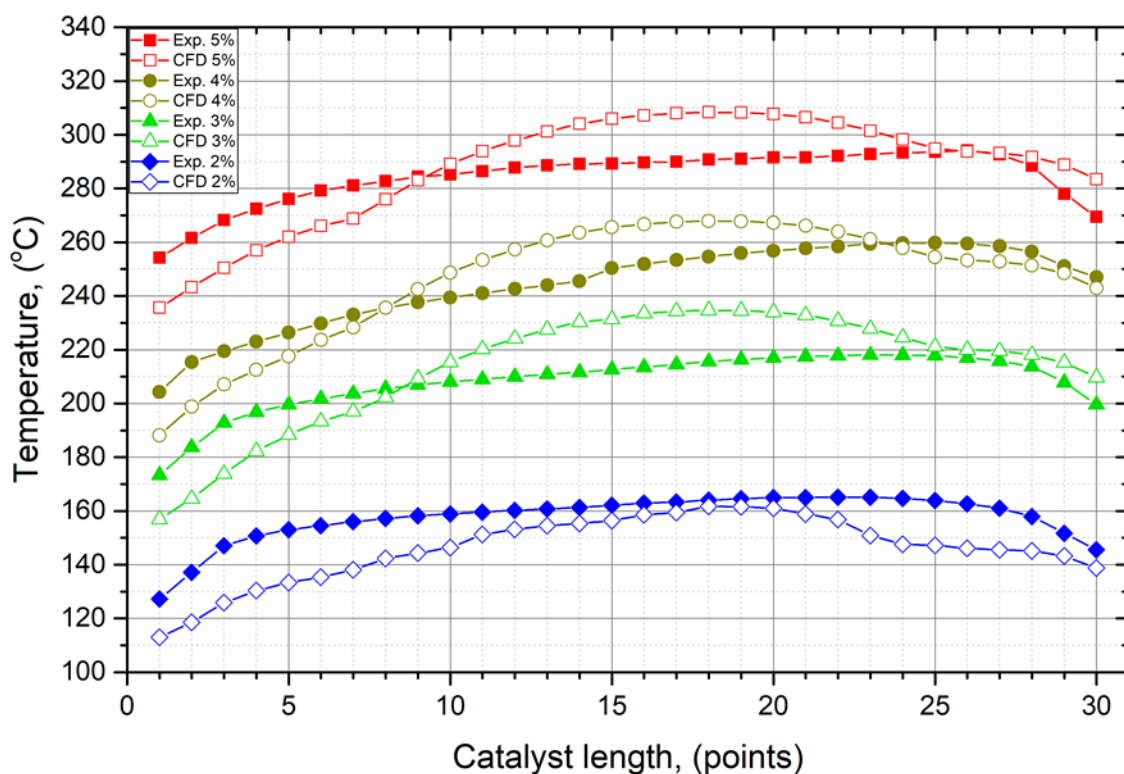


Figure 4-19: Comparison of the average of calculated (CFD) and experimentally measured (IR camera) catalyst temperature profile for all cases considered in this study.

A parameter that is quite important for our calculations is the catalyst site density. The site density is the number of available sites per unit area of the catalyst. Site density is a characteristic of a given catalyst material. The site density of pure Pt plate is taken as 2.7×10^{-8} kmol/m² (Rinnemo *et al.*, 1997; Appel *et al.*, 2002; Warnatz, *et al.*, 1990). This value is incorporated into the CHEMKIN package of the STAR-CCM+. It is quite clear that the catalyst used in the PAR may differ from other catalysts used to verify the database of the CHEMKIN package. Nonetheless, for our calculations, we decided not to vary this value—we elected to use it as such. Our calculations confirmed that such an approach was adequate to describe the experimental data here.

4.4 Conclusions

The catalytic element (frame with 14 catalyst rods) of the PAR was used to study the temperature distribution over catalyst rods and the effectiveness of hydrogen removal at low input hydrogen concentrations, that is, 2–5 vol %. Experimental data were obtained for the temperature of the

rods and the concentration of hydrogen at the outlet. The temperature in the experiment was measured with an IR camera. These data were compared with numerical CFD results making use of the STAR CCM+ package combined with the chemistry tools of CHEMKIN. The experimental and numerical results were in good agreement—hence, we consider that our numerical model has a rather high level of predictability—and can also be used for other catalyst geometries and input hydrogen concentration. In addition, we also investigated fatigued catalyst characteristics. The Pt-protecting layer decomposed during high-temperature combustion, the catalytic activity was maintained, and no Pt aggregation was observed.

Furthermore, our model can be used to predict the volume ignition of an air–hydrogen mixture at a higher input hydrogen concentration. Such investigation can be helpful with respect to safety to remove hydrogen from confined spaces where the hydrogen concentration is within the flammability range.

4.5 Acknowledgments

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CHAPTER 5: A THERMALLY CONDUCTIVE Pt/AAO CATALYST FOR HYDROGEN PASSIVE AUTOCATALYTIC RECOMBINATION

The research described in Chapter 5 has been conducted in an attempt to answer the scientific question that was defined in objective IV, “To apply and validate an innovative 3D CFD model of the catalytic hydrogen recombination process by conducting experiments in a small-scale PAR with an in-house developed Pt/AAO plate-type catalyst”. Only CFD related chapters have been written by the author.

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OVERVIEW

In this study, a Pt/anodized aluminum oxide (AAO) catalyst was prepared by the anodization of an Al alloy (Al6082, 97.5% Al), followed by the incorporation of Pt via an incipient wet impregnation method. Then, the Pt/AAO catalyst was evaluated for autocatalytic hydrogen recombination. The Pt/AAO catalyst's morphological characteristics were determined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The average Pt particle size was determined to be 3.0 ± 0.6 nm. This Pt/AAO catalyst was tested for the combustion of lean hydrogen (0.5–4 vol% H₂ in the air) in a recombiner section testing station. The thermal distribution throughout the catalytic surface was investigated at 3 vol% hydrogen (H₂) using an infrared camera. The Al/AAO system had a high thermal conductivity, which prevents the formation of hotspots (areas where localized surface temperature is higher than an average temperature across the entire catalyst surface). In turn, the Pt stability was enhanced during catalytic hydrogen combustion (CHC). A temperature gradient over 70 mm of the Pt/AAO catalyst was 23 °C and 42 °C for catalysts with uniform and nonuniform (worst-case scenario) Pt distributions. The commercial computational fluid dynamics (CFD) code STAR-CCM+ was used to compare the experimentally observed and numerically simulated thermal distribution of the Pt/AAO catalyst. The effect of the initial H₂ volume fraction on the combustion temperature and conversion of H₂ was investigated. The activation energy for CHC on the Pt/AAO catalyst was 19.2 kJ/mol. Prolonged CHC was performed to assess the durability (reactive metal stability and catalytic activity) of the Pt/AAO catalyst. A stable combustion temperature of 162.8 ± 8.0 °C was maintained over 530 h of CHC. To confirm that Pt aggregation was avoided, the Pt particle size and distribution were determined by TEM before and after prolonged CHC.

5.1 Introduction

In nuclear power plants (NPPs) and the mining industry, passive autocatalytic recombiners (PARs) are considered hydrogen (H₂) control systems for emergency gas removal based on their recombination with ambient oxygen. It is widely recognized that, in underground mines, the replacement of diesel-powered vehicles with H₂-fueled trucks will result in a cleaner environment for underground mineworkers. Water is the only byproduct of H₂ combustion/oxidation, instead of the otherwise harmful greenhouse gases (e.g., CO_x, CH₄) and NO_x generated during the combustion of hydrocarbon-based fuels. Furthermore, besides the gaseous exhausts, harmful pollutants and particulate matter form during incomplete combustion of diesel fuel hydrocarbons, which presents underground workers with further harmful exposure.

However, the utilization of H₂ in confined spaces is accompanied by the risk of accidental gas release and its accumulation. In NPPs, H₂ may be generated unintentionally as a result of the reactor fuel overheating and the chemical reaction of fuel rods' zirconium cladding with steam (Jae-Won Parka and Byung-Ryung Kohb, 2011). When the flammable concentration of H₂ (4–75 vol% in the air) accumulates, damage to/loss of structures and equipment and loss of life in mines and NPPs may occur during accidental combustion. Therefore, the issue of safety must be taken into account in the event of accidental H₂ release. PARs are considered to play a key role in accident mitigation in mines and NPPs.

A PAR is a safety device based on the idea of catalytic recombination of H₂ and O₂ according to the reaction:



PARs function without the requirement for an external power source. H₂ mitigation occurs spontaneously when the gas mixture reaches the catalyst surface. The air that contains H₂ enters at the lower end of a PAR, and exothermic reaction heat is formed as the H₂ is recombined. Natural convection forces airflow through the PAR. H₂ removal in PARs commences at nonflammable H₂ concentrations (1–2 vol%), thereby preventing the formation of explosive mixtures with the air. However, when a large amount of H₂ is released, as in the event of a severe accident, the recombiner can overheat due to the large exothermic effect. Therefore, the PAR itself may then become the H₂ ignition source.

The effect of thermal distribution throughout the PAR catalyst section on H₂ risk mitigation has been studied mainly by using numerical simulations, specifically, computational fluid dynamics (CFD) (Prabhudharwadkar, *et al.*, 2011; Malakhov, *et al.*, 2020). Results of studies have shown

that the thermal distribution over the catalytic surface plays an important role in risk mitigation related to the PAR autoignition. CFD modelling is widely recognized as a powerful numerical tool to analyze hydrogen safety issues. CFD simulations are generally in good agreement with experimental results and show a high level of predictability (Klauck *et al.*, 2014).

Catalytic hydrogen combustion (CHC) will likely play a key role in a hydrogen economy for safety purposes (in PARs) as well as for heating appliances (cooking and spatial heating). The reaction is relatively safe (no flashback phenomenon and NO_x emission, under certain conditions) and controllable (Bockris, 1982). Among the platinum group metals, Pt and Pd are considered to be the most suitable catalysts for CHC (Haruta and Sano, 1981, 1982; Haruta, *et al.*, 1982; Wierzbna and Depiak, 2004; Choi, *et al.*, 2008). They have also found diverse applications as catalytic materials, such as chemical and biosensing systems (Zaitsev, *et al.*, 2018; Melnikov, *et al.*, 2019; Alexandrovskaya, *et al.*, 2020), proton exchange membrane fuel cells (Gasteiger, *et al.*, 2005; Jung, *et al.*, 2014), electrochemical H₂ compressors (Rohland, *et al.*, 1998; Ströbel, *et al.*, 2002). When addressing research on CHC, it should be emphasized that the catalyst support significantly affects the activity of the catalytic system as it improves the dispersion of a reactive metal, affects the heat distribution throughout the catalyst surface, and prevents/limits catalyst deactivation (support degradation/reactive metal aggregation). As far as we could determine, catalyst supports, such as ceramics, metal oxides ZrO₂, TiO₂, SiO₂ (Hanson and Boudart, 1978; Haruta, *et al.*, 1982; Mercea, *et al.*, 1982; Inui, *et al.*, 1983; Choi, *et al.*, 2008; Deshpande and Madras, 2010), γ -Al₂O₃ washcoat (Kramer, *et al.*, 2002), SiC foam (Fernández, *et al.*, 2016; Fumey, *et al.*, 2018), and stainless steel mesh (SSM) (Du Preez, *et al.*, 2019) have been examined for CHC.

Kramer *et al.* studied PdOx and Pd catalysts supported on a γ -Al₂O₃ washcoat for CHC. They observed < 40% H₂ conversion at low inlet temperatures (<125 °C). Furthermore, there was an increase in H₂ conversion with an increase in the inlet temperature (100% conversion at 200 °C). Of importance here is that the presence of water vapor caused a reduction in H₂ conversion; furthermore, it was found that the lower the inlet temperature, the more significant was the effect of water vapor (Hanson and Boudart, 1978). These results of Kramer *et al.* could be expected, as the presence of water accelerates catalyst aggregation, hence reducing the catalytic activity (Bartholomew, 2001). In a study by Du Preez *et al.*, aggregation of Pt catalyst occurred on the SSM support during CHC at 420–520 °C. This occurrence was ascribed to the fact that the SSM surface allows significant Pt mobility at high temperatures. However, these authors demonstrated that calcination of the SSM support at 500–1000 °C resulted in the stabilization of Pt particles, effectively preventing their aggregation during CHC (Du Preez, *et al.*, 2019).

Deshpande and Madras compared the use of ZrO_2 and TiO_2 as supports for Pt and Pd catalysts for CHC. The activity of the Pt and Pd catalysts was found to be higher with TiO_2 support than with ZrO_2 ; complete conversions of H_2 over TiO_2 supported catalysts were obtained at a temperature of 100 °C (Deshpande and Madras, 2010). Hanson and Boudart studied the reaction between H_2 and O_2 over Pt/ SiO_2 catalyst in excess H_2 and excess O_2 . The catalyst with smaller Pt particles (higher catalyst dispersion) exhibited higher catalytic activity in excess H_2 ; the catalytic activity was almost independent of Pt particle size in excess O_2 (Hanson and Boudart, 1978). They then proposed that the latter observation can be related to the passivation/deactivation of the catalytic surface in excess of O_2 , especially in the case of smaller Pt particles. It was noticed that smaller Pt particles had higher O_2 adsorption capacity, which resulted in the formation of Pt oxide. In turn, the presence of Pt oxide decreased the H_2 combustion reactivity.

The use of SiC as catalyst support for CHC has been reported (Fernández, *et al.*, 2016; Fumey, *et al.*, 2018). In a study by Fernández *et al.*, the SiC support was found to be an appropriate material for the design of heating devices due to its high thermal conductivity (Fernández, *et al.*; 2016). The ability of catalyst support to dissipate/distribute heat is of critical importance when a catalytic system is employed for heating purposes. For example, the formation of hotspots (areas where localized surface temperature is higher than an average temperature across the entire catalyst surface) can be avoided if the catalyst support provides a uniform temperature distribution throughout the catalytic surface. Schefer *et al.* found that the presence of hotspots can result in H_2 ignition if its autoignition temperature is exceeded (Schefer, *et al.*, 1980). Fumey *et al.* employed SiC foam with Pt coating as a catalyst for a catalytic burner, suitable for domestic cooking use. They found a uniform catalytic reaction of H_2 combustion with a burner surface temperature <715 °C at an H_2 flow rate of 5–15 Nl/min. The burner could achieve temperatures exceeding that of the H_2 ignition temperature (>585 °C) due to specialized burner design. The layered structure and alternation of SiC foam discs (diffuser and catalytic disks) allowed the controlled H_2 ignition in an air atmosphere between disks, allowing burner surface temperatures >585 °C (Fumey, *et al.*, 2018).

In a recent study, in their preliminary investigations, Kozhukhova *et al.* found the Al/AAO support to be suitable as catalyst support for CHC purposes. The Pt/AAO catalyst was found to be highly stable over a prolonged CHC reaction time of 530 h. The stabilization of Pt particles was achieved, possibly due to the high thermal conductivity of the Al/AAO system. The heat produced during CHC was displaced from the AAO to the Al core, and a mild average catalyst surface temperature was achieved, which most likely limited Pt aggregation (Kozhukhova, *et al.*, 2020).

In the present work, we now demonstrate the use of Pt/AAO as a catalyst in an in-house developed recombiner section testing station. The design of the testing station allows for the characterization of the thermal distribution of the catalyst section under conditions similar to those in real-world PAR applications (Malakhov, *et al.*, 2020). The Pt/AAO catalyst performance was determined for CHC using lean H₂ mixtures (0.5–4 vol% H₂). The utilization of the Pt/AAO catalyst for PAR application is a prospective solution for low thermal conductive catalysts currently used in commercial PARs. Moreover, cheap Al alloy used as a substrate material for catalyst support preparation affords significant cost savings when compared to ceramic support materials. Therefore, the catalyst cost reduction along with the increase in its performance may afford a widespread penetration of PAR technology.

The temperature distribution across the catalytic surface during CHC was determined using an infrared (IR) camera. Structural and chemical characteristics of the catalyst and catalyst support were determined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A numerical model was created in STAR-CCM+ in combination with the chemistry tools of CHEMKIN to investigate temperature distribution throughout the Pt/AAO catalyst and to compare it with the experimental data (CD-adapco, 2017).

5.2 Results and Discussion

5.2.1 Catalytic Test in the Recombiner Section Testing Station

Preliminary work by Kozhukhova *et al.* showed the potential of an AAO as suitable catalyst support for CHC purposes (Kozhukhova, *et al.*, 2020). The high thermal conductivity of an Al/AAO system afforded a mild average surface temperature throughout the catalyst surface that likely prevented catalyst deactivation during CHC. Moreover, due to the AAO's structural features (hexagonally organized array of pores) and the high dispersion of the reactive metal (Pt), catalysts with high catalytic activity are obtained. In addition, the Al6082 alloy used in the present study is inexpensive and can be machined to any shape before the anodization, affording such a catalyst with a wide variety of practical applications. Therefore, the use of AAO as catalyst support affords not only significant cost savings (compared to the expensive ceramic catalyst support currently used in commercial PARs) but provides high catalytic activity and stability that extends the operation time of such a catalytic system.

The AAO morphology, and Pt particle size and morphology, were determined before CHC procedures. Figure 5-1 shows representative bright-field and high-resolution TEM (HRTEM) images of the Pt/AAO catalyst.

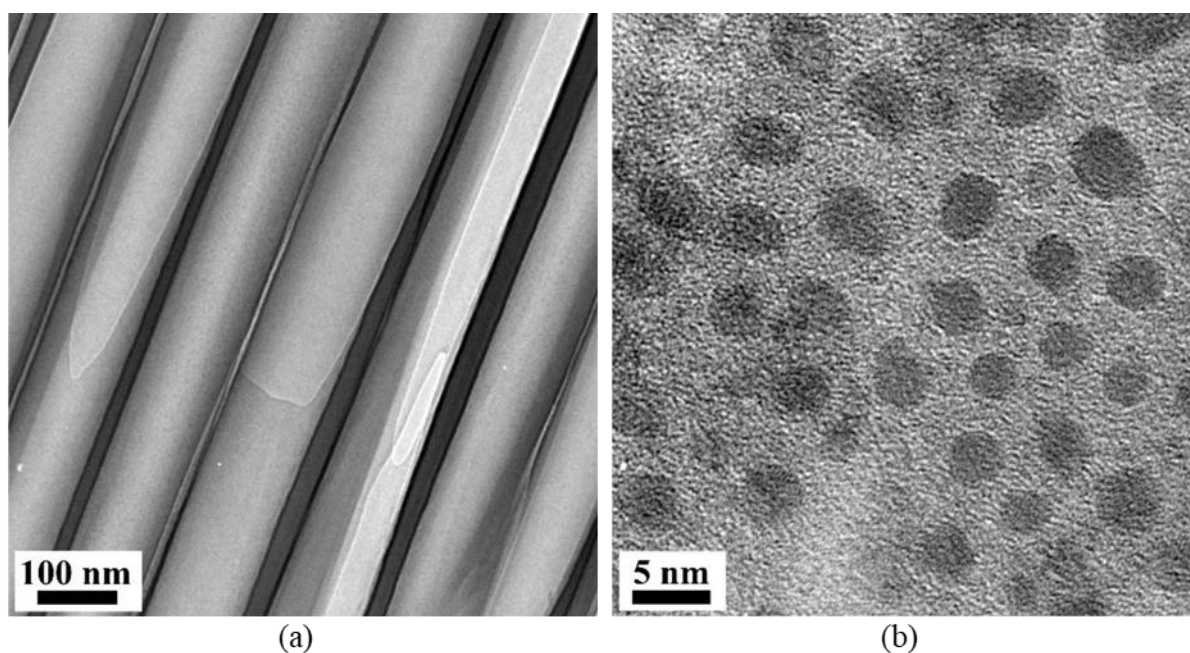


Figure 5-1: Pt/AAO catalyst before catalytic hydrogen combustion (CHC): (a) TEM bright-field image of cross-sectioned AAO pore channels; (b) HRTEM image of inter-pore-channel Pt particles.

Figure 5-1a shows the nanopore walls and channels of the Pt/AAO catalyst and suggests that the pores were tubular and relatively well constructed. Figure 6-1b shows that Pt particles are present within the AAO channels. Particle size measurements were carried out over several TEM images taken of different areas of a FIB lamella. The average diameter of Pt particles for the Pt/AAO catalyst was 3.0 ± 0.6 nm.

CHC over the prepared Pt/AAO catalyst was studied in the recombiner section testing station at a 3 vol% H_2 concentration, at a gas mixture flow velocity of 9.5 m/s. Five Pt/AAO catalysts (prepared similarly) were placed inside the testing station constituting the catalyst section. During CHC procedures, thermal measurements of each catalyst were recorded every 1 s. The CHC tests were repeated in triplicate, and the standard deviation was calculated for each catalyst. There was a period of seven days between each repetition. During these aging periods between tests, catalysts were kept in the ambient atmosphere to investigate the behavior of the catalyst under conditions comparable to real-world PARs. The aging procedure was assumed to have a detrimental effect on the catalyst due to passivation by O_2 and fouling. Poisoning by oxidants may cause changes in the oxidation state of the active catalyst and, hence, decrease the catalytic activity of the catalyst (Bartholomew, 2001). Hanson and Boudart observed that the passivation

of Pt catalysts in excess O₂ at low temperatures (0–100 °C) resulted in a loss in catalytic activity (Hanson and Boudart, 1978). Ostermaier et al. reported the deactivation of a Pt/Al₂O₃ catalyst due to the formation of Pt oxide in an O₂ atmosphere (Ostermaier, *et al.*, 1976). The deactivation of the catalyst was studied at temperatures of 95–200 °C. Deactivation was found to have a greater effect at low temperatures on catalysts with smaller Pt particles. Another important issue to consider is the inevitable dry deposition of fine solid material (dust) from the ambient atmosphere onto the catalysts used in PAR devices. This occurrence is referred to as fouling and prevents H₂ from accessing the reactive sites of a catalyst (Bartholomew, 2001). Figure 5-2 shows average combustion temperature profiles for five catalysts for 1 h of CHC.

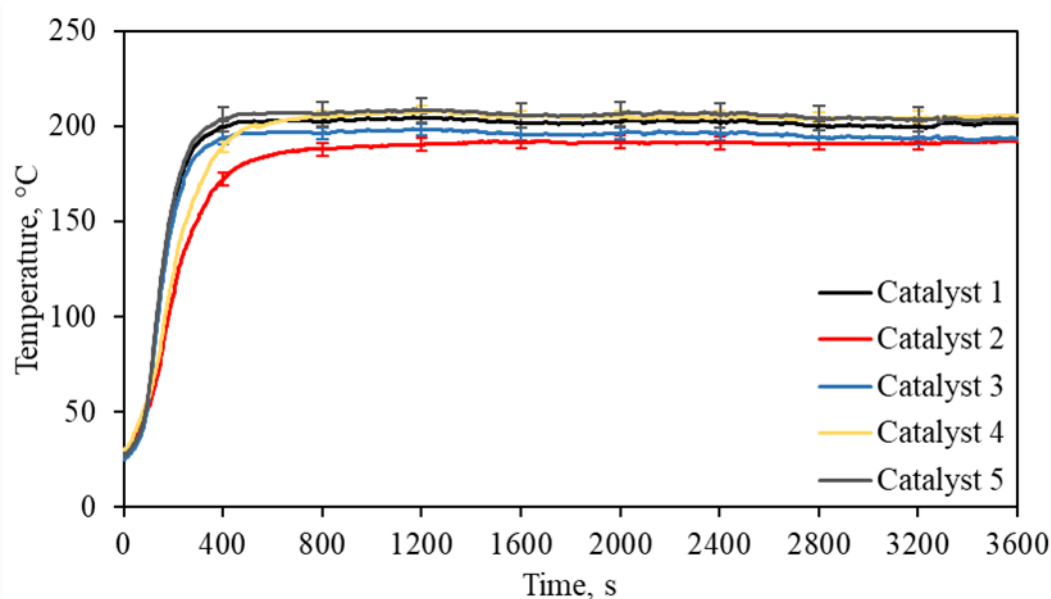


Figure 5-2: Combustion temperature profiles of Pt/AAO catalysts for 1 h of combustion at 3% H₂ volume fraction in air.

Figure 5-2 shows a steady increase in catalyst temperature for each catalyst during the first 400 s of CHC. Here, CHC was initiated spontaneously at room temperature (26–28 °C). The average combustion temperature was calculated for each catalyst based on three repeats. Stable combustion temperatures of 201.5 ± 2.6 , 191.0 ± 3.3 , 195.3 ± 3.3 , 205.1 ± 3.1 , and 204.9 ± 6.5 °C were reached for the catalysts 1–5, respectively. Considering that a relatively consistent average combustion temperature was achieved for each catalyst per test and that the CHC reaction initiated spontaneously suggests that the catalysts maintained their catalytic activity. The latter observations may be ascribed to the fact that the AAO support promotes the stabilization of Pt particles at the temperatures, as shown in Figure 6-2 (Kozhukhova, *et al.*, 2020). Furthermore, the spontaneity of the reaction suggests that the catalyst preparation method yielded samples

with relatively similar CHC reaction kinetics. It is also interesting to note the detrimental effects of catalyst exposure to ambient conditions during the periods between the tests (i.e., deactivation by ambient oxygen). An important perspective is to also determine the effect of prolonged exposure to air (several months) on the catalytic activity of Pt/AAO catalysts.

To characterize the Pt/AAO catalyst from a kinetic point of view, a series of experiments were carried out at the initial volume fraction of H_2 in air ranging from 0.5 to 4.0 vol% (0.132–1.031 mmol/s, respectively). The conversion and combustion temperature were measured at an inlet flow velocity of 9.5 m/s H_2 /air. Close to 100% H_2 conversions were observed for the initial H_2 volume fractions of >4 vol%. (H_2 volume fractions of >4 vol% were, therefore, not considered here.) Figure 3 shows the differences between the catalyst temperature before exposure to H_2 /air mixture ($T_{initial}$) and after achieving steady-state conditions (T) (primary y-axis). The conversion of H_2 at the various initial molar fractions of H_2 is shown on the secondary y-axis. The initial temperatures of the catalyst were in the range 29–30 °C. For simpler comprehension of further results, the temperature and initial concentration of H_2 are presented in Arrhenius equation units.

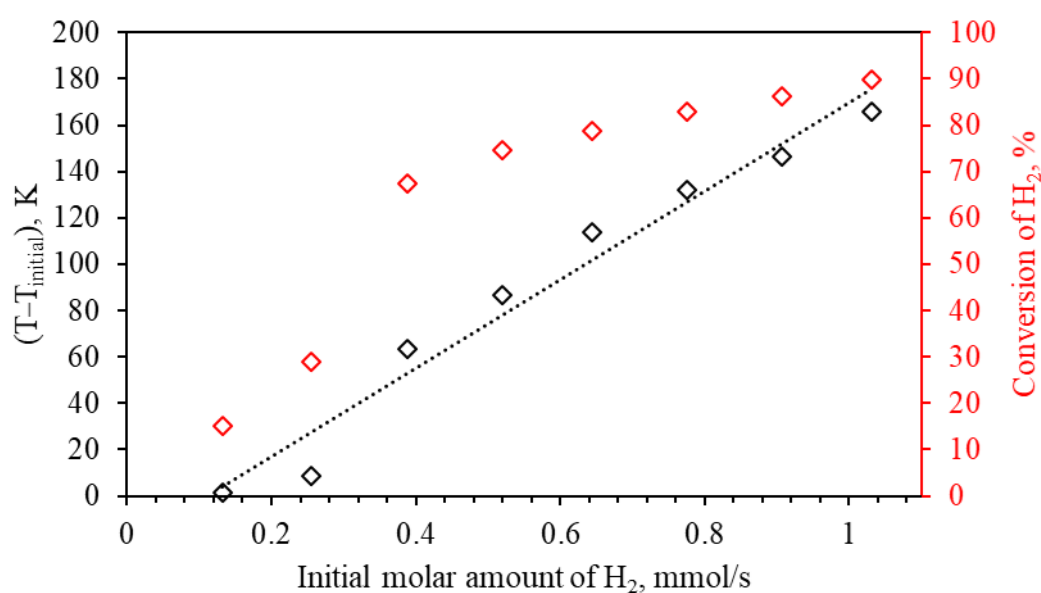


Figure 5-3: Catalyst surface temperature differences between initial temperature and temperature at steady-state conditions ($T - T_{initial}$, primary y-axis) and conversion of H_2 (secondary y-axis) as a function of the initial molar amount of H_2 in air.

As is evident in Figure 5-3, the temperature of the catalyst at steady-state increased linearly with an increase in the initial molar amount of H_2 , which is in agreement with the results obtained by

Nguyen et al. (Nguyen, *et al.*, 2018). Figure 5-3 further shows that the conversion of H₂ is dependent on the initial amount of H₂. The H₂ conversion increased from 15% to 90%, with an increase in the initial amount of H₂. The maximum H₂ conversion of 90% was obtained at the highest initial molar amount of H₂ in air. The data obtained was used to determine the activation energy (E_a) of CHC on the Pt/AAO catalyst.

Due to the high exothermicity of the CHC reaction, the performance of the experiment under isothermal conditions is problematic and inconvenient. Therefore, in this work, the data obtained under adiabatic conditions were used to determine the reaction kinetics of the CHC reaction. According to Nguyen et al., the transformation of adiabatic data to isothermal is possible (Nguyen, *et al.*, 2018).

Figure 5-4a shows the change in the relative H₂ fraction overtime during CHC at constant temperatures. The Arrhenius plot is shown in Figure 5-4b. Figure 5-4a shows that the relative fraction of H₂ dependence as a function of time gives an exponential function at different constant temperatures (except in the case of 311 K), thus corresponding to a first-order reaction. The latter observation corresponds with those made by Nguyen et al. and Hanson and Boudart (Hanson and Boudart, 1978; Nguyen, *et al.*, 2018). The rate constant can then be calculated as follows (Nguyen, *et al.*, 2018):

$$\ln(\chi_{H_2,0}) - \ln(\chi_{H_2}) = k\tau \quad 5-2$$

$$k = (\ln(\chi_{H_2,0}) - \ln(\chi_{H_2}))/\tau \quad 5-3$$

where τ is the time required to reach a stable combustion temperature, $\chi_{H_2,0}$ and χ_{H_2} are the H₂ compositions at $\tau = 0$ and time required to reach steady-state conditions (τ), respectively.

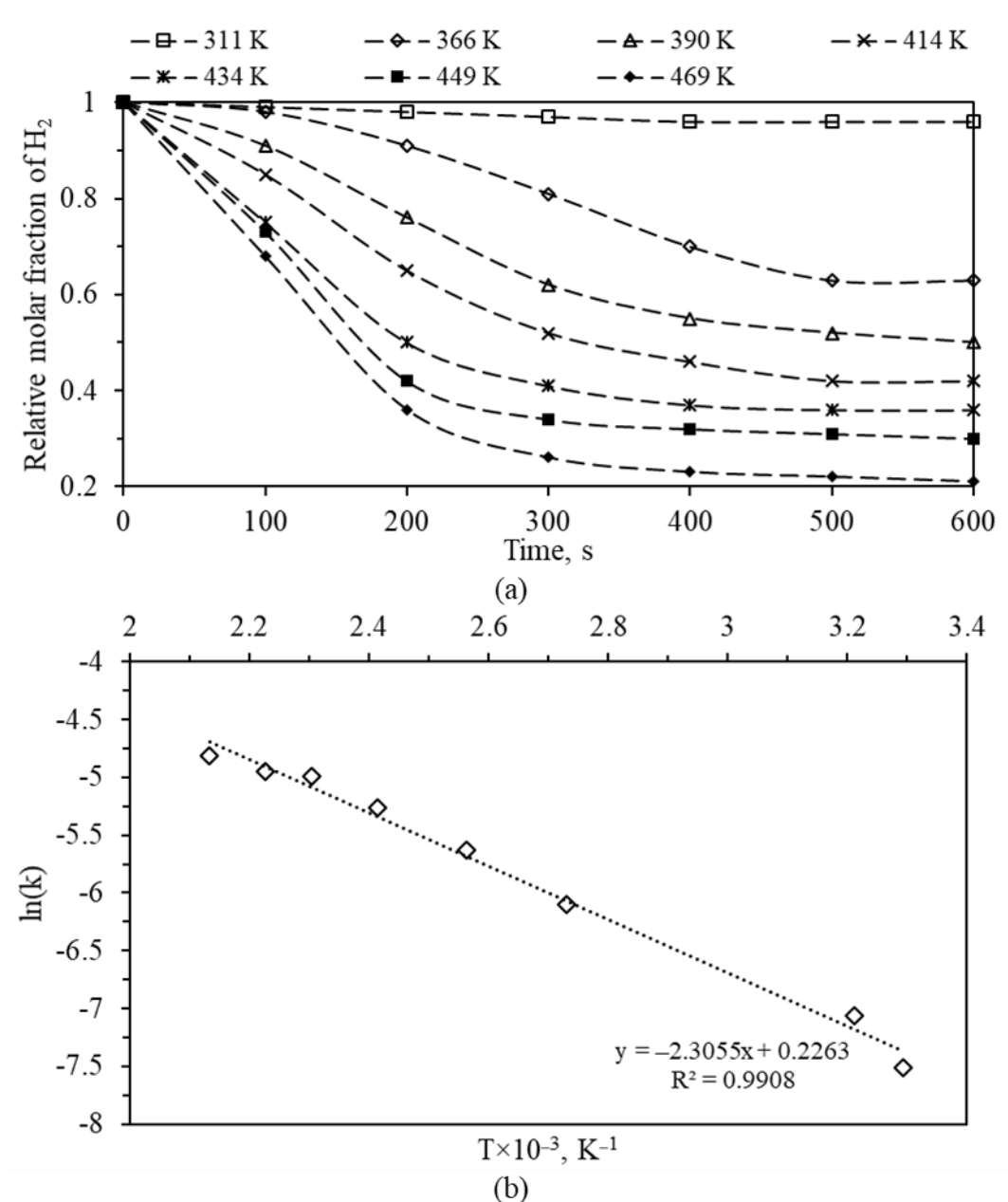


Figure 5-4: (a) Relative molar fractions of H_2 as a function of time at constant temperatures under steady-state conditions; (b) Arrhenius plot for CHC on the Pt/AAO catalyst.

Figure 5-4b shows that the temperature dependence of the reaction rate represents a linear function. The E_a calculated from the data presented in Figure 5-4b is 19.2 kJ/mol. A similar E_a value of 22.3 kJ/mol for CHC on a Pt/AAO catalyst has been reported by Joshi *et al.* (Joshi, *et al.*, 2011). However, the E_a value of various catalytic systems used for CHC can range from 7 to 46

kJ/mol. For instance, a $\text{Co}_3\text{O}_4/\text{Cr}_2\text{O}_3$ catalyst has an E_a of 10.3 kJ/mol (Younis, 2006), whereas a Pt/washcoat catalyst has an E_a of 8.7 kJ/mol (Bhatia, *et al.*, 2009). For CHC using a Pt/ SiO_2 catalyst, Hansen and Boudart reported an E_a of 7.5 kJ/mol and 46 kJ/mol in excess of O_2 and H_2 , respectively (Hanson and Boudart, 1978). Meanwhile, Fernández *et al.* reported an E_a of 35 kJ/mol for a Pt/SiC catalyst with an excess of O_2 (Fernández, *et al.*, 2016). Joshi *et al.* studied catalytic kinetics of the oxidation of a lean H_2 /air mixture on a Pt/ Al_2O_3 washcoat monolith catalyst at low temperatures ($<90^\circ\text{C}$) and determined the effect of aging space velocity and temperature (Joshi, *et al.*, 2011). They reported an E_a of 45 kJ/mol for the freshly prepared catalyst and 22.3 kJ/mol for a catalyst aged at 800°C for 1.5 h. In summary, the E_a of a specific catalyst for CHC is strongly dependent on the catalyst support, reactive metal loading, and experimental conditions. The E_a value reported here coincides with values reported in the literature.

5.2.2 Effect of the Support Structure on Catalyst Performance

It is generally accepted that the structure of the AAO support has an appreciable effect on the catalytic performance of a Pt/AAO catalyst. AAO formed on a high purity Al substrate can represent an ideal hexagonally organized structure reminiscent of a honeycomb assembly. Due to regularly organized pore distribution and parallel pore channel arrangement, the AAO support offers advantages for high catalyst dispersion, heat, and mass transfer (Rui, *et al.*, 2012; Rui, *et al.*, 2014). When lower purity Al is used as a substrate for the catalyst support, the formation of the AAO layer with ordered pore arrangement is confounded by the presence of impurities. Impurities cause nonuniform localized electric field flow at the AAO/electrolyte boundary during anodization due to differences in resistivity (Chung, *et al.*, 2011; Ostermaier, *et al.*, 1976; Chung, *et al.*, 2017). As a result, pits and hillocks, branched pores, nanowires, and other imperfections are formed on and within the AAO layer. The presence of AAO layer imperfections may adversely affect the catalytic activity of an AAO supported catalyst, decreasing the active surface area and the reactive metal dispersion and particle size distribution.

To investigate the effect of the AAO support structure on the catalytic performance in CHC, the Al substrate was exposed to a 4 h anodizing procedure. This anodization time of 4 h was chosen to intentionally form nanowires on the Al surface (Ostermaier, *et al.*, 1976). Figure 5-5 shows representative SEM micrographs of the AAO samples prepared by 1 h and 4 h anodization.

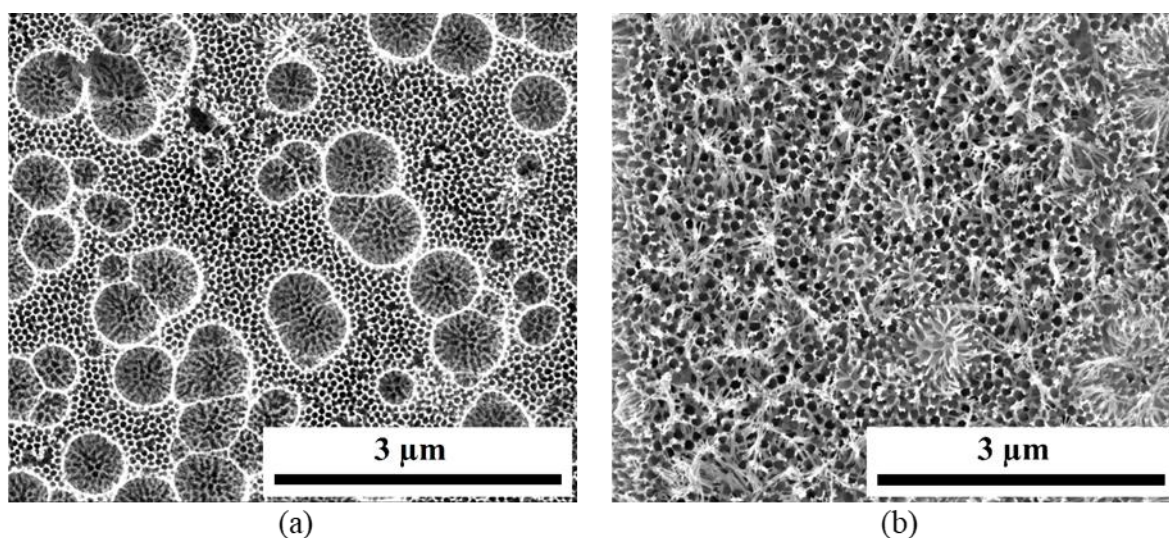


Figure 5-5: SEM micrographs of AAO samples prepared by 1 h (a) and 4 h (b) anodization.

Figure 5-5a shows that the 1 h AAO layer had a relatively ordered pore distribution, but pits were present. The 4 h AAO layer presented in Figure 5-5b underwent extensive AAO dissolution during prolonged anodization, and nanowires formed throughout the AAO layer surface. Although the AAO layer presented in Figure 5-5b did not maintain the hexagonal structural integrity, nanowires are assumed to increase the active surface area after catalyst deposition due to the large exposed surface area. The morphological characteristics of the samples were determined over several SEM images using ImageJ software (National Institutes of Health (NIH), Bethesda, MD, USA). Results are presented in Table 5-1. The D_p and D_c were determined manually, and the areas where the pits (Figure 5-5a) and nanowires (Figure 5-5b) occurred were excluded from the calculations of the average values.

Table 5-1: Morphological characteristics (D_p , D_c , n , and P) of AAO samples.

Time of second anodization step (h)	D_p (nm)	D_c (nm)	n , (pores/ μm^2)	P
1	55.7 ± 5.7	79.5 ± 11.0	193	48
4	86.9 ± 9.5	121.0 ± 188.8	85	52

D_p —diameter of pores. D_c —interpore distance. n —pore density. P —porosity

Table 5-1 shows that the 1 h AAO sample had a D_p of 55.7 nm compared to a D_p of 86.9 for the 4 h AAO sample. The D_c of samples increased from 79.5 nm to 121.0 nm with increasing anodization time from 1 h to 4 h. The increase in D_p and D_c may be ascribed to AAO layer dissolution during prolonged anodization and extensive acidic exposure of the sample (Ostermaier, *et al.*, 2011; Nguyen, *et al.*, 2018; Kozhukhova, *et al.*, 2020). The n value decreased from 193 to 85 pores/ μm^2 for AAO samples prepared by 1 and 4 h anodization, respectively. The decrease in n is likely also caused by layer dissolution during anodization. The thinnest pore walls will undergo dissolution until they are completely dissolved, which causes pores to merge. The latter results in an increase in the D_p of pores and, consequently, a decrease in the number of pores. Table 1 further shows that P remained relatively unchanged. This could be expected, as P is defined as a ratio of D_p to D_c ; both D_p and D_c increased, at a similar rate, with an increase in the anodization time. Generally, the morphological characteristics of the catalyst support affect the particle size distribution of the supported reactive metal, its dispersion, mass transfer rates, and, in turn, the catalytic activity (Hanson and Boudart, 1978; Khodakov, *et al.*, 2002). For instance, Khodakov *et al.* showed a direct correlation between catalyst support pore size and Co_3O_4 particle size and correlation for a wide variety of mesoporous silica supports (Khodakov, *et al.*, 2002).

Pt/AAO samples were prepared using the 1, and 4 h anodized supports and their catalytic activities were compared. The catalytic activity tests were performed in the recombiner section testing station at a 3 vol% H_2 concentration in air. The CHC tests were performed in triplicate, with seven days between each repetition, i.e. Test 1 is the original test, Test 2 is the test after seven days, and so though. The average combustion temperature profiles for the 4 h AAO catalysts are presented in Figure 6. The average combustion temperature of the 1 h AAO catalysts presented in Figure 5-2 is included in Figure 5-6 (red dashed line) and serves as a reference value.

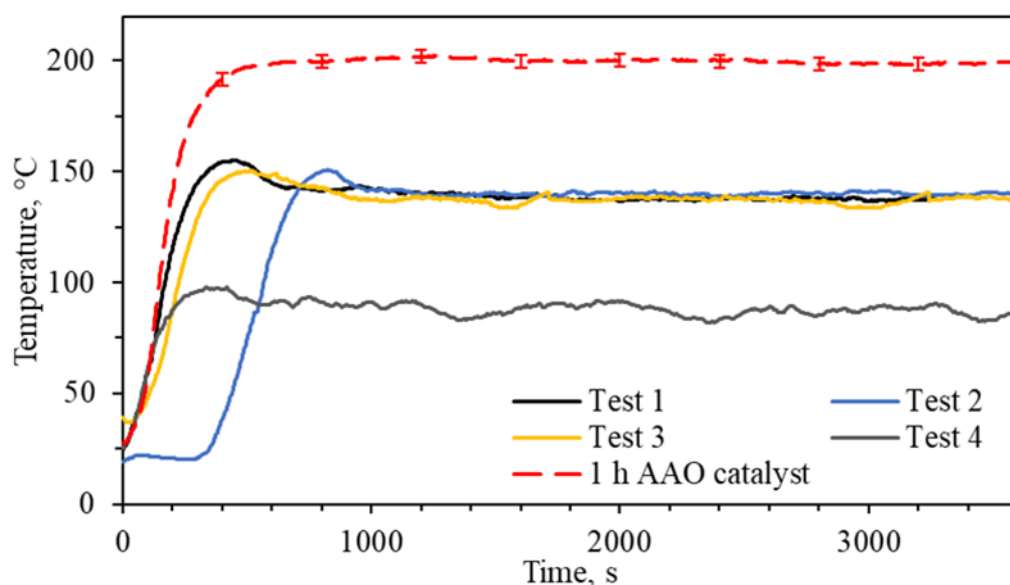


Figure 5-6: Combustion temperature profiles of Pt/AAO catalysts prepared using AAO supports anodized for 1 h and 4 h for 1 h of CHC.

Figure 5-6 shows an average combustion temperature of 199.6 ± 2.9 °C for the 1 h AAO catalysts. A stable combustion temperature was reached after 300 s of H₂ exposure. Figure 5-6 also shows combustion temperature profiles for the 4 h AAO catalyst. The latter catalyst exhibits very different combustion behavior to the 1 h AAO catalyst (see Figure 5-2). During Tests 1 and 2, stable combustion temperatures of 138.9 ± 1.9 and 140.1 ± 0.9 °C were reached after approximately 600 and 900 s of H₂ exposure, respectively. The CHC was initiated at temperatures of 19–24 °C. The Pt/AAO catalyst had to be preheated to 40 °C to initiate the CHC reaction during Test 3, whereafter a stable combustion temperature of 138.9 ± 4.0 °C was reached after 700 s of H₂ exposure.

Considering that the time required for the CHC reaction to being initiated increased from 600 to 900 s for Tests 1 and 2, respectively, and that the catalyst had to be preheated during Test 3, this offers a clear indication of catalyst deactivation. The latter is likely caused by Pt aggregation occurring during CHC. As shown in Figure 5-5b, the surface of the 4 h AAO contained numerous nanowires; therefore, it is likely that Pt was deposited onto nanowires, as well as inside the AAO pore channels. It is further likely that the deposition of Pt on the nanowires might have led to a nonuniform active site distribution, causing differences in heat and mass transfer. In turn, these differences might cause a decrease in catalytic activity. For example, the effect of heat and mass transfer on the catalytic activity of the Pt/ γ -Al₂O₃ catalyst for CO oxidation was studied by Arnby et al. (Arnby, *et al.*, 2004). The heat evolved from the exothermic reaction is removed from the active sites to the support material and ambient air; however, heat can accumulate in catalyst

particles, causing a constant temperature gradient between the catalyst and the surroundings (Arnby, *et al.*, 2004). Therefore, if the distribution of catalyst particles is nonuniform, the appearance of hotspots is likely. The latter may result in catalyst aggregation, which reduces the catalytic activity of the catalyst. Furthermore, first, the heat transfer limitation in the present study may occur due to an elongated and sophisticated pathway from the surface of the nanowire to the Al core. Heat present in nanowires may not be transferred as easily and rapidly when compared to the AAO layer directly adhering to the Al core. Furthermore second, the mass transfer limitation may cause a decline in the reaction rate due to the long diffusion path of the gas phase between the active sites and the catalyst support (Arnby, *et al.*, 2004). Mass transfer limitations locally decrease the concentration of the reactant on the active sites, resulting in a concentration gradient and a decrease in the reaction rate. Figure 6 further shows that although the CHC initiated spontaneously during Test 4, the combustion temperature of 88.4 ± 3.6 °C was reached after 200 s of H₂ exposure, thus suggesting a further decrease in catalytic activity. The initiation temperature for Test 4 was 25 °C. It is noteworthy that Test 4 initiated spontaneously after the catalyst had to be preheated during Test 3. However, previous findings indicate that the catalytic activity of a catalyst can be reactivated by increasing its temperature up to 60 °C (Rozeń, 2015). Future work should include the determination of the specific deactivation route.

To compare the efficiency of the 1 and 4 h AAO catalysts, the conversion of H₂ was measured for all CHC tests. The stable average conversions of H₂ during CHC for 1 h AAO catalysts were found to be 96.5%, 96.8%, and 98.2% for all three CHC tests, respectively. Similar values for percentage conversion might have been expected, as a similar observation was made for the combustion temperatures (Figure 5-2). The conversion of H₂ for the 4 h AAO catalyst varied over a wide range, which also might have been expected from Figure 5-6. The stable conversions of H₂ were 88.1%, 87.9%, 88.1%, and 66.9% for the four CHC tests, respectively. By plotting the values of combustion temperatures and the corresponding conversions of H₂, one may find an obvious correlation between them; the higher the combustion temperature that can be achieved during CHC, the higher the conversion of H₂ that may be expected.

From the results in Figure 5-6 and the values of H₂ conversion discussed above, it may be further concluded that the 1 h AAO catalyst exhibited higher catalytic activity (higher combustion temperatures and H₂ conversion) than the 4 h AAO catalyst. This is ascribed to the structural differences of the AAO layers formed during the 1 and 4 h of anodization, such as the absence/presence of nanowires (Figure 5-5). The 4 h AAO layer is likely susceptible to support collapse due to mechanical, thermal, and chemical stresses induced during the CHC reaction, leading to the loss in catalytic activity (Bartholomew, 2001). On the other hand, the differences in the catalytic activity of the catalysts may be caused by the different D_p values of the AAO layers.

As shown in Table 5-1, the D_p of the 1 h and 4 h AAO catalysts were 55.7 and 86.9 nm, respectively. As mentioned above, the greater the D_p of the support, the larger the catalyst particles that are formed within the support. Therefore, we assumed here that the Pt particles within the 4 h anodized AAO layer was larger than those within the 1 h anodized AAO layer. Kozhukhova *et al.* have obtained Pt nanoparticles with an average diameter of 4.7 nm for a Pt/AAO catalyst with an AAO D_p of 59.9 nm, which is in some agreement with the Pt nanoparticle diameter obtained here in the present study for a similar-sized AAO D_p (Pt particles diameter of 3.0 nm within AAO with D_p of 55.7 nm) (Kozhukhova, *et al.*, 2020). In both cases, the Pt/AAO catalysts have high activity towards CHC—the reactions initiated spontaneously at room temperature. Khodakov *et al.* have also investigated the deposition of cobalt (Co) onto silica supports with different D_p values (Khodakov, *et al.*, 2002) and found that the Co particle size increased with increasing D_p ; Co particles with an average size of 57–230 Å were formed in silica supports with D_p of 20–330 Å.

Based on the results presented in this section, it is concluded that the structural and morphological characteristics of the AAO layer significantly affect the catalytic activity of the Pt/AAO catalyst. Considering that the 1 h AAO catalyst did not show any evidence of catalytic deactivation, this catalyst was selected for prolonged CHC applications.

5.2.3 Catalyst Fatigue Test

Prolonged CHC was performed to assess Pt/AAO catalyst durability. The H_2 content in the exhaust stream was measured after the combustion temperature reached a steady-state value. A H_2 concentration of <1 vol% was determined in the exhaust stream, suggesting near-complete CHC at the specific flow rate, Pt loading, and catalyst size and orientation.

Figure 5-7 shows the combustion temperature profiles of Pt/AAO catalyst during the first 900 s and for the entire fatigue test (530 h). Figure 5-7a shows a steady increase in combustion temperature during the first 170 s, which is indicative of the onset of the CHC reaction. Here, the initiation temperature was 27 °C. After the initial 170 s of the catalyst fatigue test, the combustion temperature rapidly increased but then stabilized after approximately 550 s of H_2 exposure. The heat generated during CHC accelerated the reaction rate; therefore, a rapid increase in the combustion temperature was observed after 170 s of CHC. A temperature of 168.6 °C was achieved after 550 s of CHC reaction. In earlier studies, spontaneous CHC on Pt/SSM and Pt/Ti mesh catalysts was found at temperatures >40 and 70 °C, respectively (Du Preez, *et al.*, 2019; Du Preez, *et al.*, 2020). The higher activity of Pt/AAO catalyst (lower initiation temperature) in the present study is related to the smaller Pt particles (3.0 vs. 119.8 nm for the Pt/AAO and Pt/SSM catalysts, respectively). Zang *et al.* showed that CHC proceeded spontaneously on 1 wt%

Pt/MgAl₂O₄ and Pt/Ce_{0.6}Zr_{0.4}O₂/MgAl₂O₄ catalysts at initial temperatures as low as –10 °C and H₂ inlet concentrations of 4 vol%. The authors found that a lower CHC initiation temperature could be expected with higher H₂ inlet concentrations and space velocities (Zhang, *et al.*, 2012). Reinecke et al. investigated CHC over a Pt/washcoat catalyst. The authors found that the CHC reaction initiated spontaneously at a temperature of 25 °C and H₂ concentrations of 0.5–4 vol%. However, a temperature gradient of up to 200 °C throughout the catalyst surface was observed for inlet H₂ concentrations of 4 vol% (Reinecke, *et al.*, 2004).

Figure 5-7b shows that an average combustion temperature of 162.8 ± 8.0 °C was maintained over 530 h of CHC. Because the experimental setup used for the catalytic fatigue test is open to the atmosphere, the temperature of the ambient air affects the catalyst temperature. Therefore, the temperature profile deviations observed in Figure 5-7b may be ascribed to day/night cycles. Kozhukhova et al. have earlier shown that the combustion temperature of a Pt/AAO catalyst is sensitive toward external airflow, which has a rather significant cooling effect on the catalytic system (Ostermaier, *et al.*, 1976). In the present study, the external airflow interference was significantly reduced by introducing the vertical enclosure along the full length of the catalyst. However, the enclosure did not allow adiabatic investigations, and heat transfer was inevitable.

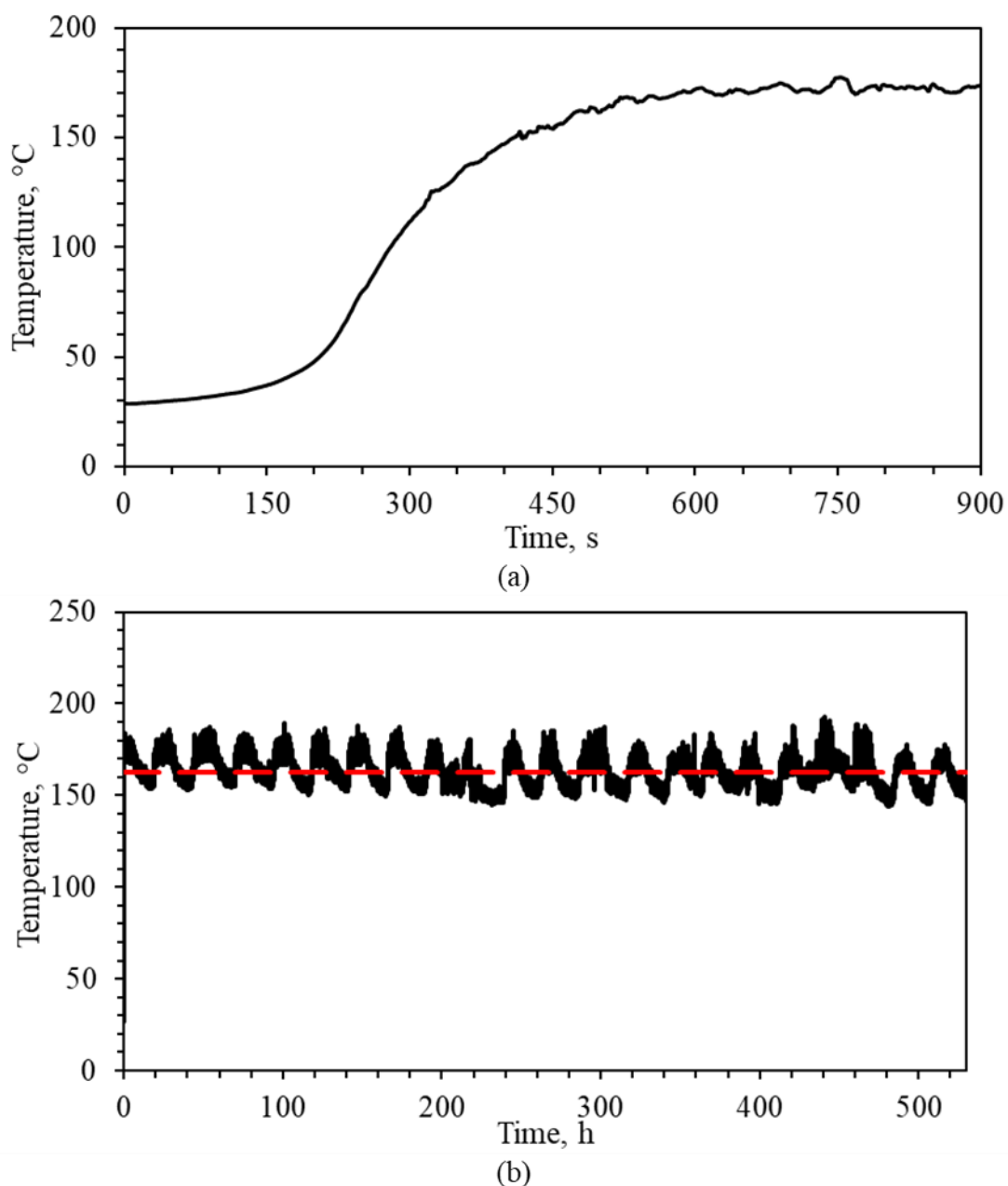


Figure 5-7: Combustion temperature profiles of Pt/AAO catalyst: (a) during the first 900 s; (b) 530 h of CHC at a H₂ flow rate of 138 NmL/min.

To then investigate any change in the Pt particle size and morphology, the fatigue tested Pt/AAO catalyst was cross-sectioned by FIB and examined using TEM (Figure 5-8). The average Pt particle size determined over several TEM images for the spent Pt/AAO catalyst was 3.9 ± 1.9 nm (based on 220 particles). Therefore, a relatively small increase in particle size occurred (compared with the particles shown in Figure 5-1b). This was even more evident when considering the morphology of the particles indicated in Figure 8—some evidence of particle

aggregation is present, i.e., particles were not as circular as the particles presented in Figure 1b. This suggests that some Pt aggregation did occur during the prolonged CHC procedure. Furthermore, the formation of PtO_2 was likely avoided in the present study. In a study by Olsson and Fridell, a $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst was analyzed by X-ray photoelectron spectroscopy (XPS) to investigate the formation of Pt oxides after catalyst pretreatment in H_2 , O_2 , and NO_2 atmospheres. The formation of PtO was observed for catalysts treated in O_2 and NO_2 at 400 and 350 °C, respectively. In addition, the NO_2 treated catalysts showed significant PtO_2 formation. Traces of PtO_2 formation was observed for the catalysts pretreated in H_2 at 500 °C and O_2 at 400 °C (Olsson, *et al.*, 2002). Hwang and Yeh found PtO_2 formation on $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst when oxidizing in a 5 vol% O_2 atmosphere at temperatures >300 °C (Hwang, and Yeh, 1996). In the present study, a CHC temperature of <200 °C was reached during the fatigue test; this suggests that the formation of Pt oxides was absent or insignificant (considering the relatively stable prolonged CHC temperature, Figure 5-7). It is proposed that the Pt/AAO catalyst prepared here be characterized after CHC procedures to determine the presence and/or extent of Pt oxidation.

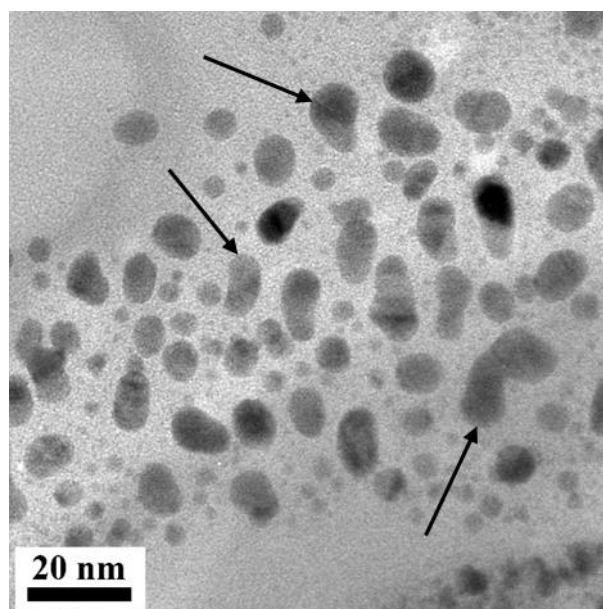


Figure 5-8: TEM bright-field image of a cross-sectioned Pt/AAO catalyst after 530 h of H_2 exposure.

It is known that Pt and reactive metal-based catalysts are susceptible to thermal degradation, which reduces the catalytic activity of such catalysts (Nagai, *et al.*, 2006; Du Preez, *et al.*, 2019; Du Preez, *et al.*, 2020). The effect of reactive metal aggregation can be facilitated by exposure to high temperatures (>500 °C) in the presence of oxygen and chlorine; the presence of water vapor increases the rate of aggregation of the supported metal catalyst (Bartholomew, 2001). Du Preez

et al. have reported that the combustion temperature of a Pt/SSM and Pt/calcined Ti catalyst decreases significantly as Pt aggregation proceeds during the first several hours of CHC (Du Preez, *et al.*, 2020; Kozhukhova, *et al.*, 2020). One also must consider the bond energy between Pt and the support material. For instance, it has been found that the aggregation rate for Ni/Al₂O₃ is less than for Pt/Al₂O₃ catalyst due to a greater Ni–Al₂O₃ interaction (Bartholomew, 2001).

Although some Pt aggregates were observed after a CHC reaction time of 530 h (Figure 5-8), the effect of Pt aggregation on the average combustion temperature over this period was not evident (Figure 5-7). This suggests that the Pt aggregation that occurred was insignificant and did not affect the catalytic activity of the Pt/AAO catalysts. This could be ascribed to the high thermal conductivity of the Al/AAO support.

5.2.4 Thermal Distribution of the Pt/AAO Catalyst

The ability of the catalytic system to distribute heat generated during CHC is a key parameter when the catalyst is intended to be used in PAR applications. Of importance here is that the low thermal conductivity of the PAR catalytic system may itself cause a self- ignition. Uniform temperature distribution is achieved only when exothermic reaction heat is efficiently distributed throughout the entire catalyst. Moreover, localized reactive metal aggregation is prevented in the absence of hotspots; thus, the catalytic activity of a catalyst is preserved. Therefore, the thermal distribution of the catalyst should be investigated before the catalyst is introduced into commercial PARs.

The mechanism involved during CHC of a Pt/AAO catalyst was presented in an early study by Kozhukhova *et al.* (Kozhukhova, *et al.*, 2020). They showed that the use of an Al metallic core adjacent to the AAO layer as part of the catalyst support allowed high thermal conductivity of the Pt/AAO system for 530 h of CHC. Due to the absence of hotspots, flashing (H₂ ignition) would only be possible if the temperature of the entire catalyst surface exceeded the H₂ autoignition temperature (585 °C), which is considered an unlikely event.

In the present study, a detailed investigation into the thermal distribution of the Pt/AAO catalyst was carried out. To investigate the significance of hotspot formation during CHC reactions, three samples with nonuniform Pt distribution were prepared. These samples are henceforth referred to as nonuniform catalysts. Catalysts with uniform Pt distribution are defined similarly. Figure 9a presents an image of the thermal distribution of the uniform and nonuniform catalysts obtained with an IR camera. Figure 5-9b represents the change in catalyst surface temperatures throughout 70 mm of the catalyst length as a function of H₂ exposure time. The two samples on the left and three on the right represent the uniform and nonuniform catalysts, respectively.

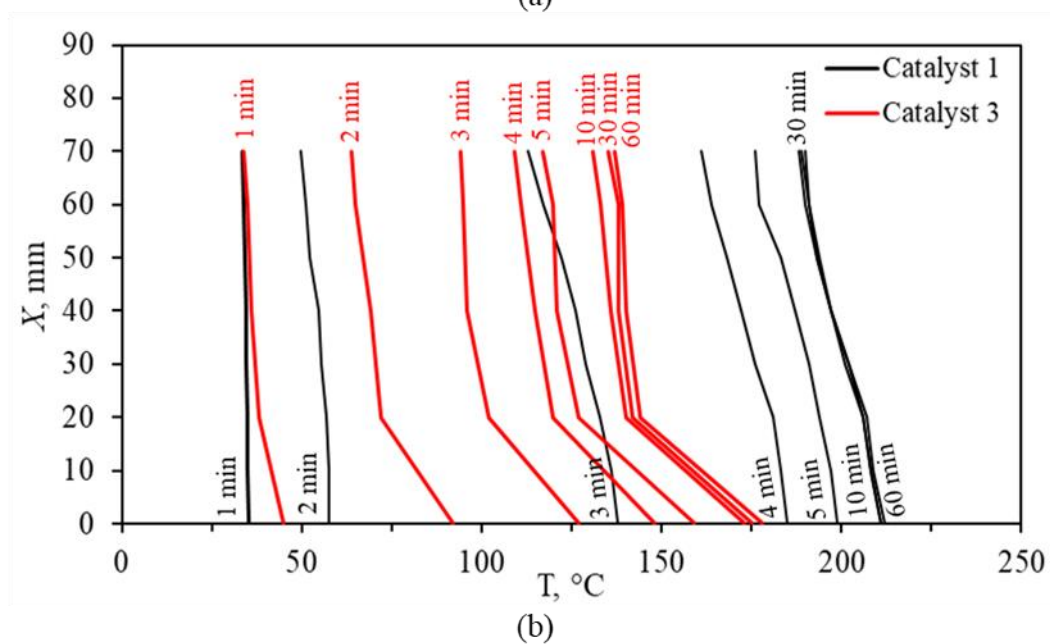
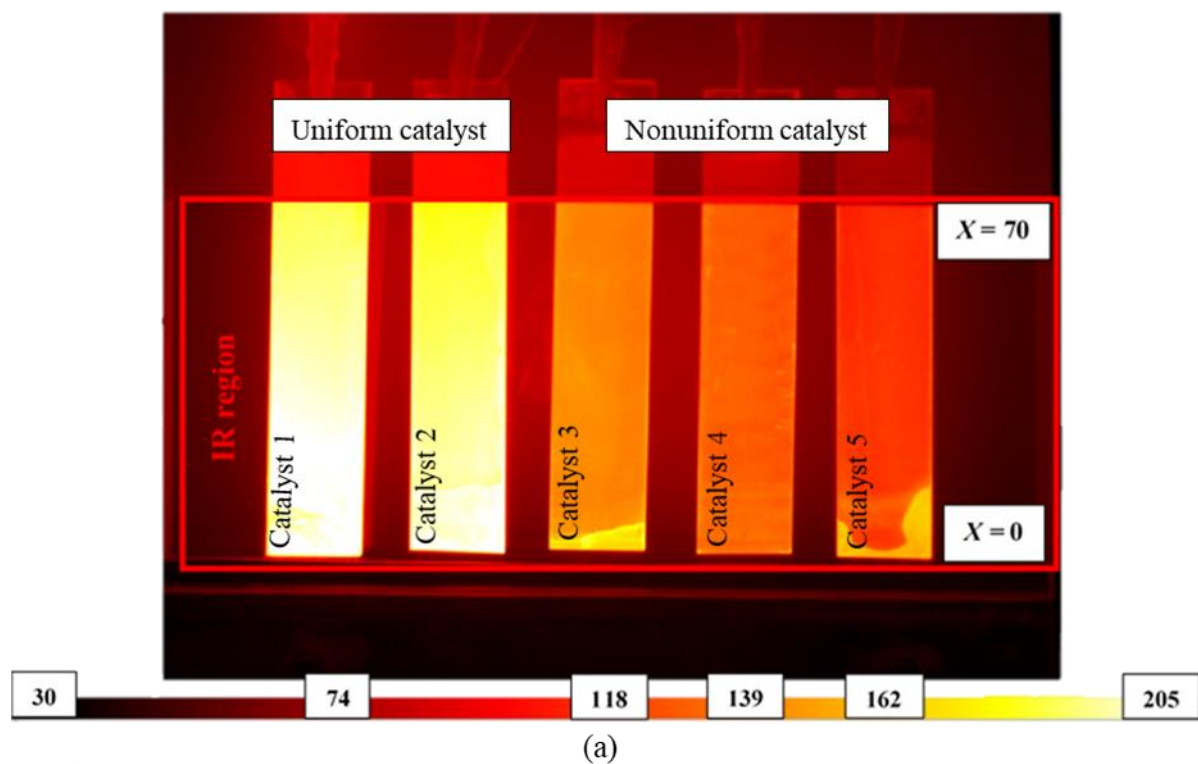


Figure 5-9: Infrared (IR) camera temperature map of Pt/AAO catalyst at steady-state conditions (a) and the change in catalyst surface temperature as a function of catalyst position (b) in a 3 vol% H_2 /air mixture after 3600 s of CHC.

Catalyst surface temperatures are presented on a color scale, ranging from black (low-temperature) to bright yellow (high-temperature), as indicated by the temperature scale bar. The region highlighted with a red rectangle indicates the area captured by the IR camera during the CHC test.

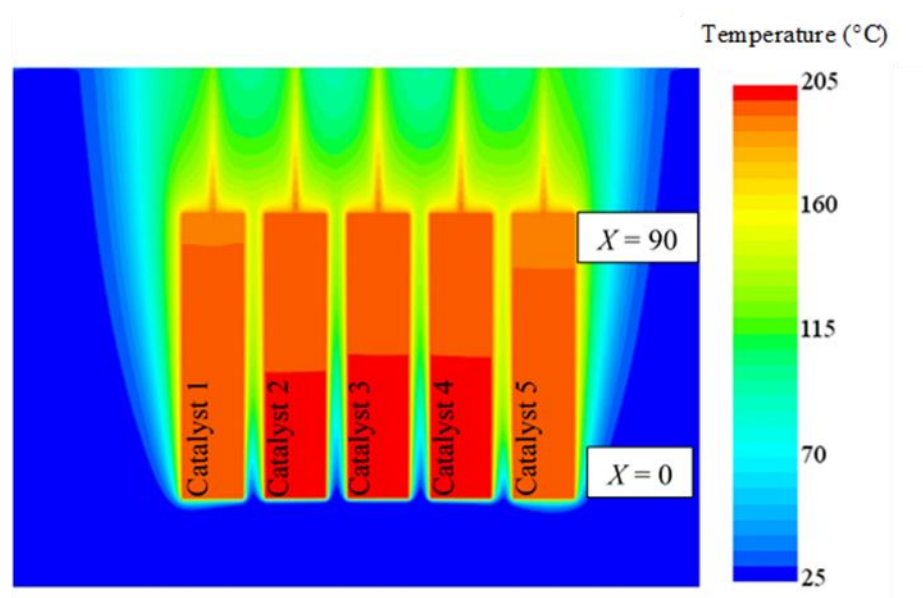
Figure 5-9a shows the thermal mappings of the catalysts during steady-state CHC conditions. The thermal mapping is relatively consistent for the uniform catalysts. This was expected, as the catalyst preparation method applied here allowed a relatively uniform distribution of Pt throughout the AAO layer. The opposite was observed for the nonuniform catalysts, where the bright yellow areas at the bottom of the images for catalysts 3 and 5 are representative of hotspots. Although catalyst 4 did not include hotspots, the catalyst was prepared with the intent to disrupt uniform Pt distribution. The hotspots presented on the surfaces of catalysts 3 and 5 correlate with higher Pt contents relative to the rest of the catalyst surface, suggesting that a larger fraction of H_2 is recombined in this localized area. As mentioned earlier, these hotspots may cause the unintentional ignition of H_2 /air mixtures.

Figure 5-9b presents the quantified temperature distribution of the thermal mapping presented in Figure 5-9a of catalysts 1 and 3. In Figure 5-9b, X refers to the distance from the bottom of the catalyst, with X = 0 and X = 70 mm referring to the bottom and top of the catalyst (as indicated in Figure 5-9a), respectively. An appreciable temperature increase caused by the catalytic activity of the catalysts is observed after approximately 120 s of H_2 exposure. The temperature of catalysts 1 and 3 was 211 and 173 °C after 10 min of CHC, respectively. Of importance is the temperature gradient (ΔT) over the length of the catalyst (from X = 0 to X = 70). Catalysts 1 and 3 had ΔT of 23 and 42 °C, respectively.

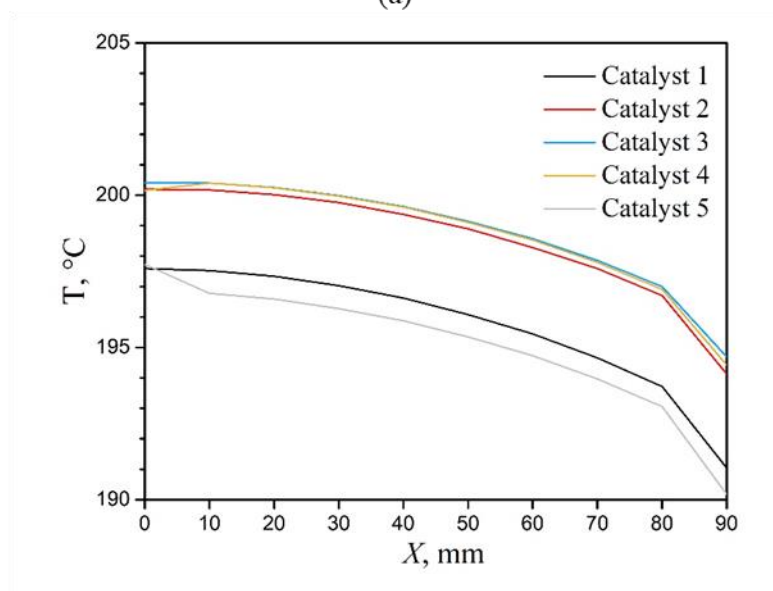
According to Reinecke et al., the exothermal CHC reaction mainly occurs in the very first surface section, resulting in a surface temperature gradient from the bottom to the top of the catalyst. A significant temperature gradient of 200 °C was found for the stainless steel Pt/washcoat catalytic material (Reinecke, *et al.*, 2004). Malakhov *et al.* observed a temperature gradient of 341.2 °C over a tubular ceramic Pt/ Al_2O_3 washcoat catalyst (Malakhov, *et al.*, 2020). By comparison, a ΔT of 23 °C for the uniform catalyst over a distance of 70 mm is relatively insignificant. Moreover, a ΔT of 42 °C in a nonideal (“worst-case”) scenario is indicative of the highly effective thermal conductivity of the Al core present in the Pt/AAO catalysts prepared in this study. Based on the observed ΔT , and because it is significantly lower than commercially employed catalysts, it is proposed that the thermal distribution of the Pt/AAO catalyst at explosive H_2 concentrations (>4 vol%) should be investigated in future research.

5.2.5 CFD Calculations

Detailed research on catalytic recombiners is usually required to investigate the interactions of reaction kinetics, temperature distribution, and heat and mass transfer. The application of CFD modelling in hydrogen safety applications may be very helpful, especially when the research needs to be conducted under conditions close to the accident ones (accident conditions) (e.g., the concentration of $H_2 > 4$ vol%, high H_2 flow rate). In the present study, a model was created to investigate temperature distribution throughout the Pt/AAO catalyst under the same conditions that were used during the thermal mapping shown in Figure 9a (3 vol% H_2). If high predictability of the results is obtained, the model may be applied in further research—for example, determining the thermal conductivity of the Pt/AAO catalyst at H_2 concentrations >3 vol%. Figure 10a presents the thermal distribution of uniform Pt/AAO catalysts obtained at steady-state conditions using a CFD numerical tool. Figure 5-10b shows the change in Pt/AAO catalyst surface temperatures throughout 90 mm of the catalyst length at steady-state conditions.



(a)



(b)

Figure 5-10: IR camera temperature map of Pt/AAO catalyst obtained at steady-state conditions (a) and the change in Pt/AAO catalyst surface temperature as a function of catalyst “position” X (b), determined by computational fluid dynamics (CFD) simulation.

Figure 5-10a shows that uniform temperature distribution throughout the samples was obtained. However, a relatively small temperature decrease in catalyst surface temperature from the bottom to the top of the catalyst was observed. Figure 10b shows that the change in catalyst surface temperature decreased from 198, 200, 200, 200, and 198 °C to 191, 194, 195, 194, and 190 °C

for catalysts 1–5, respectively. The average ΔT throughout 90 mm and 70 mm of the catalyst surface was 7 and 3 °C, respectively. The numerical model did not assume any disorder of Pt particle distribution on the support surface that may occur during a real catalyst preparation procedure. Therefore, the difference in ΔT determined experimentally and by simulation (23 and 3 °C, respectively) may be ascribed to the actual distribution of Pt on the AAO surface of the Pt/AAO catalysts prepared in this study. Figure 11 presents a distribution of H_2 throughout the catalyst surface obtained at steady-state conditions.

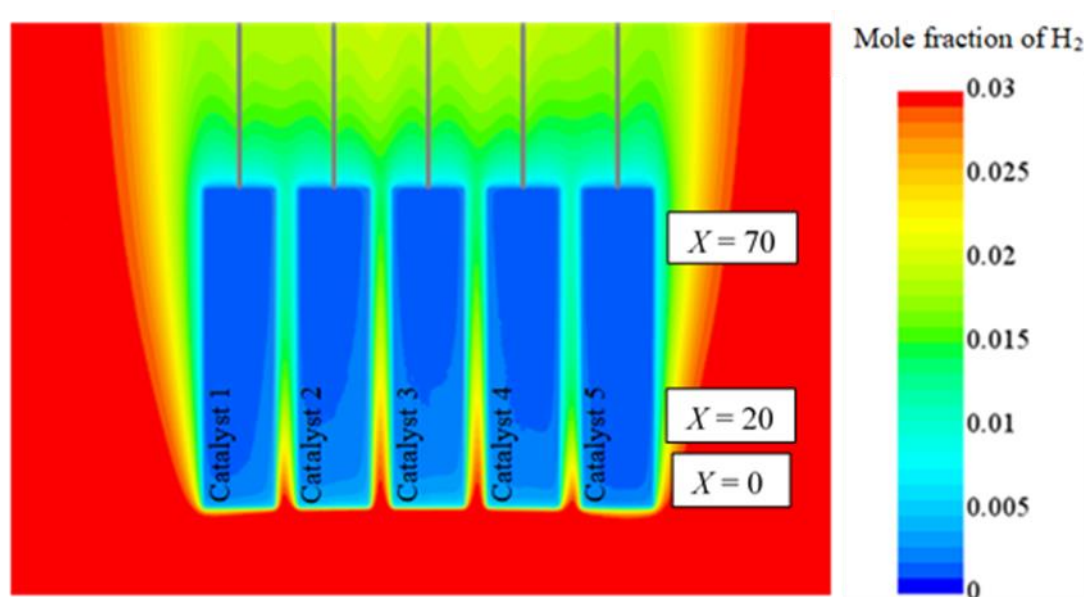


Figure 5-11: H_2 distribution map of Pt/AAO catalyst obtained at steady-state conditions, determined by CFD simulation.

Figure 5-11 shows that the H_2 concentration over the catalyst surface was relatively low, which suggests that H_2 recombination occurs rapidly on the surface of Pt/AAO catalysts. Two observations are made from Figure 5-11: first, the H_2 concentration at the bottom of the catalyst ($X = 0$) is higher when compared to $X > 0$ and, second, the H_2 concentration gradients of catalysts 2–4 were dissimilar to those of catalysts 1 and 5. Both of these observations could be ascribed to the presence of local flow fluctuations throughout the recombiner section (Frank-Kameneckiy, 1987). To investigate this, the linear velocity at the local points of the gas mixture present for catalysts 1–5 at positions $X = 0, 20$, and 70 are shown in Table 5-2. The change in the linear velocity at $X > 70$ mm was negligible. Therefore, these values were not included for further consideration.

Table 5-2: Local linear velocity of a H₂/Air mixture, determined by CFD simulation.

X, mm	H ₂ /Air mixture local linear velocity, m/s				
	Catalyst 1	Catalyst 2	Catalyst 3	Catalyst 4	Catalyst 5
0	0.037	0.147	0.219	0.182	0.053
20	0.049	0.141	0.199	0.172	0.062
70	0.075	0.131	0.153	0.142	0.085

Table 5-2 shows that the local linear velocity for catalysts 2–4 decreased with increasing position X from 0 to 70 mm, while the linear velocity increased for catalysts 1 and 5. The difference between the flow rates for the catalysts may be ascribed to the design of the recombiner section. The mixing plate present in the recombiner section testing station (see Figure 5-12) was included to allow a uniform H₂/air mixture, although it may also influence flow distribution. The presence of flow fluctuations is common considering the differing geometry of PARs and may be ascribed to dissimilar linear velocities throughout a recombiner framework (Malakhov, *et al.*, 2020). A slight decrease in H₂ concentration for catalysts 1 and 5, however, may be related to the presence of natural convection when the mass transfer occurs with a flow of heat produced by CHC. In conclusion, from the data presented in Figure 5-11 and Table 5-2, the authors assume that under the explored conditions in the present study, the CHC occurs to an incomplete extent at $X = 0$. Figure 5-11 further shows that a near-zero concentration of H₂ was obtained at $X = 70$, suggesting that, for the investigated catalyst, near-complete H₂ recombination occurred throughout the catalyst surface.

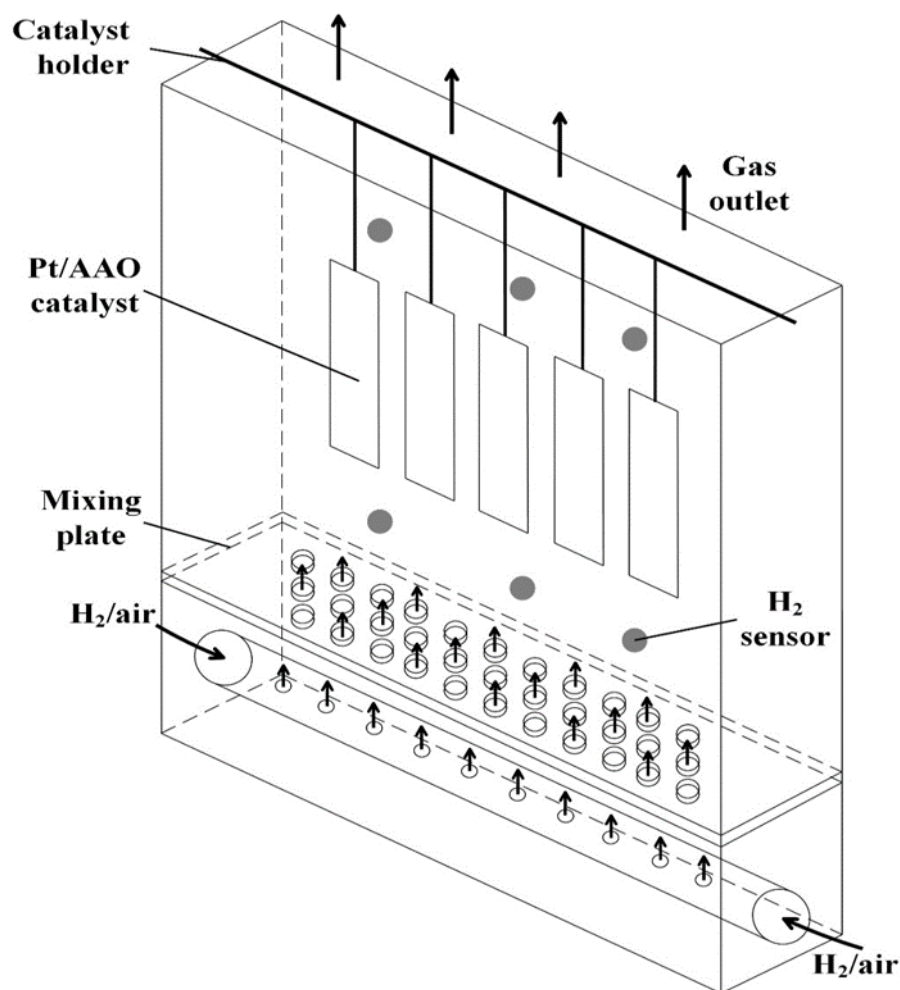


Figure 5-12: Schematic of the experimental setup used to determine the Pt/anodized aluminum oxide (AAO) catalytic activity and thermal distribution of the catalyst section.

5.3 Experimental

5.3.1 Preparation of Pt/AAO Catalyst and Its Characterization

The AAO support was prepared by two-step anodization of 0.2 cm-thick Al alloy plates sized 2 cm × 9 cm (Al6082 alloy, 97.5% Al, Aluminium and Metal Traders CC, Welkom, South Africa). Each plate included a 1 cm handle, which was not anodized. The anodization procedure has been described in early studies by Kozhukhova *et al.* (Kozhukhova, *et al.*, 2019, 2020). In short, the sample surfaces were degreased by ultrasonication in acetone, rinsed with deionized water, and then subjected to electropolishing in a mixture of HClO₄ (Sigma-Aldrich, Schnelldorf, Germany) and ethanol (Rochelle Chemicals and Lab Equipment, Johannesburg, South Africa) at a voltage of 20 V for 1 min. Next, two-step anodization was carried out in a 0.3 M oxalic acid (Rochelle

Chemicals and Lab Equipment, Johannesburg, South Africa) solution. As described in an earlier study of Kozhukhova et al., AAO formed in oxalic acid at a temperature of 30 °C and voltage of 60 V had a relatively ordered pore distribution when the anodization time of the second step was kept to 1 h (Kozhukhova, *et al.*, 2020). Therefore, we selected this AAO layer to use as catalyst support in the present study. Accordingly, the first anodization step was performed at a temperature of 30 °C and a voltage of 30 V for 30 min. Thereafter, the AAO layer formed during the first step was removed by submerging the sample in a mixture of 5% H₃PO₄ (Sigma-Aldrich, Mainland, China) and 1.8% CrO₃ (Sigma-Aldrich, Modderfontein, South Africa) at 60 °C for 5 min. The second anodization step was performed at a temperature of 30 °C and a voltage of 60 V for 1 or 4 h. Isothermal conditions were maintained using a refrigerating–heating circulating system (Julabo, CORIO CD-200 F, Seelbach, Germany). An adjustable DC power supply (Elektro-Automatik, EA-PSI 5200-10A, Morfelden-Walldorf, Germany) with a voltage range of 0–200 V and a current range of 0–10 A was used to control the applied voltage.

The Pt/AAO catalyst was prepared by the incipient wet impregnation method. This method includes the immersion of samples in a 22.8 g/L ethanol-based hexachloroplatinic acid solution (H₂PtCl₆·6H₂O, Sigma-Aldrich, Milano, Italy) for 4 h. Ethanol was used as the solvent to prevent AAO layer dissolution (Kozhukhova, *et al.*, 2020). Next, samples were dried in ambient air, and Pt was reduced in a hydrogen atmosphere at 350 °C for 2 h. A vertical tube furnace (CTF 12, Carbolite Gero, Derbyshire, England) was used for the reduction procedure.

The morphology of AAO samples was characterized using an FEI Quanta FEG 250 field emission gun scanning electron microscope (Thermo Fisher Scientific, Waltham, MA, USA). Before SEM analysis, the AAO samples were coated with a thin layer of carbon using a carbon coater (Emscope TB 500, UK). The morphological characteristics (diameter of pores D_p , interpore distance D_c , pore density n , and porosity P) were determined from SEM images using the ImageJ program.

The Pt/AAO catalyst was analyzed by TEM before and after being subjected to prolonged CHC. Before TEM analysis, the Pt/AAO catalysts were sectioned by a focused ion beam (FIB). FIB lamellas were prepared using an FEI Helios Nanolab 650 dual-beam scanning electron microscope (Thermo Fisher Scientific, Waltham, MA, USA). TEM analyses were then carried out using a Technai F20 FEI instrument (Thermo Fisher Scientific, Waltham, MA, USA).

5.3.2 Catalytic Test in the Recombiner Section Testing Station

The prepared Pt/AAO catalysts were tested as a catalyst section in an in-house developed recombining section testing station (Hydrogen South Africa Infrastructure, Potchefstroom, South Africa). The schematic of the experimental setup is presented in Figure 5-12.

The testing station represents a rectangular box allowing a vertical flow of an H₂/air mixture under defined conditions (e.g., flow rate, H₂/air inlet volume ratio). Digital thermal mass flow controllers (EL-FLOW F-201AV, Bronkhorst, The Netherlands) were used to control the inlet concentrations of H₂ and air. High-purity H₂ (>99.9% H₂, Hydrogen South Africa Infrastructure, Potchefstroom, South Africa) and compressed air were used as the inlet gas mixture. The H₂/air mixture with a H₂ concentration of 0.5–4 vol% was fed into a pipe at the bottom of the experimental setup at an inlet flow velocity of 9.5 m/s. A relatively uniform gas flow distribution was achieved by using a mixing plate placed above the inlet pipe; the mixing plate had uniformly distributed holes. Thereafter, the gas mixture reaches the catalyst section, where the recombination reaction occurs. The reaction products (water vapor) and any unreacted H₂ pass through the gas outlet at the top of the experimental setup. In this study, the catalyst section consisted of five Pt/AAO catalysts (10 × 2 cm each) placed inside the recombining testing station. Catalysts were placed vertically and spaced 1 cm from each other. The catalyst section was fixed 8 cm above the mixing plate using clamps.

Six H₂ sensors (Model XEN-5320, Xensor Integration, Delfgauw, The Netherlands) were positioned inside the experimental setup to evaluate the H₂ content before and after CHC. Measurements were logged every 1 s, using LabVIEW software. All combustion procedures were performed in triplicate, and the average values are presented.

The thermal distribution of the catalytic surface was recorded using a high-resolution IR camera (M100hd, Telops, Ontario, Canada). The camera was fitted with a lens designated to capture thermal data in the temperature range 0–325 °C. A synthetic sapphire glass panel was installed in the testing recombining station to enable the camera to capture thermal data. Thermal data were recorded every 1 s, using Reveal IR software (v. 1.7.0) (Telops, ON, Canada).

5.3.3 Catalyst Fatigue Test

The Pt/AAO catalyst was subjected to a fatigue procedure to evaluate the stability and catalytic activity of the catalyst during prolonged high-temperature CHC. A similar fatigue procedure was applied in an earlier study by Kozhukhova *et al.* (Kozhukhova *et al.*, 2020). For the fatigue test, the vertically placed Pt/AAO catalyst was exposed to a flow of a H₂/air mixture with a high H₂ content (138 NmL/min; instrument maximum flow rate). H₂ was supplied using an in-house-

developed electrolytic hydrogen generator (Hydrogen South Africa Infrastructure, Potchefstroom, South Africa). The sample was placed 3 mm above the hydrogen nozzle, allowing premixing of H₂ and air before it reached the catalyst surface. The temperature of the catalyst surface was measured at the center of the sample using a K-type thermocouple. Thermal measurements were recorded every 1 s. The fatigue test was performed for 530 h.

5.3.4 CFD Calculations

The computational domain was created in STAR-CCM+ (Siemens PLM Software, TX, USA) as a vertical rectangular box with the dimensions 24.2 × 4.55 × 28.0 cm (length × width × height). These dimensions matched the recombiner section testing station. The computational mesh was generated by a polyhedral cell based on a minimum cell size of 4.0 mm. The refinement by surface and volumetric mesh control was applied around the catalyst area. The total number of cells was approximately 3.3 million. Steady-state analyses were performed for all calculations. A realizable k-epsilon (k-ε) model with a two-layer approach was used for a turbulent flow simulation (Rodi, 1991). Reynolds-averaged Navier–Stokes equations were solved to simulate a gas flow. An initial temperature of 25 °C and pressure of 105 Pa were set. A detailed mechanism of the CHC reaction on a Pt/AAO catalyst was used in previous work (Rinnemo *et al.*, 1997). The Pt/AAO catalyst plates were 90 mm in length and had Pt active sites over the entire surface. The site density for Pt was taken as 2.7×10^{-8} kmol/m² (Rinnemo *et al.*, 1997).

5.4 Conclusions

In this study, a Pt/AAO catalyst was prepared and evaluated for passive autocatalytic recombination of hydrogen. The AAO support was prepared by anodizing a low Al purity Al alloy Al6082 in oxalic acid. The metallic Al core was preserved during the anodization procedure, and it acted as a thermal conduit during CHC reactions, affording a Pt/AAO catalyst with high thermal conductivity. The prepared Pt/AAO catalyst had an average Pt particle size of 3.0 ± 0.6 nm and an E_a of 19.2 kJ/mol for CHC. The catalyst maintained a combustion temperature of 162.8 ± 8.0 °C for 530 h at a H₂ flow rate of 138 NmL/min. Although some Pt aggregation was observed after the aforementioned 530 h of CHC, the significance thereof was not evident, as a decrease in the combustion temperature during prolonged CHC was not observed. Thermal imaging revealed a temperature gradient of 23 °C over 70 mm of the catalyst surface. To simulate a nonideal (“worst-case”) scenario, Pt/AAO catalysts were prepared to contain hotspots. They were formed by nonuniform Pt distribution and had a temperature gradient of 42 °C over 70 mm of the catalyst surface. In both cases, the reported temperature gradients were well below those of catalysts used for PARs reported in the literature. CFD modelling revealed a 3 °C temperature gradient; the CFD model assumed perfect Pt distribution over the catalyst surface. Moreover, CFD calculations

showed that although flow fluctuation was present within a simulated recombiner section, which is inherent for any PAR, the Pt/AAO could combust the majority of the H₂ introduced to the recombiner section. However, the concentration of H₂ in the case of accidents in NPPs and mines can reach values much higher than that considered in the present study (1–4 vol% of H₂). Considering that, future research should be focused on the investigation of the Pt/AAO catalyst for CHC at higher inlet concentrations of H₂ (>4 vol%). In conclusion, due to the high thermal conductivity of the Pt/AAO catalyst, its fast self-start characteristic, and high stability, the authors assume that the catalyst reported in this study can be used for PAR application.

5.5 Acknowledgments

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CHAPTER 6: STUDY OF THE EFFICIENCY OF A PAR PT CATALYST AND CFD VERIFICATION OF DETAILED MECHANISM OF H₂/O₂ OXYDATION

The research described in Chapter 6 has been conducted by the author in an attempt to answer the scientific question that was defined in objective V, “To develop and validate a detailed 3D CFD model and verify the surface and gas-phase mechanisms of hydrogen recombination reactions, by performing experiments in a PAR’s cylindrical-type catalyst section under high inlet hydrogen concentrations of 6–7 vol %”.

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OVERVIEW

The existing numerical models for passive autocatalytic recombiners (PAR) are mostly based on the empirical correlations of various experimental results. In many cases, they are hardly applicable to conditions at severe nuclear reactor accidents. To more adequately establish a highly predictive model, some new experiments along with high-performance computational fluid dynamics (CFD) simulations are required. A series of experiments was performed in a small-scale vertical test set-up (cross-sectional area 45.5 x 242.0 mm). The thermal distribution on a catalytic surface as well as recombination efficiency were investigated at 6 vol % and 7 vol % hydrogen. The catalyst unit included fourteen cylindrical ceramic elements, arranged in parallel inside a synthetic sapphire glass box for the purpose of visibility in thermal images. A high-resolution infrared camera was installed to provide images of the temperature profile at steady-state conditions. CFD analysis was conducted with the commercial code STAR-CCM+. The detailed surface mechanism and the mechanism of the gas-phase reaction were applied together to simulate a hydrogen autocatalytic recombination reaction. Moreover, in event of high hydrogen concentrations, a detailed gas-phase reaction mechanism and a radiation model are required, in order to predict unintended gas-phase ignition under accident conditions. The objective of this study is to apply the gas-phase chemical kinetic mechanism together with the detailed surface kinetic mechanism to develop the numerical CFD model and validate it against experimental results.

6.1 Introduction

Hydrogen is widely recognized as one of the advanced “clean” fuels of the future. However, the use of hydrogen as an energy carrier is accompanied by the risk of accidental releases due to leaks, component failures, or human error. The wide flammability range of hydrogen in the air (4–74 vol %) (Du Toit, *et al.*, 2018) means that, under accident conditions, unintentional hydrogen releases can start forming a flammable mixture in a confined space. During the hypothetical case of a severe accident in a nuclear reactor, the cooling water in contact with high-temperature cladding in the core can generate large amounts of hydrogen into the containment (IAEA, 2011). Then, the local concentration of hydrogen may become significantly high and may exceed the lower flammability limit. To prevent the potential hazard, one must maintain the hydrogen concentration in the confined space to a concentration that is lower than the flammability limit to this end, numerous strategies have been proposed and investigated (Markert *et al.*, 2007; Paladino *et al.*, 2012; Malakhov, *et al.*, 2020).

One of the most frequently accepted approaches towards hydrogen safety mitigation strategy is to use a passive autocatalytic recombiner (PAR) (Bachelierie *et al.*, 2003). A PAR is usually constructed as a vertical flow channel containing a number of catalytic units. The catalytic units can be of various geometric shapes, such as stainless steel plates coated with platinum or palladium (Klauck *et al.*, 2014), or aluminium ceramic cylinders coated with a platinum washcoat (Anpilov *et al.*, 2013; Malakhov, *et al.*, 2020). The operation of a PAR is maintained by means of the natural convection that is initiated when hydrogen passes through the PAR framework. The exothermic surface chemical reaction leads to the heating of the catalyst and then activates natural convection inside the PAR.

In efforts to research and define the characteristics of PARs, as well as to develop and validate a new detailed numerical model, numerous experimental programs have been conducted in small- and full-scale recombiner facilities, worldwide. Braillard *et al.* have reported on a test program that supports the introduction of PAR technology as a safety device to control and remove combustible hydrogen-air mixtures from the containment of nuclear power plants (Braillard, *et al.*, 1997). Experimental investigations into the temperature distribution on the catalyst surface of a small PAR, designed as a cut-out of a commercial recombiner section, have been performed during a test series in the REKO-3 test facility (Jülich, Germany) (Reinecke, Tragsdorf and Gierling, 2004). Within the scope of that project, the REKO-DIREKT (JÜLICH/RWTH) numerical code was developed to describe the chemical reaction processes inside a PAR (Reinecke *et al.*, 2005). The one-dimensional computational fluid dynamics (CFD) model of the passive autocatalytic hydrogen recombiner has been presented by Rożeń (Rożeń, 2015). A single-step reaction model of

hydrogen recombination at the catalytic surface was used to simulate chemical surface reactions in Ansys Fluent software. The developed model can well predict the catalyst thermal profile, gas temperature, and gas composition along a single recombiner channel.

Studies of a detailed chemical reaction mechanism of hydrogen oxidation on a platinum catalyst have progressed significantly over the past few years, especially aided by CFD methods. Heterogeneous reaction schemes for the oxidation of H_2 on platinum catalyst have been developed and applied by many research groups (Ljungström *et al.*, 1989; Deutschmann, *et al.*, 1994; Rinnemo *et al.*, 1997). Appel *et al.* carried out computations using a two-dimensional numerical model that included a conjugated approach with both gas-phase (homogeneous) and surface (heterogeneous) reactions (Appel *et al.*, 2002). They have also tested four homogeneous and three heterogeneous mechanisms in the model against experimental homogeneous ignition characteristics. The best agreements found with the experimental measurements were the surface mechanism proposed by Deutschmann (Deutschmann *et al.*, 1996) and the gas-phase mechanism proposed by Warnatz (Warnatz, *et al.*, 1990).

The objective of the present study is to develop, and validate, a three-dimensional (3D) numerical CFD model that includes a conjugated approach with a detailed chemical reaction mechanism of hydrogen oxidation on a platinum catalyst in terms of modelling a small-scale testing facility. CFD methods are helpful to provide the analysis of the experimental results and to extend the capacity of the investigation with parameters that cannot be included in an experimental scheme. The numerical model was built in the STAR-CCM+ software package. Chemical kinetics of the autocatalytic recombination of hydrogen was employed in the model utilizing the CHEMKIN software package.

6.2 Experimental study

Experiments are currently underway at DST HySA Infrastructure Center of Competence (HySA), North-West University, Potchefstroom (South Africa), in efforts to investigate and to create innovative technology for safety in the hydrogen energy field. In earlier work (Malakhov, *et al.*, 2020), a series of tests was performed to obtain the temperature profile of the commercial PAR catalytic section under defined flow conditions. In addition, experimental data were obtained to estimate the catalyst efficiency and mass transfer phenomena based on the effect of different inlet hydrogen concentrations. The presented experiments were performed to complete the existing database regarding to cylindrical-type catalytic elements in terms of sufficiently high inlet hydrogen concentrations. For the purposes of this latest research, the experimental set-up used in earlier studies had been upgraded. The catalytic section was taken from a nondisclosed

commercial PAR manufacturer (Russia). The schematic of the latest experimental set-up is presented in Figure 6-1.

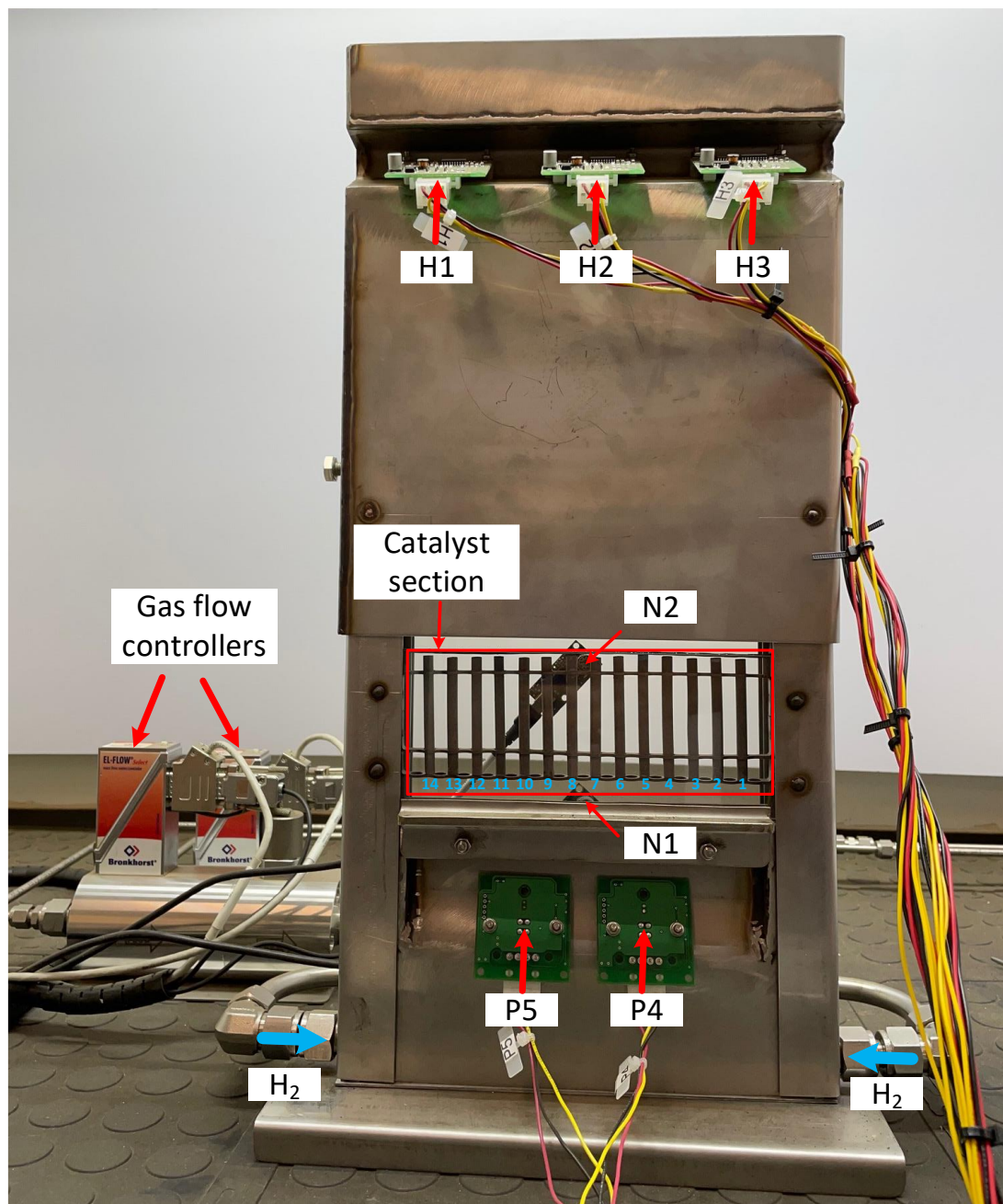


Figure 6-1: The recombiner section testing station; general view of the flow channel (HySA Infrastructure, Potchefstroom, South Africa).

6.2.1 Experimental Set-up

The recombiner section testing station represents a vertical rectangular flow channel. The cross-sectional area of the channel is 45.5 x 242.0 mm. Digital thermal mass flow controllers were used

to supply high-purity hydrogen (> 99.999% H₂, HySA Infrastructure, South Africa) and compressed air for the gas inlet mixture. Gas mixture components are fed into the inlet pipeline on the bottom part of the set-up at the mass flow rates as tabulated in Table 6-1. The initial conditions are tabulated in Table 6-1. In the present study, two inlet air–hydrogen mixtures were considered: C[H₂] = 6 vol % and C[H₂] = 7 vol %.

Table 6-1: Test series: Initial conditions.

Computational case, no	H ₂ inlet concentration C[H ₂], vol %	Mass flow rate $\dot{m}$, g/min	Volume flow rate $\dot{V}$, NL/min
1	6.0	35.0 ± 0.2	31.0 ± 0.15
2	7.0	35.0 ± 0.2	31.0 ± 0.15

The hydrogen is passed through the catalyst from bottom to top to represent the real PAR operation conditions. The velocity and turbulence smoothing element is serve to reduce intensive turbulence flow. Thereby, based on CFD simulations, the average flow velocity is less than 0.2 m/s across the catalyst area (Malakhov, *et al.*, 2020). The values for mass flow rate were extracted from mass flow controller software. The reaction products and unreacted hydrogen pass through the gas outlet at the top of the flow channel. To evaluate the inlet and outlet hydrogen concentrations, XEN-TCG3880 sensors, based on the measurement of the thermal conductivity of ambient gas, are used in the experiments (see Figure 6-1, N1 and N2). In turn, the points that labelled as H1, H2, H3, P5, P4, are Neodym ProtiSEN hydrogen sensors. LabVIEW software is used to log the measurements every 1 s.

The catalyst element is a frame that contains fourteen cylindrical rods (height 64.0 ± 0.1 mm and diameter 5.2 ± 0.1 mm). The ceramic cylinders are coated with a Pt catalyst washcoat and arranged in parallel, upright and hold by a stainless-steel frame. Within fatigue tests, carried out during a previous study, it was found that the catalyst is based on an Al-rich oxide support with a fluorine-containing protective coating (Malakhov, *et al.*, 2020). Considering the platinum particle size (5–6 nm), the platinum aggregation did not occur over a wide temperature range (168.2–509.4 °C). Furthermore, the platinum catalyst does continue functioning at the same productivity (hydrogen removal efficiency) even if the catalyst surface morphology changes, due to the increased surface temperature (Malakhov, *et al.*, 2020).

The temperature distribution profiles of the catalyst surface were captured using a high-resolution infrared (IR) camera (Telops Midwave HD Series (M100hd)). The study requires the use of a filter that captures thermal images in the temperature range 147–600 °C. The IR camera is suitable for use in the 3–5 μm IR spectral range. It was calibrated for four filter wheels, which allow the camera to capture electromagnetic intensities corresponding to up to 2500 °C. The manufacturer specified a lens emissivity of >93%. Furthermore, the set-up is equipped with sapphire glass, which is placed in front of the investigating catalytic section for thermal and optic visibility. Thermal data were recorded every 1 s using Reveal IR software (v. 1.7.0).

Tests were carried out consistently; the inlet hydrogen concentration was increased from case to case. The steady-state conditions were reached approximately 40 min after the experiment commenced. All measurements were carried out to achieve steady-state conditions of the hydrogen concentration and catalyst temperature.

6.2.2 Experimental results

The temperature distribution over the catalytic section (the frame with 14 catalytic cylinders) and the efficiency of hydrogen removal at low inlet hydrogen concentrations (2–5 vol %) was studied by the authors in previous work (Malakhov, *et al.*, 2020). In the present work, the catalytic section was investigated inside the vertical flow channel of the recombiner section testing facility at high inlet hydrogen concentrations: 6 vol % and 7 vol %. Test series were performed in triplicate and the average values are presented. Test series were conducted sequentially and following the initial conditions given in Table 6-1.

6.2.2.1 The temperature of the catalyst section

The steady-state temperature on the catalyst surface measured by the IR camera for each case of the inlet hydrogen concentration is presented in Figs 6-2 and 6-3. Catalytic cylinders are numbered from the right to the left. These lines of the temperature distribution were obtained by dividing the cylinder length by points (320 measured points). Thereafter, the experimental values (from the top to the bottom of the cylinder) were plotted (see Figs 6-2 and 6-3) to illustrate the temperature distribution along the vertical axis for all the cylinders. The horizontal axes in Figs 6-2 and 6-3 represent the length of the cylinder, while the vertical axes represent the temperature on the catalyst surface. The two minima of the temperature profile reflect the lower and upper stainless steel frame locations holding the catalytic cylinders.

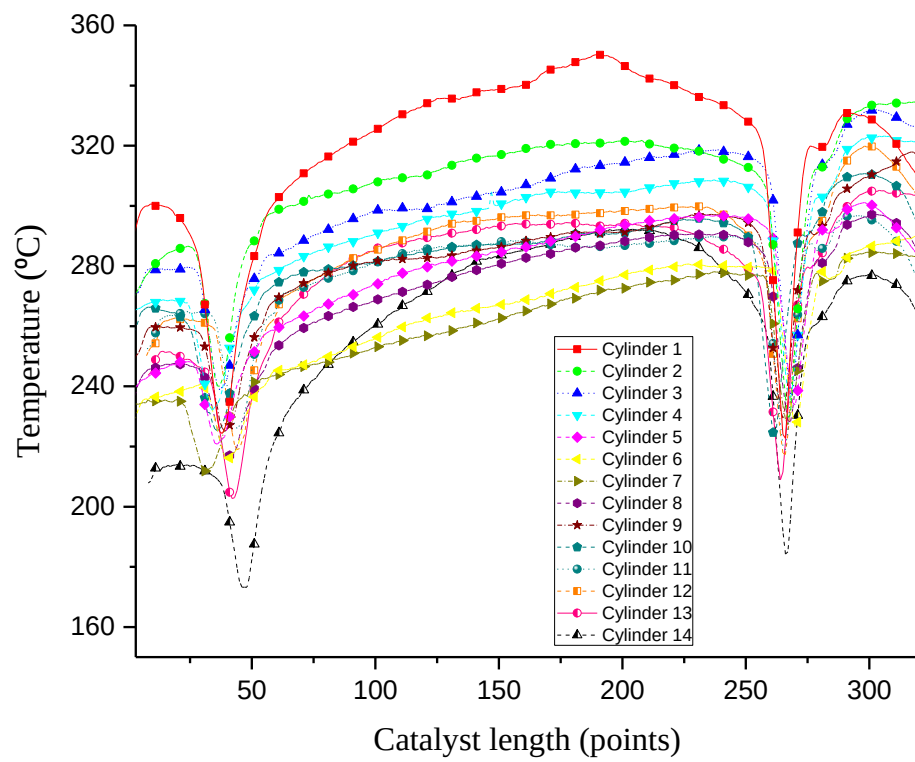


Figure 6-2: Experimental temperature distribution for each catalyst cylinder for case no. 1, $C[H_2] = 6$ vol %.

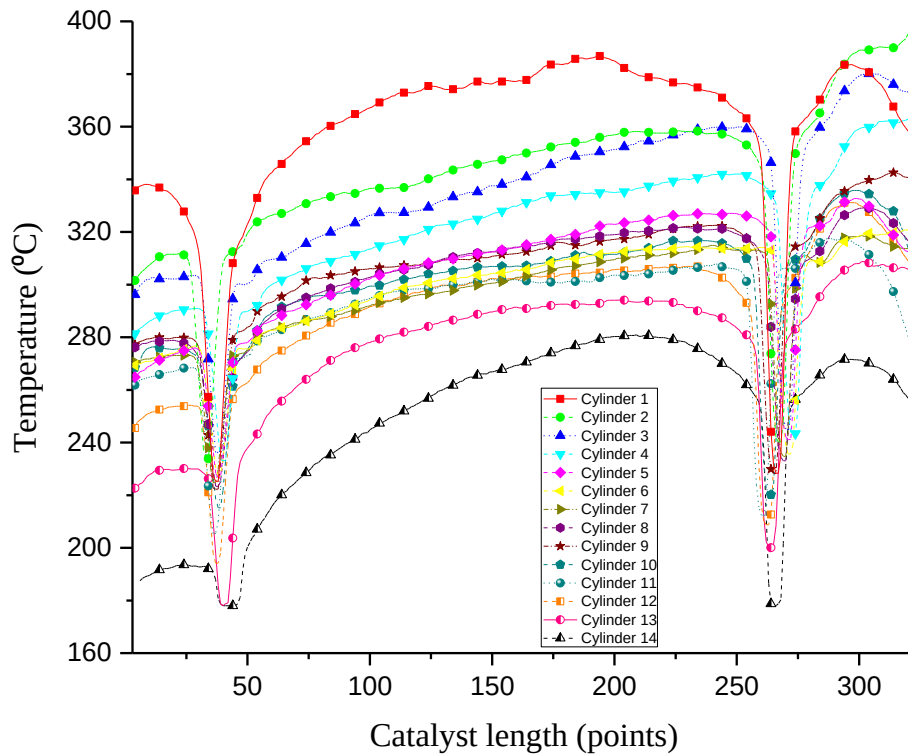


Figure 6-3: Experimental temperature distribution for each catalyst cylinder for case no. 2, $C[H_2] = 7$ vol %.

The exothermic reaction between hydrogen and oxygen is accompanied by heat release that leads to the overheating of the catalytic cylinders and by the gaseous products of the reaction. Once the gas mixture components arrive at the catalyst surface, the catalyst becomes the heat source. This heat source initiates the flow conditions for natural convection inside a PAR (Malakhov, *et al.*, 2020; Kozhukhova *et al.*, 2021). As expected, the temperatures measured by the IR camera showed a clear dependence on the hydrogen concentration. A stable temperature of the catalyst was reached after 600 s of H_2 exposure for all the cylinders. Representative temperature profiles were obtained at 6 vol % and 7 vol % inlet hydrogen concentrations, and the maximum temperature were obtained at 352 °C and 402 °C, respectively. Figs. 2 and 3 shows the temperature gradient from cylinder no. 1 to cylinder no. 14 for both considered cases. The maximum temperature of cylinder no. 1 is 352 °C, while the maximum temperature of cylinder no. 14 is 285 °C, in case of $C[H_2] = 6$ vol %. In case of $C[H_2] = 7$ vol %, the cylinder no. 14 is heated up to 395 °C, while cylinder no. 14 maximum temperature is 280 °C.

The temperature gradient along horizontal axis from left to right can be partly explained by the rather complicated shape of stainless-steel frame which hold catalytic cylinders. Figs. 2 and 3 indicates that the temperature of the catalyst 2 (on the right of catalyst section) increases as the inlet H_2 concentration increases. Although the temperature for catalyst 13 (on the left side) for both inlet H_2 concentrations are quite similar. This indicates that the asymmetry increases as the inlet H_2 concentration increases.

Considering some factors of asymmetry in the geometry of the PAR, these fluctuations may be addressed to dissimilar linear velocities throughout a recombiner framework (Kozhukhova *et al.*, 2021). The turbulent flow may also be caused by the gaps that let cylinders inertial moving up and down under the force of gas flow (short moving around cylinders location, that is limited by stainless-steel frame (± 0.1 mm)). In this concern, the hydrogen distribution across catalytic section may not be as fully homogeneous as it was expected. Another possible cause of the asymmetry along horizontal direction can be explained by the temperature damage to the frame which caused the frame to bend. Besides, it is important to admit that during experiments some of the catalyst cylinders are not that reactive than others.

Nevertheless, the ignition temperature was not observed under the experimental conditions considered here. The maximum temperature obtained on a catalyst surface does not exceed the self-ignition temperature limit of hydrogen in the air (about 560 °C) (Du Toit, *et al.*, 2018). In conclusion, from the temperature profiles we obtained, it is evident that the catalyst exhibits a high level of safety performance at inlet conditions that can be considered dangerous to ignite (i.e., H_2 concentration > 4 vol %).

6.2.2.2 The hydrogen recombination efficiency

To characterize the catalyst from the point of view of hydrogen removal efficiency, the hydrogen concentration was measured during a series of experiments at the outlet of the experimental set-up. Hydrogen concentrations were measured at an inlet mass flow rate of 35.0 g/min. The initial temperature of the catalyst was in the range 26–30 °C. Figure 4 shows the hydrogen concentration decay at the outlet of the channel for the two cases considered here (6 vol % and 7 vol % inlet hydrogen concentration).

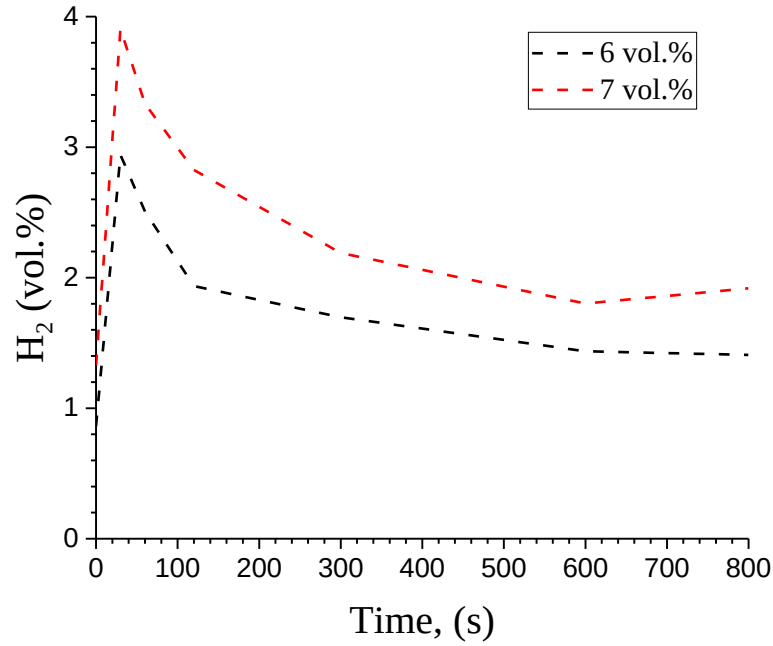


Figure 6-4: Average values of hydrogen volume fraction at the outlet of experimental setup as a function of the time at 6 %.vol and 7 %.vol in air.

During the initiation phase of recombiner operation (first 30 s), it is evident that, in cases 1 and case 2, an average hydrogen concentration reaches 2.95 vol % and 3.9 vol %, respectively (Figure 6-4). Although the H₂ concentration at the outlet increases over the first 30 s, it never reaches the inlet concentrations of 6 vol % and 7 vol %. Then, after 30 s, a continued reduction in the average H₂ concentration can be observed, which means that the autocatalytic recombination reaction has commenced. Figure 4 also shows a steady decrease in H₂ concentration at the outlet at ~120 s. The relatively constant concentration of hydrogen at the channel outlet is obtained at 300 s of operation. Steady-state average hydrogen concentration at the outlet of the set-up was achieved at 600 s (i.e., 600 after the feeding of H₂ commenced). A similar picture for the hydrogen reduction was obtained by Rożeń in the numerical study of hydrogen autocatalytic recombiner behavior under severe conditions in terms of hydrogen concentration decay (Rożeń, 2018). In accordance with the results observed in Figure 6-4, the recombination efficiency was found to be 76% and 72% for these considered cases, respectively.

6.3 CFD simulations

Numerical simulation tools were used in this study to gain a good theoretical understanding of the experiments. Extensive use was made of computational fluid dynamics software. CFD simulation

is a well recognized tool that provides an in-depth understanding of the thermohydraulics of complex objects and, in combination with the chemistry database of CHEMKIN, offers a very powerful tool to simulate the detailed process of the catalytic oxidation of hydrogen on a platinum surface (Klauck *et al.*, 2014; Meynet, *et al.*, 2014; Orszulik, *et al.*, 2015; Rozeń, 2015; Baggemann *et al.*, 2017). In this work, the CFD code STAR-CCM+ was used as the numerical tool to simulate physical–chemical processes. The STAR-CCM+ simulation environment offers all instruments required for carrying out the numerical analyses: the creation of the 3D geometries, generation of the numerical mesh, solution of the governing equations, and analysis of the results.

6.3.1 Numerical domain

As mentioned in Section 6-2, the experimental set-up was improved. The simulation model was redesigned following set-up upgrades and the assigned purpose of the study. Within the scope of its subject, a number of settings were adjusted to develop a well fitted simulation model that takes into account most of the essential parameters.

The numerical domain represents the experimental set-up in dimensions 242.0 mm x 520.0 mm x 45.5 mm. Polyhedral-type cells were selected to discretize the numerical domain with a base size of 5.0 mm, and the total number of cells was approximately 3,350,000. A prism layer mesh was created next to all surfaces and boundaries to allow the solver to resolve near-wall flow motion more accurately. Furthermore, the polyhedral mesh was improved by adjusting the surface and volume refinement around the catalyst, and all of the features in the domain. The boundary conditions on the catalytic surfaces of each cylinder express the conservation of reactant gaseous species mass and energy owing to the gas-solid contact interface. The emissivity of the catalyst surface is applied to be $\varepsilon = 0.9$. The walls in calculation domain assumed adiabatic and impermeable, the energy that could be allocated with the wall species influx or outflux is not added in simulations.

As was noted by the authors in a previous study (Malakhov, *et al.*, 2020), the flow inside the channel is turbulent due to complex geometry, hence a realizable k-epsilon model with a two-layer approach was used to simulate a turbulent flow. Reynolds-averaged Navier–Stokes equations were solved to simulate the flow motions. The discrete ordinate method as a method for simulation the radiative heat transfer in participating media was used in the CFD model (Fiveland, 1985).

In a detailed study of the hydrogen recombination processes, it is necessary to take into account physicochemical processes occurring both on the surface of the catalyst (a surface chemical mechanism) and in the gas volume (a gas-phase chemical mechanism). The surface mechanism

proposed by Deutschmann *et al.*, (1996), accompanied by the gas-phase mechanism proposed by Warnatz *et al.*, (1990), was introduced to simulate an autocatalytic recombination reaction of hydrogen.

6.3.2 Simulation results

Numerical simulations were conducted to investigate the recombiner section behavior under severe hydrogen conditions, to develop and validate a CFD model that includes the surface and gas-phase reactions' mechanism of hydrogen oxidation on a platinum catalyst.

A numerical evaluation of the temperature profile was conducted to validate experimental results. Figure 6-5 presents a comparison between simulation and experimental results for the 6 vol % case now considered.

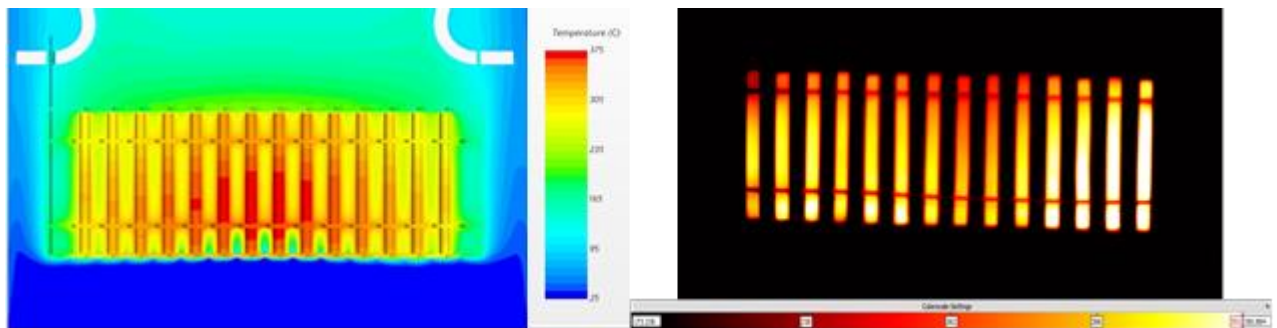


Figure 6-5: Comparison of catalyst temperature profile for case no. 1, $C[H_2] = 6$ vol %: calculated (STAR-CCM+) and that experimentally measured (IR camera).

Figure 6-5 shows that the highest temperature is around the bottom part of the cylinders. The calculated maximum temperature was obtained on the surface of the cylinders in the middle (372 °C), while the experiments indicate that cylinder nos 1 and 2 are the hottest (352 °C). It is evident the hottest catalyst may expect to be in the centre due to the thermal radiation causes larger heat losses across the side walls, while in the centre the radiation is heating neighbour cylinders. This thermal distribution behaviour can be observed from CFD simulation results (Figure 5, left), specifically because the simulation model assumed symmetry. Overall, the calculated and measured temperature profiles are in reasonable agreement.

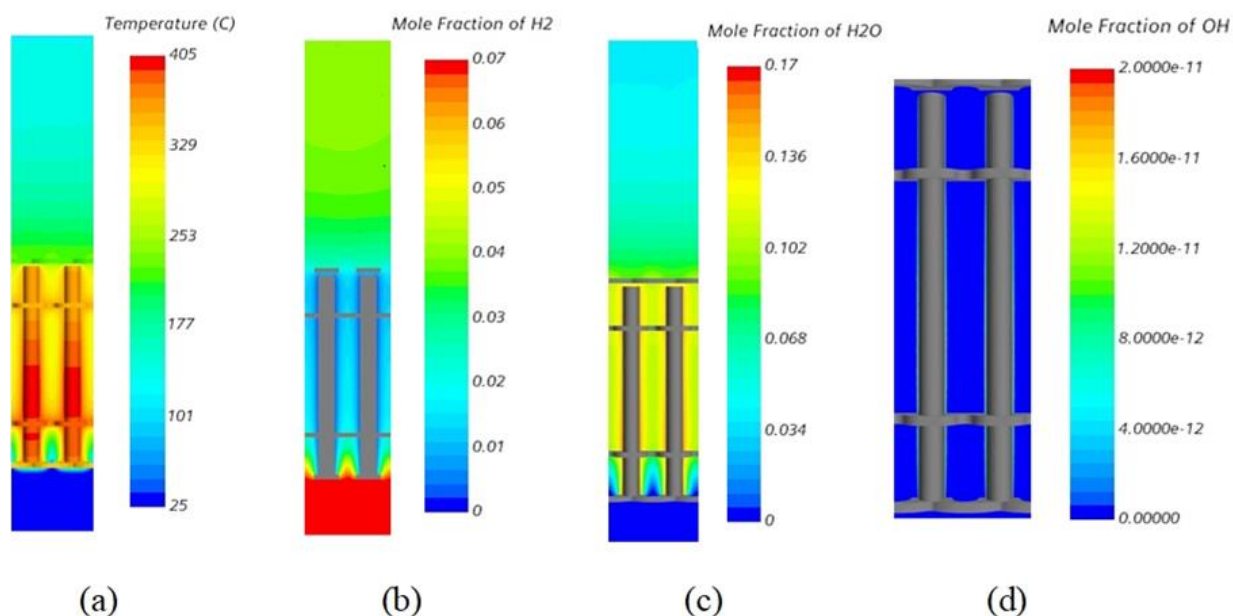


Figure 6-6: Calculated profiles: (a) surface temperature for the two cylinders in the middle; (b,c) hydrogen and H₂O products; and (d) OH concentration for case no. 2, C[H₂] = 7 vol %.

Calculated profiles for the surface and environment temperatures, reactants, and product concentrations between two middle cylinders are presented in Figure 6-6. (Experimental details applicable here: 7 vol % inlet H₂ concentration.) Here, the calculated maximum catalyst surface temperature was obtained from case no. 2, at ~405 °C. Taking the common knowledge that the gas phase self-ignition temperature for the air–hydrogen mixture is about 560 °C, one can see that the maximum experimentally obtained catalyst surface temperature does not reach this limit. However, in some studies it has been found the ignition limit could be reached at much lower inlet hydrogen concentrations. For instance, a plate-type PAR catalyst had already reached the hydrogen self-ignition temperature at 4 vol % of H₂ (Reinecke *et al.*, 2005; Klauck *et al.*, 2014; Rozeń, 2018). Furthermore, Meynet *et al.* have reported that the gas-phase heat release has a strong increase at 5.4–5.6 vol % of inlet H₂, for a similar plate-type catalyst (Meynet, *et al.*, 2014; Meynet and Bentaib, 2017).

Yet another indicator of the presence of the hydrogen gas-phase ignition processes can be identified through the OH radical in the reaction products (Dogwiler, Benz and Mantzaras, no date). Ljungstrom *et al.* established that the catalytic surface reaction promotes a gas-phase reaction via radicals (OH, O, and/or H) emitted from the surface, which then cause gas-phase chain reactions (Ljungström *et al.*, 1989). As an example, Meynet *et al.* carried out studies and

demonstrated the availability of OH radicals as a chemical reaction product, with a maximum 1.0×10^{-3} mole fraction of OH at 8 vol % of inlet H_2 , while a temperature of 800 °C was achieved on the catalyst surface (Meynet, *et al.*, 2014). From the data obtained in our study, and demonstrated in Figure 6-6(d), the numerically calculated outlet mole fraction of OH does not exceed 2.0×10^{-11} . Moreover, all emitted OH species are located around the catalyst surface and does not flowing up, following by main gas motions direction (Figure 6(d)) (Ljungström *et al.*, 1989). A more detailed discussion, along with further calculations on this matter, will be published at a later study.

Figure 6-7 shows the comparison of experimental and numerical temperature profiles on an average scale for all fourteen cylinders. The local two peaks that identify the lower and upper stainless-steel frames holding the catalytic cylinders are omitted here.

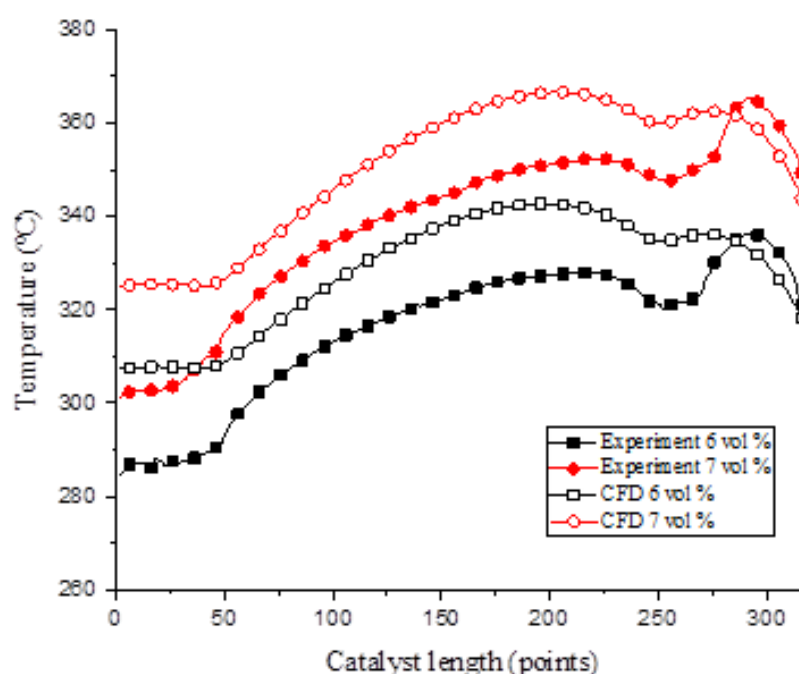


Figure 6-7: Comparison of the average of calculated and experimentally measured catalyst temperature profiles at 6 vol % and 7 vol % inlet H_2 .

6.4 Conclusions

In the recombiner section testing station, located at HySA Infrastructure, a test series of experiments with 6 vol % and 7 vol % of inlet H_2 (inlet mass flow rate 35.0 ± 0.2 g/min) was performed. The catalytic section of the PAR, which contains fourteen cylinders, was studied in

terms of the temperature distribution and hydrogen recombination efficiency. The experimentally obtained data were successfully used to develop and validate a 3D CFD model that includes both the surface reactions as well as the mechanism of the gas-phase reactions of H_2/O_2 catalytic oxidation. The experimental and simulation results were largely in good agreement; there was a rather high level of predictability in terms of the hydrogen recombination efficiency, temperature distribution across the catalyst section and the temperature maximum. The temperature gradient along horizontal axis from left to right was observed for both considered cases and can be addressed to the factors of asymmetry in geometry and appearance of flow fluctuations in the PAR channel. Besides, during experiments some of the catalyst cylinders are not that reactive than others. In addition, the initiation phase, and the start-up behaviour of the recombiner operation, were determined experimentally. The time to reach steady-state hydrogen concentration at the outlet of the set-up was determined approximately 600 s after initiation of the hydrogen exposure.

The conjugated approach that includes the surface and gas-phase chemical reaction mechanism was successfully applied to the 3D CFD model. This test series was carried out at high hydrogen inlet concentrations; however, ignition inside the experimental set-up was not observed. Moreover, under considered conditions, the simulation results demonstrated that mole fraction of OH radical does not exceed the ignition limit.

In a subsequent step (to be reported on later), a test series is planned in order to study the reaction kinetics under high inlet hydrogen concentrations of up to 10 vol %. Furthermore, as oxygen starvation conditions may act in a gas-phase hydrogen ignition, this issue will be also addressed in a further study.

6.5 Acknowledgments

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CHAPTER 7: CONCLUSIONS AND RECOMMENDATIONS

This chapter presents the conclusions to the work described in the thesis (with reference to the objectives denoted in Chapter 1), as well as recommendations for the future development and application of the CFD models.

7.1 Conclusions

The worldwide general interest in hydrogen energy has grown rapidly in recent years, particularly after the wider use of modern computer simulations. Nevertheless, associated with efforts towards fully substituting hydrocarbon fuel, the issue of safety remains most essential for the development, commercialization, and implementation of hydrogen technologies. Numerical simulations, utilizing the computational fluid dynamics (CFD) approach, demonstrate relevance towards providing a stable foundation for related safety issues. Accurately predicting safety requirements will go a long way to enable hydrogen to become a future energy carrier and to establish a hydrogen economy.

In this thesis, the mitigation technologies for hydrogen safety were investigated experimentally, in relation to the development and validation of innovative CFD models for hydrogen leakage in confined spaces and autocatalytic recombination processes.

- I. In Chapter 2, a review of the literature identified that utilization of forced ventilation (FV) systems and passive autocatalytic recombiners (PARs) are worldwide accepted technologies to prevent the formation and dispersion of flammable mixtures of hydrogen with air. (i) The ventilation systems can promote flow circulation, thereby mixing the hydrogen with air to below the flammability limit. Currently, ventilation technology is used in residential garages, subsea tunnels, and underground mine tunnels to effectively remove the unintended release of flammable hydrogen away from the space/facility/environment where hydrogen is used. However, the literature review identified that in most cases, only vertical-direction hydrogen release has been investigated. (ii) Elsewhere, PARs as safety devices are used in the nuclear industry to reduce the concentration of hydrogen utilizing an exothermic chemical reaction on a noble metal catalyst. In current literature, there appears to exist only one- and two-dimensional numerical models to simulate the chemical mechanism of hydrogen autocatalytic recombination. Furthermore, the focus of existing studies is mostly on employing the plate-type catalyst—cylindrical-type has not been considered. In the other hand, the utilizing of CFD can be extremely useful to investigate technologies for hydrogen safety. CFD could

offer a number of advantages to examine the parameters of the simulated phenomena by assessing variables that cannot be accurately measured experimentally.

- II. In Chapter 3, the hydrogen distribution under a leakage accident in a confined space was analysed experimentally, in efforts to determine the hydrogen removal efficiency. Focus was on two different sizes of leak orifice and the use of various hydrogen release pressures, in the presence or absence of FV. Results revealed a difference in behaviour of hydrogen distribution, i.e., for a small orifice and at high pressure compared with a large orifice and at low pressure. In the case of the latter (large orifice, low-pressure), a greater amount of hydrogen is released into a confined space. Nevertheless, a case with a small orifice and high-pressure release demonstrated a relatively lower amount of released hydrogen. The experimental results and numerical validation demonstrated that the FV provides a high level of hydrogen removal efficiency. The ventilation flow velocity of 6.5 m/s is sufficient to dilute unintended hydrogen leak to below 4 vol %. The effect of forced air, causes potentially flammable hydrogen cloud to mix with air and move away from the leak point much faster in contrast with the absence of ventilation. Thereby, FV is strongly recommended to be deployed to the facility which is using hydrogen. The experimental results confirm improved mitigation strategies for hydrogen safety. The numerical model extends the current database in terms of predicting the hydrogen distribution behaviour in a hypothetical case of the release in a confined space.
- III. In Chapter 4, a three-dimensional (3D) CFD model of a small-scale PAR with a cylindrical-type Pt catalyst section was developed in STAR-CCM+ and validated by experimental evaluation. The multi-step surface reaction mechanism of hydrogen oxidation on the Pt catalyst was implemented to simulate hydrogen autocatalytic recombination. The cylindrical-type catalytic elements were investigated in terms of the surface temperature increase due to the exothermic reaction and hydrogen recombination efficiency. The developed CFD model demonstrated a high level of predictability and it can be employed in the analysis of other catalyst geometries and inlet hydrogen concentrations. Results indicated that the cylindrical-type catalyst performance was safe at low inlet hydrogen concentrations. The temperature from the top to the bottom of the catalyst cylinders showed a homogeneous profile. The maximum was observed at the middle of the catalyst surface (~ 310 °C at 5 vol % of inlet H_2), where most of the hydrogen recombination reaction takes place. The efficiency of hydrogen recombination for considered cases here was estimated to be $\sim 55\%$, according to measured and simulation results. It is interesting to note that the recombination efficiency slightly increased with an increasing inlet hydrogen concentration. Moreover, the numerical results demonstrated that the operation

is in the diffusion regime, which means that the hydrogen diffusion for the catalyst utilized here is slow under the considered experimental conditions. According to experimental evaluation and numerical validation, the cylindrical-type catalyst was determined to be reliable and safe (up to 5 vol % H₂).

- IV. Chapter 5 included a description of the design and characterization of an in-house developed Pt/AAO (Pt/anodized aluminum oxide) catalyst as well as the applicability of the CFD model (developed in Chapter 4) to investigate interactions of temperature distribution, heat and mass transfer, and hydrogen recombination efficiency. The experimentally obtained temperature gradient over the length of the catalyst was 23 °C for a uniform Pt distribution catalyst. The CFD model, which utilizes a multi-step surface chemistry mechanism, has been successfully applied to simulate the safety performance of a thermally conductive aluminum catalyst. A difference in temperature gradient was observed at 23 °C and 3 °C for experiments and simulations, respectively. This deviation can be ascribed to the actual distribution of Pt on the AAO surface of an in-house developed catalyst—it could not be accounted for numerical simulations (at the present time). In terms of hydrogen recombination efficiency, the simulation results indicate a near-zero (0–0.005 vol %) H₂ concentration, thus near-complete H₂ recombination occurred over the length of the catalyst surface. A thermally conductive Pt/AAO catalyst has exhibited satisfactory performance for application in the passive autocatalytic recombination of hydrogen. The 3D CFD model developed in Chapter 4 demonstrated an ability to be further applied for various types of PAR catalyst elements and can predict experimental performance satisfactorily.
- V. Chapter 6 included a description of the development and characterization of a detailed 3D CFD model in STAR-CCM+ to verify the multi-step mechanism of surface and gas-phase hydrogen recombination chemistry for a cylindrical-type Pt catalyst. The thermal distribution of the catalyst as well as the outlet hydrogen concentrations were obtained experimentally to validate the detailed CFD model. The experimentally measured maximum temperatures of 352 °C for 6 vol % and 402 °C for 7 vol % hydrogen were obtained at a relatively low position, at the bottom of the catalyst. Although the test series was conducted at high hydrogen inlet concentrations, the hydrogen self-ignition temperature was not observed in the experimental set-up. Moreover, under the considered conditions, the simulation results demonstrated that the mole fraction of the OH radical does not exceed the ignition limit. In addition, the initiation phase, and the start-up behaviour of the recombiner operation, were determined experimentally. The time to reach steady-state hydrogen concentration at the outlet of the set-up was ~600 s after initiation

of the hydrogen feed. The experimental results demonstrated that the cylindrical-type catalyst behaved well under conditions of high hydrogen concentrations, even at 7 vol % hydrogen (which is already beyond the minimum flammability hydrogen concentration in air), while the numerical results provided a new extension of a database in terms of 3D CFD modelling to simulate, in detail, hydrogen autocatalytic recombination reactions on the Pt catalyst.

7.2 Recommendations for future work

Although this thesis attempted to encompass a wide number of safety aspects pertaining to hydrogen technologies, there remains many more different tests, simulations, and interesting analyses that warrant attention in future work.

One suggested focus area of future research pertains to the hydrogen leakage into large-scale confined spaces, representing an underground mining tunnel. The outcome of such research should provide valuable safety recommendations, towards accelerating the gradual replacement of diesel vehicles with hydrogen fuel cell (HFC) vehicles in the mining industry. In addition, having identified that the presence of FV is very effective in the case of hydrogen leakage (Chapter 3), it is apparent that the value of ventilation flow must be determined with respect to the pressure of the hydrogen release. Future research findings could provide specific values. Meanwhile, CFD investigations of the hydrogen release need to include the revision of several model details to simulate the release of hydrogen in a large-scale confined environment/space. For example, a 'coupled flow' model could be considered to simulate flow motions instead of using a 'segregated flow' model. The turbulence model may also be revised. The specifying of molecular diffusivity of components in a mixture by means Schmidt number must be taken into account for high-turbulence flow motions and require further study.

Yet another area of future work includes a more in-depth analysis of chemical mechanisms of the hydrogen autocatalytic recombination reaction as well as the cylindrical-type catalyst performance under inlet hydrogen concentrations above 7 vol %. In this case, the advantages of a CFD approach will be able to provide a wide number of relevant knowledge to understand physical–chemical processes in a PAR. Moreover, the parametrical study in terms of different inlet mass flow rates and velocities and their effect on catalyst performance is essential to be conducted.

According to the catalyst study, it will be interesting to conduct the study of characteristics of supporting material for cylindrical-type catalyst. Moreover, the determination of the site density of real catalyst can contribute to the accuracy of CFD simulation results.

An important parameter of numerical validation of a PAR is to estimate the Soret effect. The Soret effect is the mass diffusion due to the presence of a temperature gradient and it may be an important phenomenon showing itself in localized hydrogen spots with concentrations beyond the ignition limit. It may be difficult to study the effects of thermal diffusion experimentally; however, CFD methods can offer this opportunity.

Meanwhile, the ability of the model (see Chapter 6) to be applicable for the various shapes of catalytic elements could be applied in future work. For instance, the Pt/AAO catalyst (see Chapter 5) can be investigated numerically utilizing a developed detailed 3D CFD model, from a safety viewpoint for PAR application under accident conditions.

Another opportunity for further investigation is the testing of cylindrical-type PAR (RVK-500) catalysts for scalability. Although the recombiner consists of a number of catalytic units, the efficiency of a PAR fully loaded with catalytic units can be numerically simulated by adjusting the CFD model for scalability. Instead of simulating all catalytic units, the CFD model can be rescaled to predict the hydrogen recombination efficiency of a fully-loaded PAR. Therefore, the development of a scalability model is considered valuable for the terms of validation of a full-size PAR's performance and effectiveness.

APPENDIX A: MATH HYDROGEN CATALYTIC RECOMBINER: ENGINEERING MODEL FOR DYNAMIC FULL-SCALE CALCULATIONS

The Appendix A described the development of the hydrogen recombiner numerical model (2D). It is included in this thesis as the theoretical background of numerical methods focusing on the hydrogen autocatalytic recombination mechanisms.

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OVERVIEW

To protect a hermetic enclosure and the equipment and systems of a reactor installation housed in it from damage caused by the ignition (explosion) of hydrogen, most nuclear power plants with pressurized water reactors are provided with a hydrogen concentration monitoring system and an emergency hydrogen removal system. These systems prevent the formation of explosive mixtures in the accident localization zone by maintaining the concentration volume of hydrogen in the mixture below the safety limits, which ensures the preservation of the density and strength of the hermetic enclosure and the operability of other localizing safety systems. A key component of an emergency hydrogen removal system is a passive autocatalytic hydrogen recombiner that operates on the principle of the catalytic recombination of hydrogen and oxygen. There is an urgent need for a full-scale dynamic calculation of the development of emergency conditions in a nuclear power plant containment accompanied by a large release of hydrogen. In efforts to achieve this, we constructed, and justified, a simple engineering thermohydraulic model of hydrogen removal in the operation of a passive autocatalytic recombiner based on the available experimental data. This paper presents the application results of the model as a part of contour industry codes RELAP, TRACE and CORSAR, intended, among other things, for carrying out multi- factor and full-scale calculations of the dynamics of emergency processes with the release of hydrogen into nuclear power plant premises. This model allows us to substantiate the dynamics of local concentrations of gas components of a mixture in a confined space; the temperature of the mixture, the catalyst and the walls of the box; and the pressure when hydrogen or steam is supplied to the box. We have analysed various rates of hydrogen supply to a closed box to numerically substantiate the time at which the concentration reaches the maximum level. Furthermore, we have calculated the performance for several entrance concentrations of hydrogen and

obtained a satisfactory agreement between the dynamics of the concentrations, the temperatures of the catalyst and gas, and the productivity of the passive autocatalytic hydrogen recombiner. These calculations are based on the results of comparisons between calculated and available experimental data.

8.1 Introduction

LIST OF SYMBOLS

B Flow coefficient, kg/s

C Molar concentration, mol/m³

C_v Volumetric concentration, kg/m³

D Current mass flow of hydrogen, kg/s

D_g Hydraulic diameter of the beam of catalyst rods, mm

D_h Thermal diameter of the beam of catalyst rods, mm

F Flow section of the recombiner, m²

G Current mass flow rate of natural air circulation, kg/s

ΔH Enthalpy of reaction, J/kg

K Reaction rate, kmol/(m²·s)

K Empirical coefficient of “completeness of recombination”

M Weight of air (mixture) in the box, kg

R Universal gas constant, m² kg s⁻² K⁻¹ mol⁻¹

Pressure, Pa

Temperature, °C

t Time, min, s

Air speed, m/s

W Heat dissipation power, W

The accident at the Fukushima-1 NPP on 11 March 2011 clearly showed the need to revise the approaches to severe accident management (SA). Taking into account that the buildings of the two power blocks of the NPP were destroyed by hydrogen explosions, special attention was paid, worldwide, to studying the formation of explosive mixtures in the accident location area (ALA) and

searching for effective means of preventing an explosion and maintaining the integrity of the enclosure vessel (EV) of the nuclear plant during SA. The generally accepted global practice for the removal of hydrogen from an EV is based on the principle of passive catalytic hydrogen recombination using catalytic elements containing platinum (CEC, 1992; Ferroni F., and Schiel L, 1994; Devit U.A, and Koroll J.N, 1996; SIEMENS, 1998; IAEA, 2011). Catalytic elements, of various geometric shapes, are assembled into catalytic blocks. In Russia, cylindrical ceramic catalytic elements with a platinum coating are used in equipment that implements the principle of catalytic hydrogen recombination (the main producer is INPK RET) (RVK, 2004, 2005). Fig. 8-1 shows a schematic representation of a passive catalytic hydrogen recombiner (PAR) device (RVK, 2004, 2005).

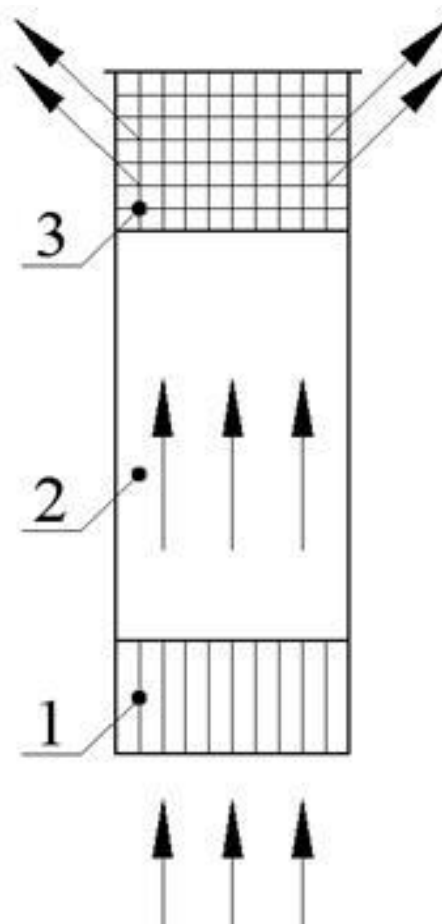


Figure 8-1: PAR construction (the arrows show the direction of movement of hydrogen-air mixture): 1 – the catalytic block with an entrance window from below; 2 – framework with the convection section; 3 – exit window.

On the surface of the catalyst, an exothermic chemical reaction occurs between the hydrogen and oxygen compounds. Simultaneously, heat release creates a useful driving pressure of the

vapour-air-hydrogen mixture and a stable natural circulation (NC) through the PAR. The stability of the circulation is facilitated by the heating of the catalyst at a temperature above the gas temperature at the exit of the device. Gas containing the products of the combustion of hydrogen (water vapour) is emitted into the atmosphere through the housing exit. Fig. 8-2 shows the appearance of the PAR (model RVK-500). Initially, numerous tests of the PAR RVK series were performed by the manufacturer (CJSC INPK RET) (Blanchat and Malliakos, 1999; Reinecke, Tragsdorf and Gierling, 2004; RVK, 2004, 2005; Reinecke *et al.*, 2010; Meynet, 2013).

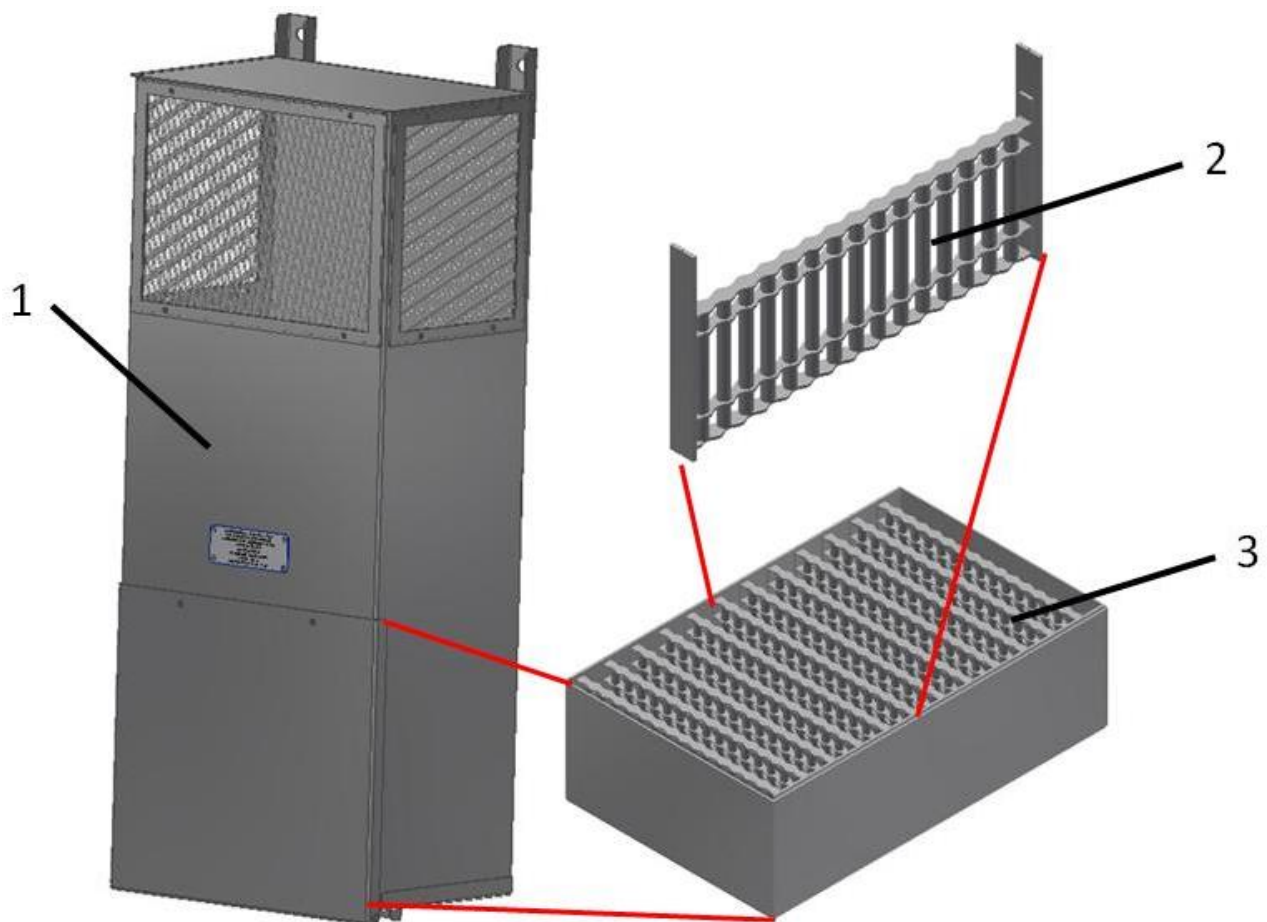


Figure 8-2: Appearance of the PAR (RVK-500): 1 – PAR framework; 2 – cylindrical catalytic element; 3 – catalytic block.

In 2016, the State Scientific Center of the Russian Federation Institute of Physics and Power Engineering (SSC RF-IPPE) conducted inspection tests at the measuring installation for the testing of hydrogen safety systems of nuclear power plants (MITHSS) (Rosenergoatom, 2015). Some of the results are presented in this paper. The purpose of these tests was to confirm the main characteristics of the PAR RVK-500 model and to justify the possibility of transferring

(scaling) the results to other PAR RVK models. In the working vessel of the MITHSS, parallel to the vertical axis, a bar was mounted on which prefabricated console elements for fixing the RVK-500 PAR were installed. The placement of the RVK-500 PAR in the working volume of the MITHSS vessel is shown in Fig. 8-3.

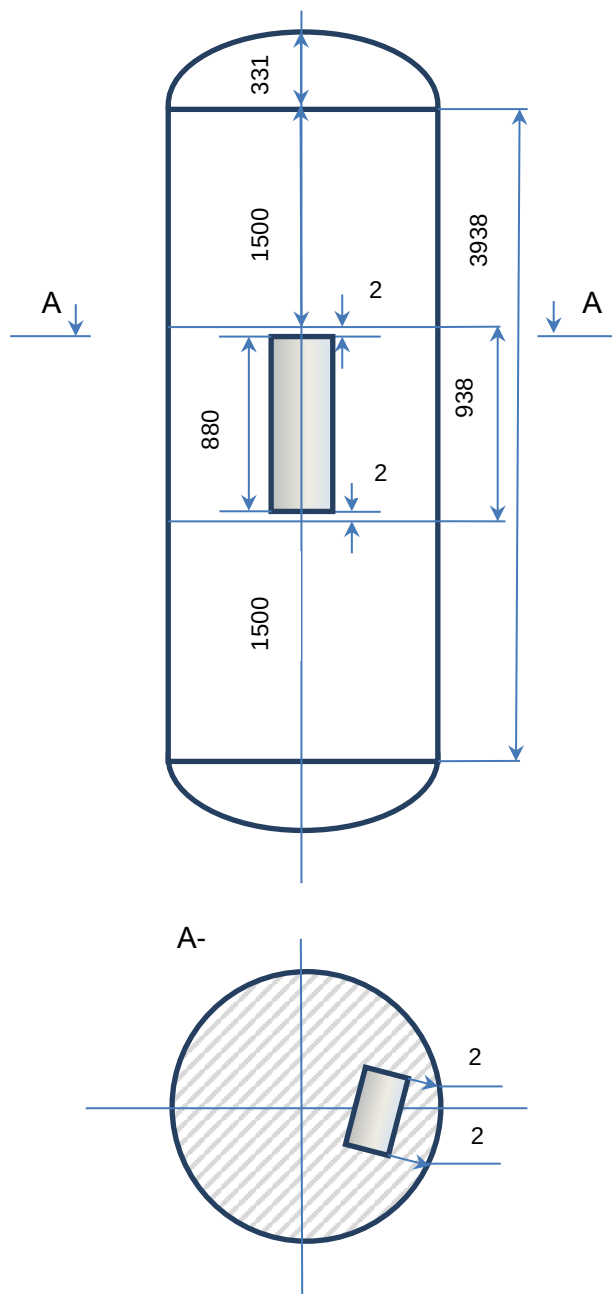


Figure 8-3: Sketch of RVK-500 deployment in the experimental vessel.

The vessel has a cylindrical shape (volume 8.9 m³) with tubes for supplying hydrogen and steam. The tests to determine the efficiency of the recombiner included four main steps:

- heating the mixture in the volume of the MITHSS vessel to the set temperature,
- supplying steam (if necessary),
- supplying hydrogen for 1-5 min,
- mixing (for testing without steam).

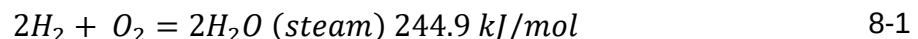
The following measurements were recorded over a period of 30-50 min:

- the temperature of the gas in the vessel,
- the gas temperature at the entrance and exit of the PAR,
- the hydrogen concentration at the entrance of the PAR,
- the concentration of hydrogen at the exit of the PAR,
- the pressure in the vessel,
- the temperature of the catalytic unit.

At present, there is no simple engineering model for the operation (the removal of hydrogen) of a recombiner which would allow full-scale dynamic calculations of the development of an emergency mode in a nuclear power plant containment that is accompanied by a large release of hydrogen. The aim of this study is to build and substantiate such a simple model of a PAR based on available experimental data.

8.1 Theoretical: physicochemical basis of hydrogen recombination

The hydrogen oxidation reaction is exothermic it occurs with the release of energy.



The detailed mechanism of hydrogen oxidation on platinum (heterogeneous mechanism of chemical reactions) is multistage. Depending on the purposes of modelling, it is desirable to consider from 14 to 16 steps (Rinnemo *et al.*, 1997; Appel *et al.*, 2002). In practice, the detailed mechanism is usually simplified to a one-step exothermic reaction, introducing a model reaction rate obtained from the detailed mechanism of kinetics with reasonable simplifications. This is done in the Kazemo model (Rinnemo *et al.*, 1997), for example. To show the recombination at low hydrogen concentrations, the reaction rate is fairly well described by the following kinetic equation:

$$K = 4,695 \times T^{\frac{1}{2}} \left(\frac{C[H_2]^2}{C[O_2]} \right) \quad 8-2$$

The Schefer kinetic model (Schefer, 1982), which is often used in the modelling of the catalytic hydrogen recombination reaction, describes the reaction rate by the following equation:

$$K = 14 \times \exp \left(-\frac{16.1 * 10^6}{R_u * T} \right) \times C[H_2] \quad 8-3$$

The latter (3) is the Arrhenius equation with empirical parameters, where the pre-exponential factor is proportional to the hydrogen concentration. It is known that the speed of a heterogeneous chemical process is determined both by the rate of the chemical reaction on the surface and by the speed of the supply of the reacting substances to the surface (mainly due to convective diffusion). These two processes determine the so-called kinetic and diffusion areas (Frank-Kameneckiy, 1987). Equation (3) and, to a lesser extent, equation (2) are obtained in the formulation of the recombination occurring in diffusion mode, that is, they are applicable to processes where the diffusion rates (delivery of reacting components) determine the speed of the entire heterogeneous chemical process. However, equations (2) and (3) in themselves do not determine the rate of delivery of components to the catalyst, but only the possible rate of recombination at given concentrations of reacting components and temperature. In a detailed study of the dynamics of the ongoing processes, it is necessary to implement the conjugate approach with the help of computational fluid dynamics (CFD) methods, taking into account physicochemical processes occurring both on the surface of the catalyst and in the gas volume. As a rule, the implementation of such an approach involves numerous calculations and is still more fundamental than practical. Experiments with the PAR in a sealed box show that when the device operates, the temperature and pressure values change almost as they do when an electrically heated device of an identical design operates, and the power decreases exponentially with time. This analogy leads to the conclusion that, within the framework of contour two-phase codes designed to simulate design accidents at NPPs in a full-scale setting (including the hydrogen yield (*Ensuring hydrogen explosion protection at a nuclear power plant*, 2002)), engineering calculation of the dynamics of hydrogen concentrations and thermophysical parameters in the NPP premises is possible, taking into account PAR operation. In order to do this, an additional model of a recombination calculation should be developed.

When selecting codes, one should first rely on the verified, widely used and industry supported contour two-phase codes, including RELAP, TRAC, TRACE (USA) and CORSAR (Russia). All these codes allow the modelling of a multicomponent vapour- gas medium of variable composition (single-velocity approximation for the gas phase) and have special models for calculations of

hydrogen generation in the active area (steam-corium reaction and radiolysis of water). It is important to take note of the solutions offered by modern CFD codes for 3D modelling of the processes under consideration in a containment with strong spatial detailing, but in a reduced-scale physical process, unlike contour codes. The model of a multicomponent mixture of gases in CFD codes is also a single-speed and single-temperature model, which assumes the identity of the main calculated results with contour codes. The difference between two types of codes lies in the application of the viscous gas model and turbulence models.

8.1.1 Simple model of the thermal hydraulics of a recombiner in a closed box

Consider a simplified single-component computational model of the PAR in an experimental box for process analysis and the implementation of this model in one of the codes. The productivity of the recombiner (the current mass flow of burned hydrogen, kg/s) is described by the theoretical equation:

$$D = k \cdot G \cdot C = k \cdot F \cdot V \cdot C_v \quad 8-4$$

where G is the current mass flow rate of NC of air through the PAR, C is the current mass concentration of hydrogen at the entrance of the recombiner (kg/kg), C_v is the volumetric concentration (kg/m³), V is the air velocity in the PAR, F is the cross-section of the recombiner (matched with velocity via porosity), k is the empirical coefficient of “completeness of recombination” of hydrogen the share of the “burned” reagent of the volume incoming to the device. Heat dissipation power (W) during combustion of hydrogen in air oxygen (irrespective of combustion method: detonation, combustion or recombination) is given by

$$W = \Delta H \cdot D \quad 8-5$$

where ΔH is the enthalpy of the reaction (see (1), in J/kg). The differential equation for the dynamics of the average hydrogen concentration in a closed box (without sources) with initial concentration C ($t = 0$) is given by

$$M_0 \cdot \frac{dC}{dt} \equiv -D = -k \cdot C \cdot G, \quad 8-6$$

where M_0 is the initial mass of the air in the box. In further calculations, the coefficient of completeness of recombination is temporarily omitted ($k = 1$). In the presence of a hydrogen

source (G_H), the balance equation for the average mass concentration of hydrogen in the box is given by

$$M_0 \cdot \frac{dC}{dt} = -C \cdot G + G_H(t), \quad 8-7$$

and is solved by an analytical method:

$$\begin{aligned} C(t) &= \frac{1}{\mu(t)} \cdot \left(\int f(t) \cdot \mu(t) dt + \text{const} \right), \\ \mu(t) &= \exp\left(\int a(t) dt\right), \\ a(t) &= \frac{G(t)}{M_0}, \\ f(t) &= \frac{G_H(t)}{M_0} \end{aligned} \quad 8-8$$

It follows from (8) that in the absence of a recombiner (or at a hydrogen concentration below the threshold level for the PAR), the concentration increases linearly with time with a constant supply of hydrogen. Ideally, at a constant air flow through the PAR and a constant flow of hydrogen, a constant value of the average hydrogen concentration (mass) is established in the box, equal to the inflow ratio per air flow ($k = 1$)

$$C = \frac{G_H}{G}. \quad 8-9$$

The complete solution of equation (7) with constant flows and zero initial concentration will be as follows:

$$C(t) = \frac{G_H}{G} \cdot \left(1 - \exp\left(-\frac{G_H \cdot t}{M_0}\right) \right). \quad 8-10$$

In the absence of a hydrogen source, $f(t) = 0$, and in the presence of a given initial concentration in the box, as a result of integrating equation (6), we obtain the exponential law of decreasing the average hydrogen concentration ($k = 1$)

$$C = C(t=0) \cdot \exp\left[-\frac{1}{M_0} \int_0^t G(t) dt\right]. \quad 8-11$$

Equation (11) has a physically obvious meaning. The rate of concentration decrease is determined (for $k = 1$ and $G(t) \approx \text{const}$) by the ratio between the NC consumption through the PAR and the initial air mass in the box. With the help of equations (4), (5) and (11), it is possible to determine the current heat release power depending on the current consumption of the vapour-gas mixture at NC through the recombiner:

$$W = k \cdot \Delta H \cdot G \cdot C(t=0) \times \exp\left[-\frac{k}{M_0} \cdot \int_0^t G(t) dt\right]. \quad 8-12$$

The empirical coefficient (parameter) of the completeness of recombination, k , has a significant effect on the power of heat release and the rate of decrease in heat release and, accordingly, the rate of decrease in the average hydrogen concentration. This parameter, under the condition of diffusion mode, namely, in the mode in which the recombiner operates, is fully determined by the properties of the catalyst. The most significant outcome in the derivation of equation (12) is that the dynamics of heat release is determined by the initial hydrogen concentration and depends on the flow rate. This makes it possible to reduce the problem to the calculation of the NC of air and then determine the flow rate of the NC through the PAR, where the catalytic block is a “heater” and the walls of the box with a large heat capacity play the role of a “refrigerator”. In this case, air is regarded as an ideal gas and a box with PAR in contour codes can be considered as a single 2D/3D porous body with a given hydraulic resistance of the bundle of catalytic elements. To solve the thermal part of the problem, it is sufficient to use the heat sink model to the case of a finite (and large) heat capacity. Indeed, even in the presence of ideal thermal insulation of the experimental box (volume $\approx 10\text{m}^3$), the total heat capacity of the steel box body weighing 200 kg exceeds, by orders of magnitude, the total heat capacity of the air. As a result, within 30-60 min of PAR testing, the temperature of the walls of the box will remain almost unchanged (cold). In the catalytic “burning” of hydrogen, the power of the heat release of a chemical reaction is generated on the catalyst. In this case, the catalyst temperature is always higher than the exit gas temperature. The chemical reaction proceeds within the boundary layer with the catalyst, and the main part of the heat is diverted to the catalyst. The thermal conductivity of the catalyst base, even for ceramics (emery), is much higher than the molecular thermal conductivity of the air. The proposed design model makes it possible to provide an experimentally observed significant delay in time until the maximum air temperature at the exit from the PAR is reached. The reason for this delay is the fact that the total heat capacity of the catalyst is 180 times greater than the total heat capacity of the flowing air in the recombiner. Therefore, in the design model, it is very important to determine the heat transfer coefficient from the catalyst beam to the gas mixture. The

coefficient value (as well as the parameter k) determines both the catalyst temperature and the thermal head between the catalyst and the gas. To verify the design scheme, we take into account the experimental results typical of hydrogen recombination in a closed box obtained and analysed elsewhere (RVK, 2004, 2005; RET, 2007; Anpilov *et al.*, 2013; RF-IPPE", 2016; Solov'ev and Mikhal'chuk, 2017) (see Figs. 8–4 and 8–5).

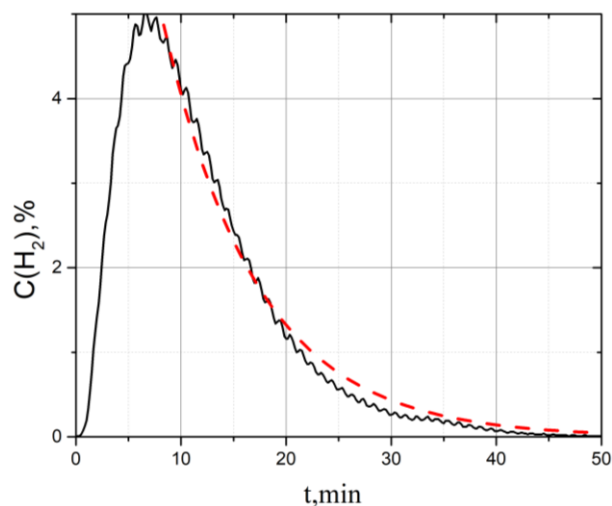


Figure 8-4: Experimental dynamics (continuous curve) of the volumetric concentration of hydrogen (in vol.%) near the input window of the PAR in the filling-stopping mode of the hydrogen supply into the vessel as a function of time (min.) and the calculated dynamics of the average volumetric hydrogen concentration in the box at the initial concentration of 0.0036 kg / kg (5% volumetric).

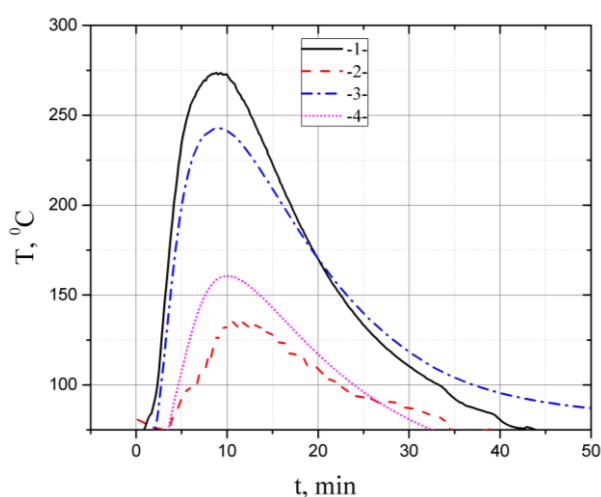


Figure 8-5: Experimental dynamics of temperatures in the filling-stopping mode of the hydrogen supply to the vessel depending on time: the temperatures on the catalyst (1 – experiment, 3 – calculation) and at the exit from the recombiner (2 – experiment, 4 – calculation).

The initial pressure is about 1.2 bar, the initial temperature in the vessel is about 50 °C. The initial mass concentration of hydrogen given is 0.0036 kg/kg (5% volumetric). The direct power supply to the catalytic elements of the PAR (block of catalytic elements is about one quarter of the PAR body) is simulated and the convective heating of the air in the flowing part of the device from the “hot” catalytic elements is simulated. The calculations were performed using a porous body model (air medium) with a specified hydraulic resistance of the PAR. One-component gas (air) is presented as ideal, which provides the useful pressure of the NC in the PAR due to changes in the density during heating, as well as pressure dynamics. The hydraulic resistance of the PAR was simulated by the square of the velocity dependence. The design code TRACE-V5 was used for the simulation. The realization of the given power function by the relationship (12) was carried out in all contour codes by means of external programmable functions. The coefficients of heat transfer in all the marked codes are calculated according to well-known empirical correlations. The design scheme of the model is shown in Fig. 8-6.

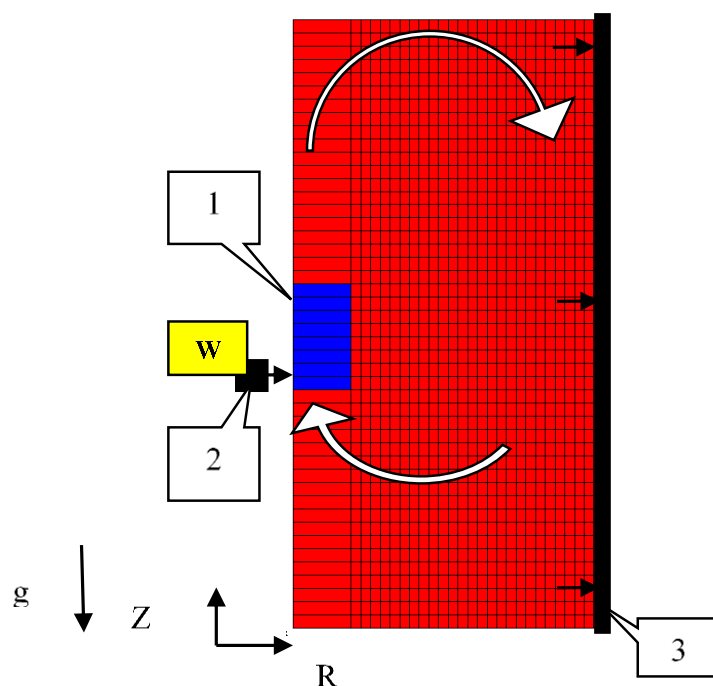


Figure 8-6: Scheme for placing the PAR in a sealed box, a two-dimensional mesh calculated in cylindrical. R-Z coordinates, and a heat flow diagram: 1 - the PAR flowing part; 2 - the catalyst; 3 - the box wall.

The model has the following components:

- box height of 4.6 m and diameter of 1.6 m;
- PAR 0.8 m high, 0.2 m high catalytic layer (bottom of PAR) and with a cross-section through the PAR box of 0.07 m²;
- catalyst: 300 rods with a height of 200 mm and an outer diameter of 6 mm;
- base: corundum

The results of this calculation, compared with the experimental data, are shown in Figs. 8-4 and 8-5. Additional initial data in the calculation were as follows: the coefficient of completeness of recombination k was 0.4 (obtained after a series of variant calculations, as a result of comparison with experimental data), hydraulic and thermal diameters of the beam of catalyst rods were $D_g = D_h = 8$ mm, and the design maximum heat transfer coefficient was 30 W/m² K. The comparison of calculated and experimental data showed a good agreement for the dynamics of hydrogen concentrations and a satisfactory one (no higher than 30 K) for temperature dynamics. Fig. 8-6 shows details of the placement of the PAR in a sealed box. During the experiment, the hydrogen supply was not instantaneous. A sufficiently homogeneous mixture was achieved after stirring (1-2 min). It should be noted that the comparison was only carried out for the curve of the drop-in hydrogen concentration. The peak of the hydrogen concentration was observed for approximately 6 min of the recombiner operation (see Fig. 8-4), that is, much later than the end of the hydrogen supply. This model should explain (among other things) such a noticeable delay in reaching the maximum concentration of hydrogen. It is also important that the exit window of the PAR is structurally located on a vertical wall (the outlet of the flow turned towards the horizon). This was not taken into account in the calculations. Figs. 8-7 and 8-8 show the calculated dynamics of mixture flow and pressure in the box.

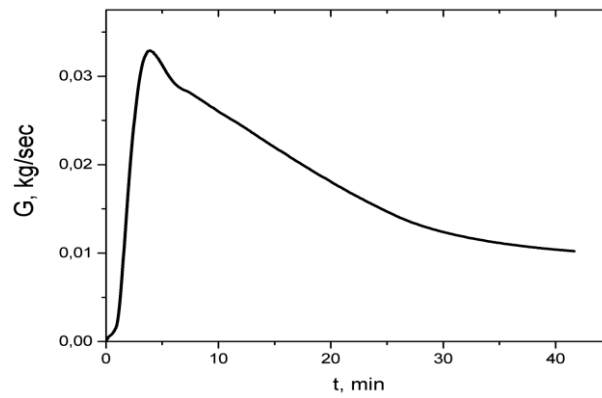


Figure 8-7: Dependence of calculated flow dynamics at natural circulation through PAR on time.

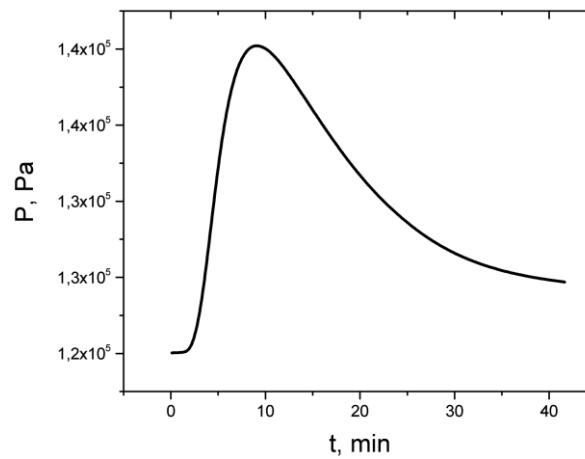


Figure 8-8: Calculated dynamics of pressure in the box.

Within 400 s (~6.7min), the heat release capacity exceeds the power drawn to the air, that is, the catalyst is heated. At the same time, the air temperature and the NC consumption increase monotonically. Furthermore, as the hydrogen concentration decreases and, consequently, the power decreases, the NC consumption is reduced (by a factor of 3 with a 10-fold decrease in concentration). This numerical calculations corresponds to the analytical solution (the quadratic law of resistance). The presented numerical dynamics of the average concentration in the box and the consumption of NC through the recombiner can also be obtained analytically for the stage of the quasi-stationary process of monotonous flow reduction (after the pre heating phase of the catalyst). In this case, the following conclusions follow from the balance equation for the hydraulic resistance of the recombiner and the developed effective head: 1) the resistance is proportional to the square of the flow, 2) the effective head is proportional to the heating of the gas in the

device, 3) the heating is equal to the ratio of power to flow, and 4) the power is proportional to the flow and concentration of hydrogen. Thus, the analytical solution for the flow is as follows:

$$G = B \cdot C^{1/2} \quad 8-13$$

where B is the flow coefficient (a complex of air properties, hydraulic resistance and PAR geometry). Substitution of (13) into (6), with subsequent integration, leads to an expression for the dynamics of concentration:

$$C(t) = \frac{1}{(C_0^{-1/2} + B \cdot t \cdot M/2)^2} \quad 8-14$$

where C_0 is the initial average mass concentration of hydrogen in the box, t is the current time, M is the mass of air (mixture) in the box. The analytical solution (13, 14) demonstrates not an exponential drop in the hydrogen concentration in the box but a quadratic one as a function of time.

8.1.2 Multicomponent model

The basic simplification of the model presented in the section “Simple Model of Thermal Hydraulics of a Recombiner ...” can be eliminated if a hydrodynamic model of a mixture of ideal gases (air, hydrogen, and steam) of variable composition is used. In this model, one equation of momentum and energy is used for a vapour-gas multicomponent mixture. Hydrogen transfer in the model of contour codes is only carried out by convection (diffusion is not considered). The mixture of gases in the contour codes is considered with a time-varying composition, which is a prerequisite for simulating typical situations with hydrogen generation. For the most important reactions with the formation of hydrogen in contour branch codes, there are corresponding special semiempirical calculation models. Change in the composition of the gas mixture (vapour-gas mixture) as a result of the reaction of hydrogen with air oxygen in the RCCORSAR and RELAP can only be provided by means of the boundary condition for hydrodynamics through the source of the incoming mass of the given mixture component (the flow rate of a particular gas components H_2 , O_2 , N_2 , H_2O - to the simulated contour). The mass flow of the dry mixture (natural to the boundary pressure condition or artificial with a predetermined negative flow rate) is only realized in the form of a flow of a mixture of gases from the last cell before the boundary condition without isolation of specific components. The latter limitation fundamentally complicates the design scheme for modelling chemical reactions with substitution of components in the marked contour codes. With reference to this, to model the recombination process (replacement of the

components of the mixture) in the circuit, it is necessary to “open” the path of the recombiner, with subsequent cross-linking of the boundary conditions, using one of the following schemes. In the complete formulation, the conjugation scheme is as follows.

- A. The current outlet pressure at the flowing part of the recombiner is equal to the pressure in the box in the flow return section.
- B. The current temperature of the components of the mixture (nitrogen, oxygen, hydrogen and vapour) in the cross-section of the return flow to the box is equal to the temperature of the mixture at the output of the recombiner.
- C. The current mass total flow rate of the mixture in the flow return section is equal to the flow rate of the mixture at the exit from the recombiner.
- D. The difference in the altitude marks of the flow part of the recombiner strictly corresponds to the difference in altitude marks between the return of the gas to the box and the mark of the entrance to the recombiner (to exclude false induced effective head of the NC).
- E. The change in the composition of the mixture in the return section is determined by individual changes in the flow of the components according to the chemical reaction coefficients:

$$\begin{aligned}
 G_{out}(H_2) &= G_{in}(H_2) - D, \\
 G_{out}(O_2) &= G_{in}(O_2) - 8D, \\
 G_{out}(H_2O) &= G_{in}(H_2O) + 9D, \\
 G_{out}(N_2) &= G_{in}(N_2),
 \end{aligned}
 \tag{8-15}$$

where D (kg/s) is the rate of “burned” hydrogen.

- F. The consumption of “combustible” hydrogen in the recombiner and the power of heat release in the recombiner are determined by the following equations:

$$D = k G_{in} G_{in}(H_2), \tag{8-16}$$

$$G_{out}(H_2) = (1 - k) G_{in}(H_2) = (1 - k) G_{in} G_{in}(H_2),$$

where $k \in [0,1]$ is the empirical coefficient of the complete-ness of hydrogen recombination.

- G. The released thermal power in the combustion of hydrogen in oxygen is calculated by equation (5).

In this setting, the box can be modelled as a spatial volume, and the flow part of the recombiner as a 1D channel with heat release. Representation of the flow part of the recombiner in the form

6 - connection at the exit of the recombiner; 7 - the boundary condition for the pressure at the exit of the recombiner; 8-11 - the boundary conditions for H_2, N_2, O_2, H_2O temperature on the return of gases to the box after the recombiner; 12-15 - boundary conditions for consumption of H_2, N_2, O_2, H_2O on return of gases to the box. 16 - the catalytic rods with heat release of chemical reaction; 17 - the lateral (thermally insulated) wall of the box; 18 - the upper side of the box; T - the transfer of the mixture temperature from the exit of the recombiner to return to the box; G - the flow of the components of the mixture - H_2, N_2, O_2, H_2O from the exit of the recombiner to return to the box taking into account the displacement; 19 - the boundary condition at the air temperature entrance; 20 - the air flow rate boundary condition; 21 - the “channel” cooling box; 22 - connection; 23 - the boundary condition on the outlet pressure (atmospheric).

The basic idea is not to calculate an instantaneous flow of the NC, but to replace it by a given function of flow depending either on time or on the input concentration (tabular or functional). As a given dependence of the flow rate on concentration, it is possible to use the information on the model of the section “Simple model of the thermal hydraulics of a recombiner ...”, the analytical dependence (10) or the direct experimental data presented in the next section. In this case, the items marked with A and partly B are not required. This calculation scheme is stable and is shown in Fig. 8-9 (RELAP). The calculation scheme for the CORSAR code is similar but with the 2D representation of the box replaced with a branched 1D contour.

8.2 Testing the model on the hydrogen vertical stratification problem

Previously, according to the presented scheme (without PAR, box walls), a multicomponent combined gas model of hydrodynamics of contour codes was tested (here it is the first numerical test) for the task of “supply-stop supply” of hydrogen in a pressurized box (4.6 m high) with air. Here, the injector is at the bottom of the box. The problem of vertical gravitational stratification of hydrogen and air was tested using the RELAP-5-3D code. A 2D box model was used. With attenuation of the oscillations of the local velocity modulus at selected points (<1 cm/s), it was concluded that the stabilization of the hydrogen concentration profile occurred 170 s after the hydrogen supply ceased. The second test (see Table 8-1) demonstrates the vertical stratification of hydrogen and water vapour when injected into the hydrogen box with steam.

Table 8-1: Stabilized profiles of gas and vapour concentrations (kg/kg) at the various height in the box (4.6 m) without PAR.

Relative height and joints of mesh, Z	Mass concentration (relative), $C(H_2)$	Mass concentration of non-condensate and (steam)	Mass concentration, $C(N_2)$	Mass concentration, $C(O_2)$
0 (1)–bottom	1,90218E-04	0,968–(0,032)	0.83984	0.15997
0,2–(10)	6,51076E-04	0,959–(0,041)		
0,4–(20)	2,38641E-03	0,947–(0,053)		
0,6–(30)	4,47233E-03	0,931–(0,069)		
0,8–(40)	4,90127E-03	0,928–(0,072)		
1 (50)–top	4,93205E-03	0,928–(0,072)	0.83586	0.15921
Z full = 4.6m	Maximum / average = 1.77	Maximum / average = 1.26		

The table shows the results of the stratification of the vapour-gas mixture components over a period of 500 s after injection of hydrogen (0.024 kg) and steam (0.24 kg) into the box during 100 s. The average non- condensate volume of the box is 0.943 kg/kg, the average concentration of steam is 0.057 kg/kg and the average hydrogen content is $2.786 \cdot 10^{-3}$ kg/kg, which corresponds to a volumetric concentration of hydrogen of 4%. It is important to note that the height of the box significantly affects the coefficient of vertical hydrogen stratification (the ratio of the maximum to the average balance concentration). Thus, with a box height of 23 m (five times higher than the base version), the design factor was 3.47 for hydrogen with an average volumetric concentration of hydrogen of 3.7% and no vapour. Similar qualitative results were obtained using CFD codes (ANSYS-CFX) with a single-velocity gas mixture model. The third test is the repeated reduction of stratified hydrogen in the air by the constant injection of water vapour into the box. The injectors were at the bottom of the box; the code was RELAP-5-3D. The results show that the initial stratification of hydrogen can be easily destroyed by the constant injection of the third component (vapour). In a more general formulation, the organization of circulation (stirring) in the box, irrespective of the method, leads to the equalization of the hydrogen concentration along the height of the box. The result obtained is important for modelling the full-scale scenario in a containment. The fourth test (with phase transition checking) is the start of a sprinkler system-supply of cold water to the top of the box with initially stratified hydrogen and steam in the air. The results of the calculations show destruction of the vertical stratification of hydrogen when the underheated water is supplied to the vapour-gas mixture in the box. Pressure reduction to a small vacuum, a decrease in temperature, and the formation of a “puddle” of liquid on the bottom of the box were tested. Thus, testing the gas mixture model within the RELAP-5-3D contour code

demonstrated a qualitative fit to the observed stratification processes and the stability of the stratification of components in large volumes.

8.2.1 Results of recombiner calculations

The test calculation with the PAR presented in the section “Simple model of the thermal hydraulics of a recombiner ...” was repeated according to the full model. The specified simplified flow dynamics through the device is shown in Fig. 8-10.

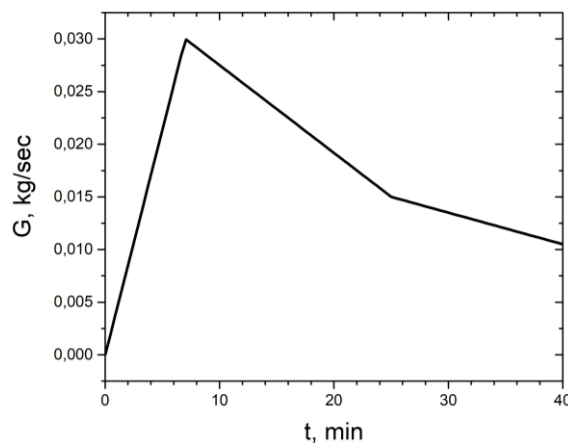


Figure 8-10: Specified flow dynamics through the PAR and hydrogen supply (from the bottom of the box).

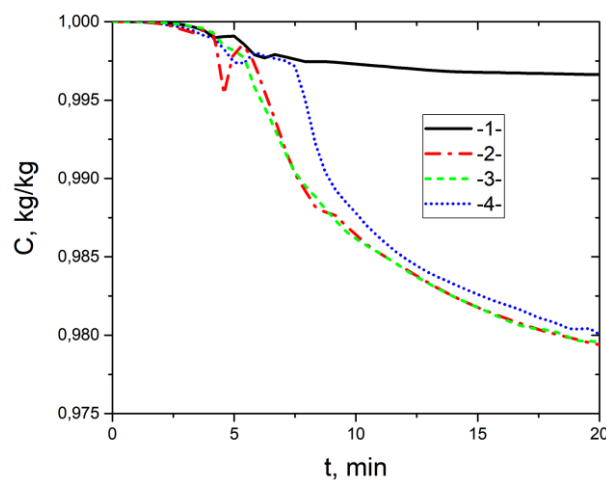


Figure 8-11: Dynamics of the hydrogen mass fraction in the box in the cross section at half of the radius. Mass fractions of hydrogen: 1 - at the bottom of the box; 2 - at the exit from the PAR; 3 - at the top of the box; 4 - near the PAR entrance.

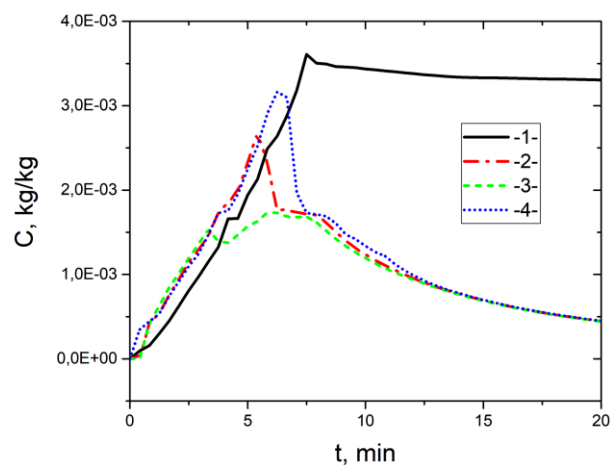


Figure 8-12: Dynamics of the mass fraction of non- condensable gases (hydrogen, oxygen and nitrogen) in a vapour-gas mixture. The total mass fraction of non- condensable gases: 1 - bottom of the box; 2 - exit from the PAR; 3 - top of the box; 4 - entrance in the PAR.

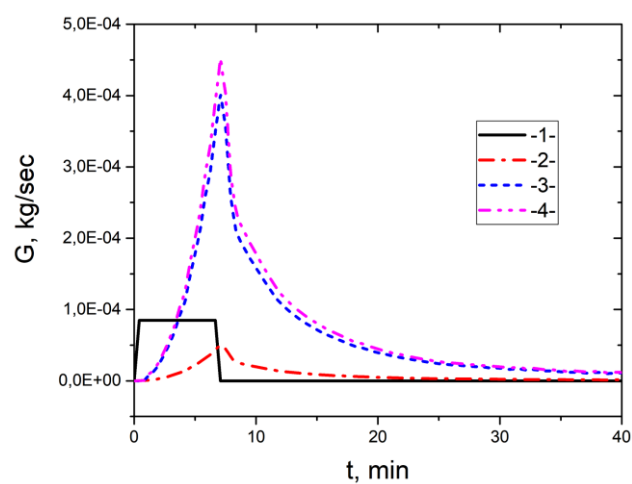


Figure 8-13: The dynamics of flow components: 1 – hydrogen flow into the box; 2 – hydrogen burning rate; 3 – oxygen combustion rate; 4 – steam generation rate.

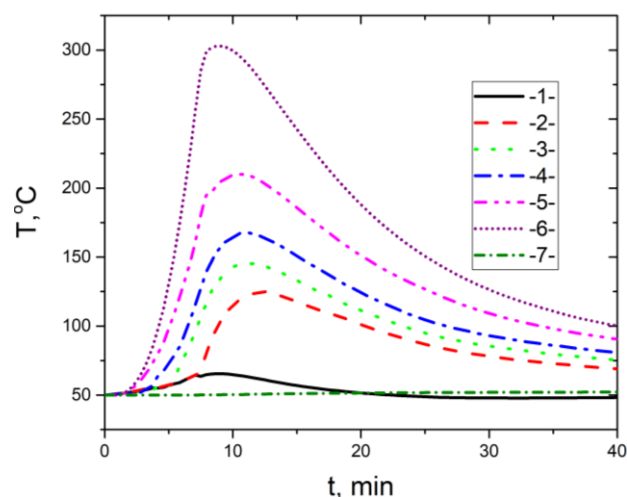


Figure 8-14: Temperature dynamics of mixture, catalyst and box walls: 1 - the bottom of the box and 0.2 height of box at half of the radius of the box; 2 - mark 0.4 of the height of the box at half of the radius (entrance to RCC); 3 - mark 0.6 of the height of the box at half of the radius (upper mark of the PAR); 4 - the top of the box; 5 - the exit from the PAR; 6 - the catalyst; 7 - the box wall at half height.

Figs. 8-11–8-14 show the main results of the calculation. The following additional parameters are accepted: the recombination coefficient is 50%, the hydraulic and thermal diameter of the catalyst beam is 6 mm, and the design heat transfer coefficient in the beam is 28 W/m² K (at maximum). Fig. 8-11 shows that at the markings below the entrance to the PAR there is practically no change in hydrogen concentration due to the absence of convection. Fig. 8-12 shows the accumulation of steam, mainly in the circulation zone. The results obtained make it possible to draw the following main conclusion. The “burning” of hydrogen occurs in the box in the zone of the NC of the vapour-gas mixture, that is, from the lower mark of the entrance to the recombiner to the upper mark of the box. In the lower stagnation zone, in the absence of a source of gas circulation (e.g., a power source), an increased concentration of hydrogen is observed, which decreases extremely slowly. The hydrogen at the bottom of the box is slowly “washed away” by sluggish circulation. The water vapour released as a result of the chemical reaction stratifies with a maximum near the upper window of the PAR and a minimum at the bottom of the box. In the presence of an external power source in the lower part of the box (realized in full-scale conditions), there is a drastic change in the dynamics of the decrease in the hydrogen concentration in this zone. This is confirmed by calculations in the presence of an additional heat source (3 kW) on the bottom cover of the box. In this version of calculation, the hydrogen concentration practically decreases homogeneously throughout the entire height of the box.

8.2.2 Generalization of experimental data during PAR tests

In equation (13), it was analytically shown that, beyond the initial stage of heating of the catalytic elements, under the quadratic law of the hydraulic resistance of PAR, the NC gas consumption is proportional to the average hydrogen concentration C to power $\frac{1}{2}$. Substituting (13) into (4) leads to the following performance relationship:

$$D = \text{const} C^{1,5} \quad 8-17$$

Fig. 8-15 presents a comparison of the experimental data on the performance of the model of the PAR in question with the calculation results (see the section “Multicomponent Model”) for the temperature in the box of 50 °C, $k = 0.5$.

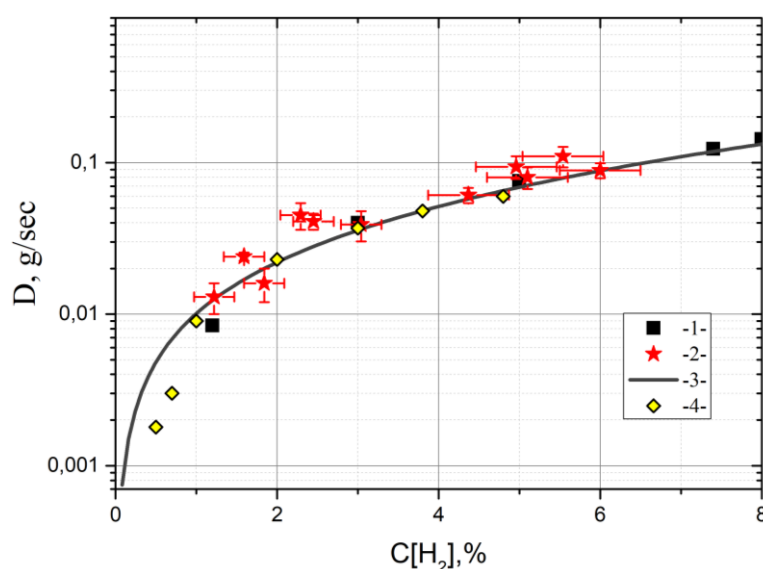


Figure 8-15: The productivity of RVK-500: 1 - the experimental data of RET; 2 - the experimental data of IPPE; 3 - the empirical calculated dependence of RET; 4 - the calculated model of the present work.

These data are described with a certain accuracy by the relationship (17), and thus the methodical basis of the calculated numerical model of the PAR is confirmed. According to the RET data (Fig. 8-15), the following semiempirical relationship for hydrogen production was obtained for the RVK-500 model:

$$D = 0,34 C_m^{1,5}$$

8-18

or

$$D = 0,34(C / 14)^{1,5}$$

Here, the performance dimension is measured in kg/c, C_m is the mass fraction of hydrogen, C is the volume fraction of hydrogen.

Using equation (4) and the recombination completeness coefficient determined on the basis of comparison of experimental and design data, $k = 0.5$, we obtain the ratio for the instantaneous consumption of NC mixture through RVK-500

$$G = 0,68C_m^{1,5} \quad 8-19$$

The final relationship is the closing correlation for using the calculated 4-component model considered in the "Multicomponent Model" section. The recommended range of heat transfer coefficient in the catalyst beam is 25-30 W/m² K.

8.3 Results of calculations

Based on the experimental data, the relationship (19) is further applied in calculations to justify the change in the hydrogen concentration with time and with the operating recombiner in the experimental vessel. The model was tested using the experimental data (see Figs. 8-4 and 8-5) corresponding to a maximum volumetric hydrogen concentration of 5%. The results of calculations and analysis of the behaviour of the main components of the mixture after the initial supply of hydrogen for 100 s, 420 s and 1000 s are presented. The total amount of the spent hydrogen remained unchanged, at 35.7 g. Calculations at different hydrogen supply rates were performed to better understand the experimental data obtained, namely, the time at which the maximum hydrogen concentration and the maximum catalyst temperature are reached, as well as the response time (delay) of the catalyst with a change in the concentration of incoming hydrogen. The response time was determined as the difference between the peaks of the hydrogen concentration and the temperature of the catalyst. Because the supply of hydrogen and the speed of its mixing can have a sufficiently large error (at present there is no certain accuracy), calculations with different hydrogen feed rates, and a subsequent comparison with the experimental data, can yield a range of estimated values of this time.

8.3.1 Hydrogen supply in the interval of 100 s at a flow rate of 0.357 g/s

Calculations presented in Fig. 8-16 confirm that the stratification of hydrogen within the zone of NC is practically not observed, and hydrogen, which is located below the lower edge of the recombiner, practically does not participate in the recombination process and it forms a stagnant zone.

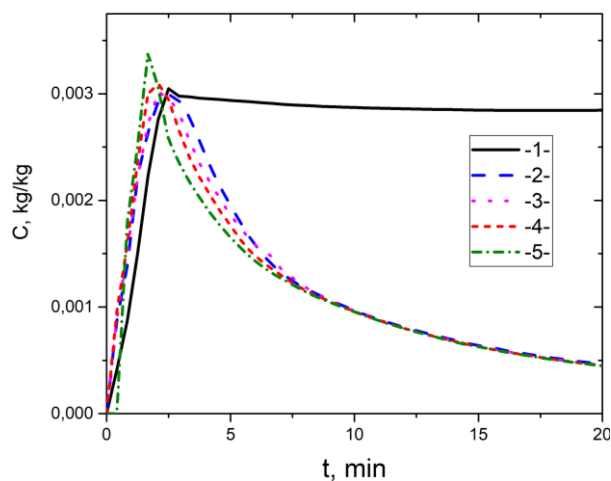


Figure 8-16: Dynamics of the hydrogen mass fraction at different marks on the height of the box at a distance of half the radius of the box: 1 - the bottom of the box; 2 - input in the PAR; 3 - half of the height of the PAR; 4 - output from the PAR; 5 - the top of the box.

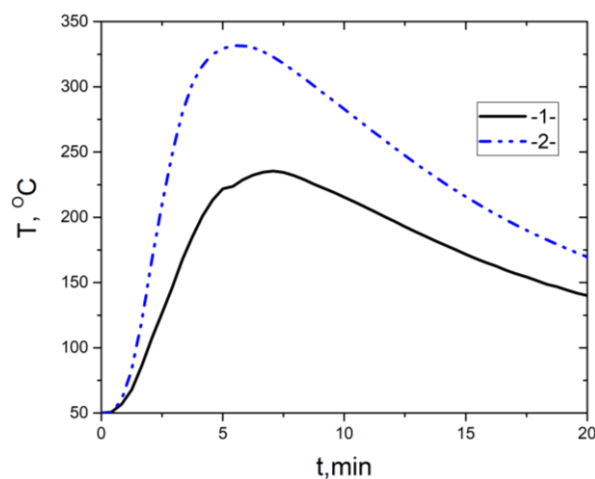


Figure 8-17: Temperature dynamics: 1 - catalyst; 2 - gas at the outlet from the PAR.

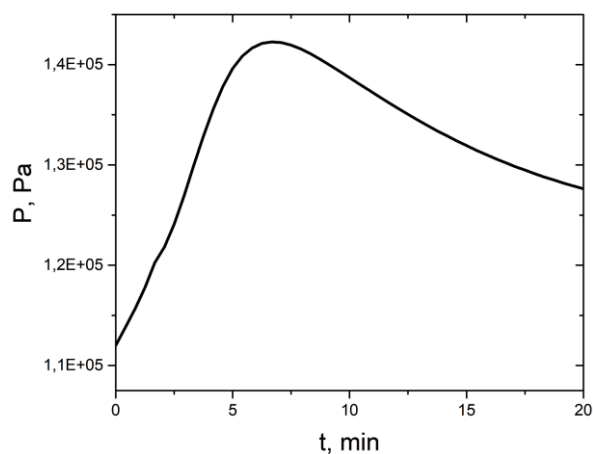


Figure 8-18: The pressure dynamics in the box.

The difference in concentration in the NC zone is maximized at the time of reaching the maximum concentration in the box and is estimated not to exceed 20%. In Fig. 8-17, the time delay (about 250 s) of the maximum temperature from the moment of stopping the hydrogen supply is clearly demonstrated. Fig. 8-18 also shows the time delay of the maximum pressure from the moment that the hydrogen supply is stopped, which is close to the maximum temperature.

8.3.2 Hydrogen supply in the interval of 420 s at a flow rate of 0.085 g/s

The numerical results presented in Fig. 8-19 clearly demonstrate a significant stratification of hydrogen within the NC zone in the hydrogen supply time interval (up to 420 s). Fig. 8-20 shows the time delay (about 150 s) of the maximum temperature on the catalyst from the moment the hydrogen supply is stopped.

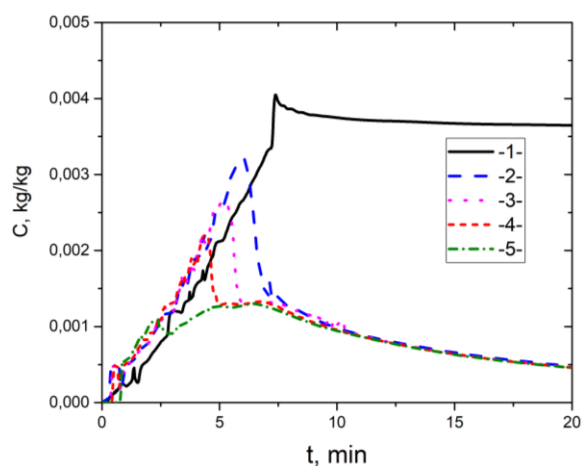


Figure 8-19: Dynamics of the hydrogen mass fraction at different marks on the height of the box at a distance half the radius of the box: 1 - the bottom of the box; 2 - entrance in the PAR; 3 - half of the height of the PAR; 4 - exit from the PAR; 5 - the top of the box.

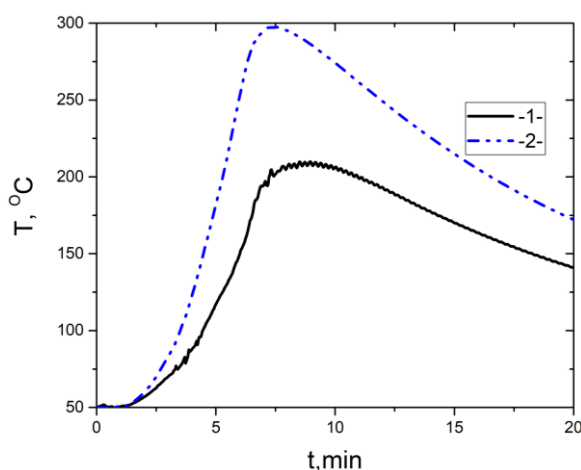


Figure 8-20: Temperature dynamics: 1 - catalyst; 2 - gas at the outlet of the PAR.

8.3.3 Hydrogen supply in the interval of 1000 s at a flow rate of 0,0357 g/s

With a slow feed of hydrogen, the maximum consumption of NC is lower than with a faster feed (in 100 s or 420 s), so hydrogen “accumulates” in the lower part of the box in larger quantities than it does at a fast feed. It should be noted that “accumulation” is a temporary effect until the redistribution of hydrogen in the NC zone and the subsequent “cooling down” of the heat cushion in the NC zone. However, such calculations were not carried out in this work. A comparison of the experimental data on the temperature dynamics of the catalyst (see Fig. 8-6) and hydrogen

concentration (see Fig. 8-4) with the results of calculations for different times of hydrogen supply gives a qualitative understanding of the speed of the processes. The experimental data on the concentration of hydrogen showed that the maximum concentration of hydrogen is reached at ~ 350 s after start (the start of hydrogen feed). Judging by the results of the numerical calculations, at the time of hydrogen feed in the interval 100 s of the peak shift, the maximum concentration of hydrogen does not occur after the end of its feeding. At the same time, the change in the concentration of hydrogen as a function of time has a smooth character (within the error limits) for the area of NC. Numerical calculations at the time of hydrogen feed in the interval 420-1000 s (Fig. 8-21) also did not reveal a peak shift of the maximum hydrogen concentration after the feed stop.

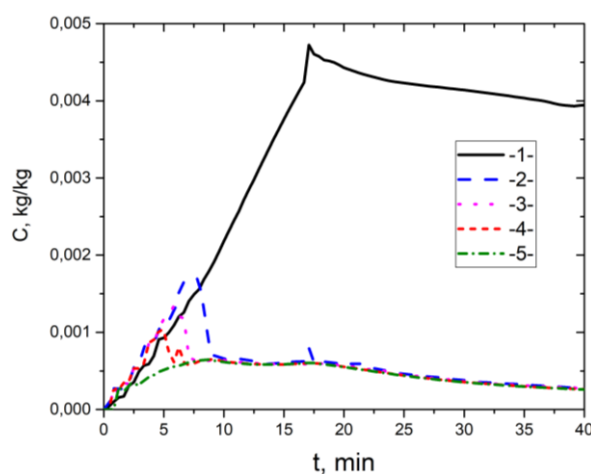


Figure 8-21: Dynamics of the hydrogen mass fraction at different marks on the height of the box at a distance of half the radius of the box: 1 - the bottom of the box; 2 - entrance in the PAR; 3 - half of the height of the PAR; 4 - exit from the PAR; 5 - the top of the box.

However, the change in the hydrogen concentration as a function of time has a sharp character, which is not characteristic of experimental data. Consequently, numerical calculations confirm that the supply of hydrogen, that included stirring, could last no more than 2 min, because with a “slower” supply the dynamics of the change in the hydrogen concentration would be severe which is related to the rate of catalyst heating. At the same time, the function of the temperature dynamics of the catalyst has a smooth character at any hydrogen feed rate. With such a slow supply of hydrogen, the time in reaching the temperature peak is almost equal with the time in reaching the concentration peak (Fig. 8-22).

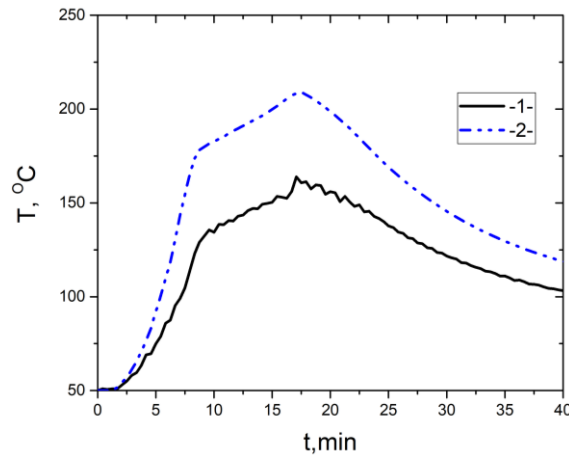


Figure 8-22: Temperature dynamics: 1 - catalyst; 2 - gas at the outlet of the PAR.

The average delay time for a concentration of 1-2% is sufficiently large, it is 5-10 min (RF-IPPE", 2016), and for a concentration of 4-6% it is 2-3 min (the case considered in this article) (RF-IPPE", 2016). At high concentrations, the delay is about 1 min or less, which indicates rapid heating up of the catalyst. The maximum concentration at 4-10% hydrogen appears within 6-8 min after the start of the feed, which, as we recall, lasted 1-2 min (RF-IPPE", 2016). At low concentrations, the peak was reached at 10 min or even later. Thus, the time delay for the appearance of a peak in hydrogen concentration can be related to the hydrogen sensor response function which may take several minutes to warm up, since it uses the same principle of hydrogen recombination on its catalyst. As the response function can only be constructed on the basis of experimental data, a detailed study of this effect of delaying will be carried out in later work. In this article, the focus of attention was on the hydrogen recombination rate after reaching its peak concentration, as the knowledge of the rate of concentration drop from the peak value is sufficient to determine the productivity of the recombiner and to construct an appropriate engineering model.

8.4 Conclusions

The contour two-phase codes such as RELAP-5-3D (USA, Idaho), TRACE (USA, Los Alamos) and CORSAR (Russia, NITI) have a multicomponent model of a gas-vapour mixture, taking into account the variable composition of the components in time and space of the circuit or volume. The model is based on a single-speed equilibrium approximation. The transfer of the concentration of the components (hydrogen) is only ensured by convection. A similar model for a viscous medium is available in CFD codes. The presented model is the methodological basis for modelling the hydrogen recombination process according to the scheme for substituting components (hydrogen and oxygen in water vapour) with additional heat generation in the

catalyst. The testing of the contour codes mentioned showed a vertical stratification of hydrogen and vapour in the atmospheric medium with the complete absence of convection sources. Specific values of the nonuniformity of the hydrogen and vapour concentrations along the height of the model box are obtained. For RELAP and CORSAR codes (within the framework of standard application), the hydrogen recombination model based on the substitution of the hydrogen and oxygen components of water vapour with additional heat generation was developed. The test results are in satisfactory agreement with the experimental data on natural convection obtained during the testing of the PAR in a sealed box. The most important parameters of the “tuning” of the model are the recombination completeness factor and the heat transfer coefficient in the catalyst beam. The former determines the power of heat release and the rate of decline in concentration and the latter (together with the former) is the temperature of the catalyst, which is important for determining the ignition limit. The numerical model of the PAR provides the calculation of the dynamics of the local concentration of four gas components of the mixture in the box; the temperature of the mixture, the catalyst and the walls of the box; and the pressure when hydrogen, steam, and water are supplied to the box from the sprinkler system, taking into account additional internal heat sources. It has been calculated that, under ideal conditions of the experimental box with PAR (no additional sources of convection), a huge decrease in the hydrogen concentration in the box after stopping its supply takes place in the zone of NC of the vapour-gas mixture: from the bottom mark of the PAR to the upper mark of the box. At the bottom of the box, the decrease in concentration occurs quite slowly with a low gas temperature. The result obtained is a consequence of the model of hydrodynamics for a mixture of gases adopted in the codes and can be verified experimentally. In real conditions, with the presence of a powerful source of heat in the lower part of the containment (reactor), ventilation, operation of the sprinkler system, specifically, in the organization of general circulation in the room, this effect is absent. This was confirmed by calculations. Based on the results of the comparison of the calculated and experimental data, the dynamics of the concentration and temperatures of the catalyst and gas at the exit from the PAR were determined. It has been established that for the tested type of PAR, the consumption factor of hydrogen recombination completeness (combustion coefficient) is 40-50% with a realistic level of the heat transfer coefficient in the catalyst beam (20-30 W/m² K), the hydraulic resistance of PAR and the heat capacity of the catalyst. The disadvantage of RELAP and CORSAR contour codes for simulating chemical reactions with substitution, in particular combustion, is associated with the inability to program the “outflow” of a particular gas component from the design cell (for example, only hydrogen and oxygen from a four-component vapour-gas mixture) during a standard utilization of the code. Accordingly, only an algorithm with a break in the contour at the exit from the recombiner area is implemented, followed by cross-linking of the component flow and temperature, with the externally determined total flow through the PAR. This

algorithm is absolutely stable. However, at present, only contour codes provide an end-to-end calculation of the dynamics of the emergency processes at the power unit, starting from neutron physics and the thermo- hydrodynamics of the active zone prior to the release of hydrogen into the nuclear power plant.

8.5 Acknowledgements

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APPENDIX B: SUPPLEMENTARY INFORMATION

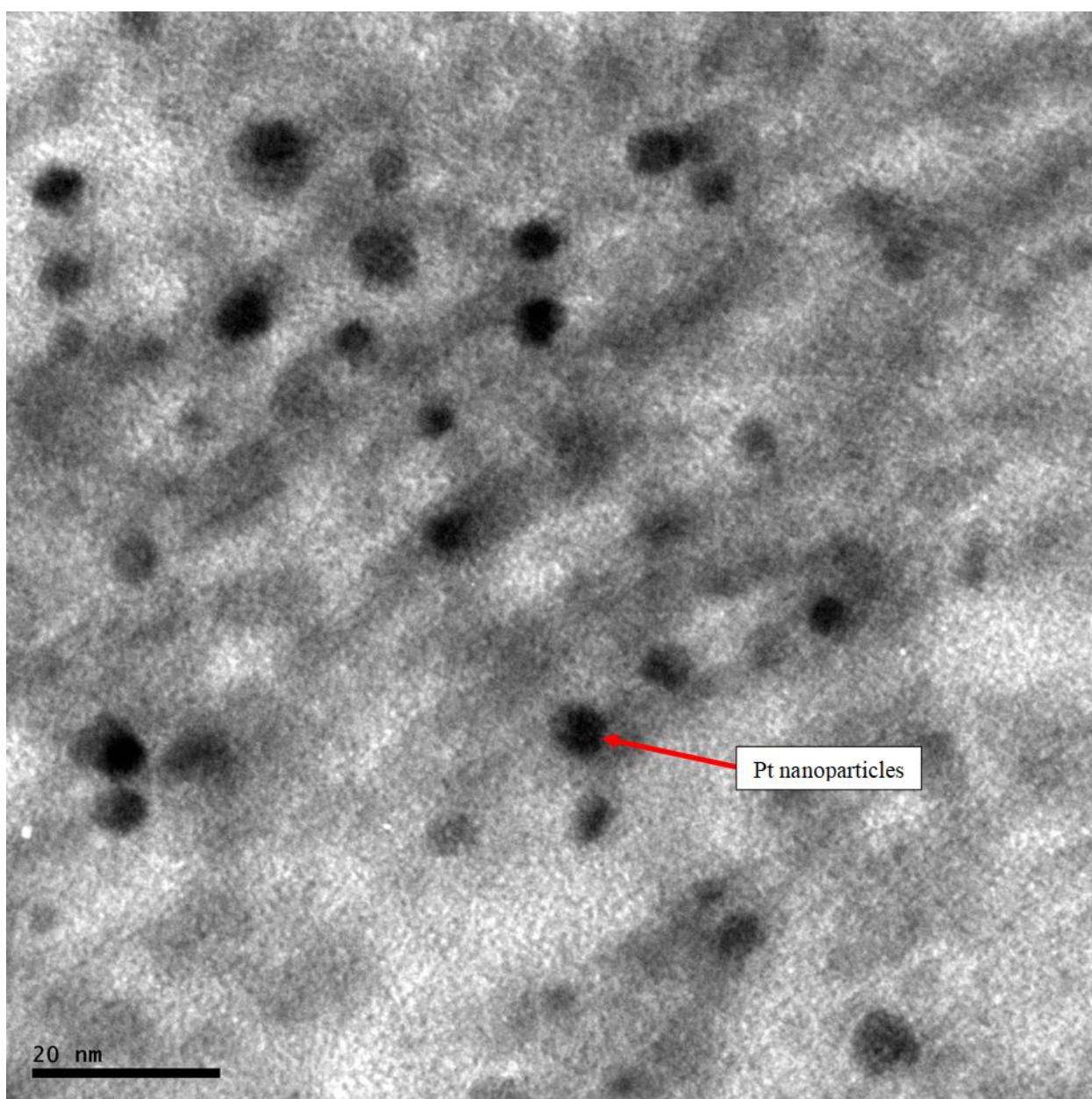


Figure B-23: Representative TEM image of mechanically separated outer layer of the catalyst (bottom) after 250 h of catalytic hydrogen combustion.

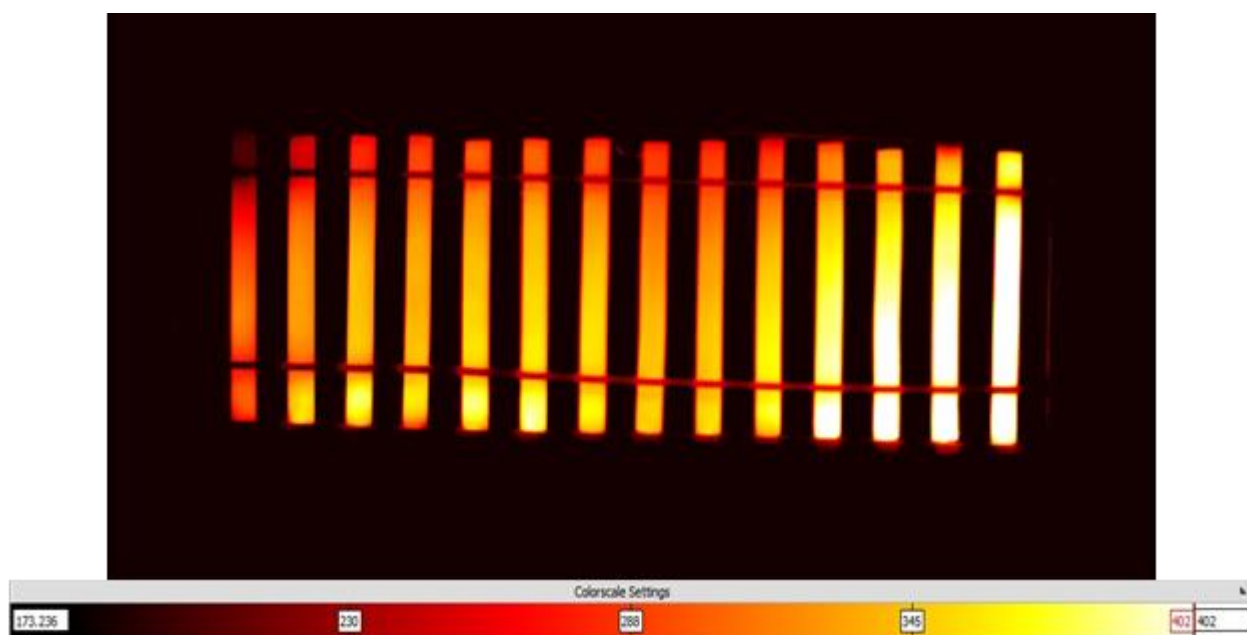


Figure B-24: Experimentally measured (IR camera) temperature profile for case no. 2 ($C[H_2] = 7$ vol %).

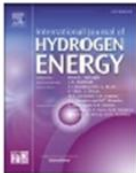
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INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (XXXX) XXX



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CFD simulation and experimental study of a hydrogen leak in a semi-closed space with the purpose of risk mitigation

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HIGHLIGHTS

- Computational fluid dynamics methods were used to analyze hydrogen leakage.
- STAR-CCM+ code was used to compare the simulation results with experimental results.
- Combinations of hydrogen release pressure and leak orifice size were considered.
- Efficiency of forced ventilation in semi-closed spaces was investigated.
- Numerical results could be useful in the analysis of safety issues in mining tunnels.

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ABSTRACT

Computational fluid dynamics (CFD) methods were used to analyze hydrogen leakage in a semi-closed ventilation facility. The goal of the research was to apply numerical simulations to verify hydrogen distribution in the semi-closed space using the commercial STAR-CCM+ code and to compare the simulation results with experimental results. Experiments were conducted in a container with the dimensions 12.11 m × 2.39 m × 2.34 m. The experimental facility represents part of an underground mining tunnel. In the study, different combinations of hydrogen release pressure and leak orifice size were considered. The efficiency of forced ventilation in semi-closed spaces was also investigated. The hydrogen distribution in the ventilation facility was studied through experimental investigation and confirmed by CFD simulation. Our numerical results could be useful in the analysis of safety issues in semi-closed ventilation facilities, such as in mining tunnels.

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Temperature Profile Mapping over a Catalytic Unit of a Hydrogen Passive Autocatalytic Recombiner: An Experimental and Computational Fluid Dynamics Study

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Supporting Information

ABSTRACT: Passive autocatalytic recombiners (PARs) are used for the removal of accidentally released hydrogen inside confined spaces. The high catalyst surface temperature is an important safety issue to be considered in the use of a PAR. The ability to predict the catalyst surface temperature could be very useful in preventing the self-ignition and explosion of hydrogen inside the PAR. This study seeks to investigate the changes in temperature profiles of the PAR catalytic section upon variation of the inlet hydrogen concentration. Experiments were conducted on a small-scale test setup. The catalytic section comprised cylindrical ceramic elements arranged in parallel and supported by a stainless-steel frame. The temperature profiles were measured with a high-resolution infrared camera. The computational fluid dynamics (CFD) code STAR-CCM+ was used as a numerical tool for modeling the gas mixture flow, the experimental setup and the chemical reaction kinetics. The results of numerical studies are presented and compared with experimental results. The presented CFD-based approach and software offer an appropriate numerical tool for the investigation of safety issues. Finally, the catalyst was subjected to a prolonged high-temperature combustion fatigue procedure to determine its stability. The surface of the fatigued catalyst was evaluated by scanning electron microscopy and energy-dispersive X-ray spectroscopy. It was found that decomposition of the protective surface layer occurred at elevated temperatures; the catalytic activity was unaffected by this. In addition, a relatively uniform reactive metal particle size was maintained over the entire temperature range, suggesting that no aggregation occurred.

1. INTRODUCTION

Hydrogen is an advanced fuel for wider future use as an energy carrier in various applications. Hydrogen fuel cell (HFC) vehicles are being developed as an alternative for powering underground mining machines.^{1–3} HFCs and vehicles based on fuel cells offer significant advantages in terms of reducing carbon emissions. However, the use of hydrogen in confined spaces is accompanied by the risk of emergency releases because of leaks, component failures, or human error. The most important safety consideration in any hydrogen application is to prevent the formation of flammable mixtures of hydrogen with air. The ignition volume fraction range for hydrogen is 4–74% in air at atmospheric pressure.⁴ The self-ignition temperature range is 845–858 K.⁵ It is therefore important that emergency hydrogen removal systems be in place to keep the hydrogen concentration below the flammability limit of ~4% vol.

Several methods are used to mitigate the risk of hydrogen deflagration or detonation, for example, catalytic recombination conducted in passive autocatalytic recombiners (PARs) and forced ventilation. The consequences of leakage and then the dispersion and accumulation of hydrogen in terms of the geometric configuration of a confined space have been reported by Matsuura.⁶ The space geometry plays a role in the selection of the natural or forced ventilation used. Analysis of the efficiency of natural ventilation has been carried out,⁷ and forced ventilation in semiclosed spaces and tunnels has been studied.^{8,9} In previous work, we investigated the

ventilation efficiency in a full-scale facility, representing a part of an underground mining tunnel, during hydrogen leakage occurrence.¹⁰

The properties of hydrogen, such as its wide flammability range, low density, and low ignition energy, increase the probability of a fire/explosion hazard in any spaces where hydrogen is present.⁵ The catalyst sections in a PAR mainly uses platinum (Pt). In the event of a severe accident in a light water reactor, high temperatures inside the reactor will result in the zirconium alloys therein being oxidized by steam to form hydrogen, in an exothermic reaction. The generally accepted global practice to remove hydrogen from containments of nuclear power plants is currently based on the principle of passive catalytic hydrogen recombination in the presence of catalysts such as Pt.^{11–14} PARs are used to mitigate the effects of hydrogen release. A PAR operates at temperatures much lower than those required for gas-phase ignition and reduces the accumulation of hydrogen and detonation risk after any hydrogen release. A key component of a passive catalytic hydrogen recombiner is the catalyst, on the surface of which a hydrogen recombination reaction with oxygen takes place.

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Article

A Thermally Conductive Pt/AAO Catalyst for Hydrogen Passive Autocatalytic Recombination

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Abstract: In this study, a Pt/anodized aluminum oxide (AAO) catalyst was prepared by the anodization of an Al alloy (Al6082, 97.5% Al), followed by the incorporation of Pt via an incipient wet impregnation method. Then, the Pt/AAO catalyst was evaluated for autocatalytic hydrogen recombination. The Pt/AAO catalyst's morphological characteristics were determined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The average Pt particle size was determined to be 3.0 ± 0.6 nm. This Pt/AAO catalyst was tested for the combustion of lean hydrogen (0.5–4 vol% H₂ in the air) in a recombiner section testing station. The thermal distribution throughout the catalytic surface was investigated at 3 vol% hydrogen (H₂) using an infrared camera. The Al/AAO system had a high thermal conductivity, which prevents the formation of hotspots (areas where localized surface temperature is higher than an average temperature across the entire catalyst surface). In turn, the Pt stability was enhanced during catalytic hydrogen combustion (CHC). A temperature gradient over 70 mm of the Pt/AAO catalyst was 23 °C and 42 °C for catalysts with uniform and nonuniform (worst-case scenario) Pt distributions. The commercial computational fluid dynamics (CFD) code STAR-CCM+ was used to compare the experimentally observed and numerically simulated thermal distribution of the Pt/AAO catalyst. The effect of the initial H₂ volume fraction on the combustion temperature and conversion of H₂ was investigated. The activation energy for CHC on the Pt/AAO catalyst was 19.2 kJ/mol. Prolonged CHC was performed to assess the durability (reactive metal stability and catalytic activity) of the Pt/AAO catalyst. A stable combustion temperature of 162.8 ± 8.0 °C was maintained over 530 h of CHC. To confirm that Pt aggregation was avoided, the Pt particle size and distribution were determined by TEM before and after prolonged CHC.

Keywords: anodized aluminum; Al6082; passive autocatalytic recombiner; catalytic hydrogen combustion

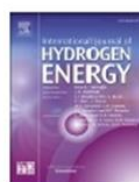
1. Introduction

In nuclear power plants (NPPs) and the mining industry, passive autocatalytic recombiners (PARs) are considered hydrogen (H₂) control systems for emergency gas removal based on their recombination with ambient oxygen. It is widely recognized that, in underground mines, the replacement of diesel-powered vehicles with H₂-fueled trucks will result in a cleaner environment for underground mineworkers. Water is the only byproduct of H₂ combustion/oxidation, instead of the otherwise harmful greenhouse gases (e.g., CO₂, CH₄) and NO_x generated during the combustion of hydrocarbon-based fuels. Furthermore, besides the gaseous exhausts, harmful pollutants and particulate matter form during incomplete combustion of diesel fuel hydrocarbons, which presents underground workers with further harmful exposure.

However, the utilization of H₂ in confined spaces is accompanied by the risk of accidental gas release and its accumulation. In NPPs, H₂ may be generated unintentionally as a result of the reactor fuel overheating and the chemical reaction of fuel rods' zirconium

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Math hydrogen catalytic recombiner: Engineering model for dynamic full-scale calculations[☆]

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ABSTRACT

To protect a hermetic enclosure and the equipment and systems of a reactor installation housed in it from damage caused by the ignition (explosion) of hydrogen, most nuclear power plants with pressurized water reactors are provided with a hydrogen concentration monitoring system and an emergency hydrogen removal system. These systems prevent the formation of explosive mixtures in the accident localization zone by maintaining the concentration volume of hydrogen in the mixture below the safety limits, which ensures the preservation of the density and strength of the hermetic enclosure and the operability of other localizing safety systems. A key component of an emergency hydrogen removal system is a passive autocatalytic hydrogen recombiner that operates on the principle of the catalytic recombination of hydrogen and oxygen.

There is an urgent need for a full-scale dynamic calculation of the development of emergency conditions in a nuclear power plant containment accompanied by a large release of hydrogen. In efforts to achieve this, we constructed, and justified, a simple engineering thermohydraulic model of hydrogen removal in the operation of a passive autocatalytic recombiner based on the available experimental data.

This paper presents the application results of the model as a part of contour industry codes RELAP, TRACE and CORSAR, intended, among other things, for carrying out multi-factor and full-scale calculations of the dynamics of emergency processes with the release of hydrogen into nuclear power plant premises. This model allows us to substantiate the dynamics of local concentrations of gas components of a mixture in a confined space; the temperature of the mixture, the catalyst and the walls of the box; and the pressure when hydrogen or steam is supplied to the box.

We have analysed various rates of hydrogen supply to a closed box to numerically substantiate the time at which the concentration reaches the maximum level. Furthermore, we have calculated the performance for several entrance concentrations of hydrogen, and obtained a satisfactory agreement between the dynamics of the

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HYPOTHESIS XV
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SOLUTIONS INTERNATIONAL SYMPOSIUM

E-BOOK OF ABSTRACTS



EDITED BY

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RHIYAAD MOHAMED
GIUSEPPE SPAZZAFUMO

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12TH INTERNATIONAL CONFERENCE ON
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E-BOOK OF ABSTRACTS



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ANTONIO VITA
GIUSEPPE SPAZZAFUMO

SEPTEMBER 19-23, 2021, ON-LINE CONFERENCE

APPENDIX D: AUTHOR CONSENT FORMS

Statement of consent: Dr. Alexander V. Avdeenkov

To whom it may concern.

I, ALEXANDER V. AVDEENKOV, declare that I have read this consent form and give my permission to ALEXANDER A. MALAKHOV to use the publication listed below, of which I am co-author, in the thesis entitled "**Mitigation strategies for hydrogen safety in the confined environment: CFD modelling and validation**". The thesis is submitted for the degree *Doctor of Philosophy in Engineering with Chemical Engineering* at Potchefstroom campus of North-West University, South Africa:

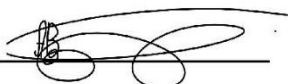
1. Malakhov, A.A., Avdeenkov, A.V., Du Toit, M.H. and Bessarabov, D.G., (2020). CFD simulation and experimental study of a hydrogen leak in a semi-closed space with the purpose of risk mitigation. *International Journal of Hydrogen Energy*, 45(15), pp.9231-9240.
2. Malakhov, A.A., du Toit, M.H., Du Preez, S.P., Avdeenkov, A.V. and Bessarabov, D.G., (2020). Temperature profile mapping over a catalytic unit of a hydrogen passive autocatalytic recombiner: an experimental and computational fluid dynamics study. *Energy & Fuels*, 34(9), pp.11637-11649.
3. Malakhov, A.A., Avdeenkov, A.V., Du Toit, M.H. and Bessarabov, D.G., (2021). Study of the efficiency of a PAR Pt catalyst and CFD verification of detailed mechanism of H_2/O_2 oxidation. *NURETH-19*. (has been accepted for publication 08/10/2021 NURETH-19)
4. Avdeenkov, A. V., Sergeev, V. V., Stepanov, A. V., Malakhov, A. A., Koshmanov, D. Y., Soloviev, S. L., Bessarabov, D. G. (2018). Math hydrogen catalytic recombiner: Engineering model for dynamic full-scale calculations. *International Journal of Hydrogen Energy*, 43(52), 23523-23537.

As Ph.D in Physics and Mathematics, and Extraordinary Professor at North-West University (Potchefstroom Campus), Faculty of Engineering, South Africa, and Director of Innovation Technology in WWER, «All-Russian Research Institute for Nuclear Power Plants Operation» JSC ("VNIIAES JSC"), I am responsible for manuscript reviewing, revising, and editing.

This statement satisfies Rule 5.4.2.8 and Rule 5.4.2.9 of the General Academic Rules 2015 of the North-West University.

Signed at Obninsk on 03 day of November 2021

Signature: _____



Statement of consent: Prof. Dmitri G. Bessarabov

To whom it may concern

I, DMITRI G. BESSARABOV, declare that I have read this consent form and give my permission to ALEXANDER A. MALAKHOV to use the publication listed below, of which I am co-author, in the thesis entitled "**Mitigation strategies for hydrogen safety in the confined environment: CFD modelling and validation**". The thesis is submitted for the degree *Doctor of Philosophy in Engineering with Chemical Engineering* at Potchefstroom campus of North-West University, South Africa:

1. Malakhov, A.A., Avdeenkov, A.V., Du Toit, M.H. and Bessarabov, D.G., (2020). CFD simulation and experimental study of a hydrogen leak in a semi-closed space with the purpose of risk mitigation. *International Journal of Hydrogen Energy*, 45(15), pp.9231-9240.
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3. Kozhukhova, A. E., du Preez, S. P., Malakhov, A. A., Bessarabov, D. G. (2021). A Thermally Conductive Pt/AAO Catalyst for Hydrogen Passive Autocatalytic Recombination. *Catalysts*, 11(4), 491.
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As Professor at North-West University (Potchefstroom Campus), Faculty of Engineering, South Africa, and Director of HySA Infrastructure (CoC), North-West University (Potchefstroom Campus), Faculty of Engineering, South Africa, I am responsible for manuscript reviewing, revising, and editing.

This statement satisfies Rule 5.4.2.8 and Rule 5.4.2.9 of the General Academic Rules 2015 of the North-West University.

Signed at Potchefstroom on 11 day of November 2021

Signature: Dmitri Bessarabov

Statement of consent: Dr. Marina H. du Toit

To whom it may concern

I, MARINA H. DU TOIT, declare that I have read this consent form and give my permission to ALEXANDER A. MALAKHOV to use the publication listed below, of which I am co-author, in the thesis entitled "**Mitigation strategies for hydrogen safety in the confined environment: CFD modelling and validation**". The thesis is submitted for the degree *Doctor of Philosophy in Engineering with Chemical Engineering* at Potchefstroom campus of North-West University, South Africa:

1. Malakhov, A.A., Avdeenkov, A.V., Du Toit, M.H. and Bessarabov, D.G., (2020). CFD simulation and experimental study of a hydrogen leak in a semi-closed space with the purpose of risk mitigation. *International Journal of Hydrogen Energy*, 45(15), pp.9231-9240.
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3. Malakhov, A.A., Avdeenkov, A.V., Du Toit, M.H. and Bessarabov, D.G., (2021). Study of the efficiency of a PAR Pt catalyst and CFD verification of detailed mechanism of H₂/O₂ oxidation. NURETH-19. (has been accepted for publication 08/10/2021 NURETH-19)

As Ph.D in Nuclear Engineering and Senior Lecturer at North-West University (Potchefstroom Campus), School for Mechanical Engineering, South Africa, I am responsible for manuscript reviewing, revising, and editing.

This statement satisfies Rule 5.4.2.8 and Rule 5.4.2.9 of the General Academic Rules 2015 of the North-West University.

Signed at Potchefstroom on 11 day of November 2021

Signature: Dr Marina du Toit
 Digitally signed by Dr Marina du Toit
Date: 2021.11.11 11:25:30
+02'00'

Statement of consent: Dr. Stephanus P. du Preez

To whom it may concern

I, STEPHANUS P. DU PREEZ, declare that I have read this consent form and give my permission to ALEXANDER A. MALAKHOV to use the publication listed below, of which I am co-author, in the thesis entitled "**Mitigation strategies for hydrogen safety in the confined environment: CFD modelling and validation**". The thesis is submitted for the degree *Doctor of Philosophy in Engineering with Chemical Engineering* at Potchefstroom campus of North-West University, South Africa:

1. Kozhukhova, A. E., du Preez, S. P., Malakhov, A. A., Bessarabov, D. G. (2021). A Thermally Conductive Pt/AAO Catalyst for Hydrogen Passive Autocatalytic Recombination. *Catalysts*, 11(4), 491.

As Ph.D in Chemistry and Postdoctoral research fellow at North-West University (Potchefstroom Campus), Faculty of Engineering, HySA Infrastructure (CoC), South Africa, I am responsible for manuscript reviewing, revising, and editing.

This statement satisfies Rule 5.4.2.8 and Rule 5.4.2.9 of the General Academic Rules 2015 of the North-West University.

Signed at Potchefstroom on 11th day of November 2021

Signature: _____



Statement of consent: V V. Sergeev

To whom it may concern

I, VLADIMIR V. SERGEEV, declare that I have read this consent form and give my permission to ALEXANDER A. MALAKHOV to use the publication listed below, of which I am co-author, in the thesis entitled **"Mitigation strategies for hydrogen safety in the confined environment: CFD modelling and validation"**. The thesis is submitted for the degree *Doctor of Philosophy in Engineering with Chemical Engineering* at the Potchefstroom campus of the North-West University, South Africa:

1. Avdeenkov, A. V., Sergeev, V. V., Stepanov, A. V., Malakhov, A. A., Koshmanov, D. Y., Soloviev, S. L., Bessarabov, D. G. (2018). Math hydrogen catalytic recombiner: Engineering model for dynamic full-scale calculations. *International Journal of Hydrogen Energy*, 43(52), 23523-23537.

As Senior Researcher at, State Scientific Center of Russian Federation Institute of Physics and Power Engineering (IPPE), Obninsk, Russia, I responsible for manuscript reviewing, revising, and editing.

This statement satisfies Rule 5.4.2.8 and Rule 5.4.2.9 of the General Academic Rules 2015 of the North-West University.

Signed at Obninsk on 16 day of November 2021

Signature: 

Statement of consent: A V. Stepanov

To whom it may concern

I, ANDREY V. STEPANOV, declare that I have read this consent form and give my permission to ALEXANDER A. MALAKHOV to use the publication listed below, of which I am co-author, in the thesis entitled **"Mitigation strategies for hydrogen safety in the confined environment: CFD modelling and validation"**. The thesis is submitted for the degree *Doctor of Philosophy in Engineering with Chemical Engineering* at Potchefstroom campus of North-West University, South Africa:

1. Avdeenkov, A. V., Sergeev, V. V., Stepanov, A. V., Malakhov, A. A., Koshmanov, D. Y., Soloviev, S. L., Bessarabov, D. G. (2018). Math hydrogen catalytic recombiner: Engineering model for dynamic full-scale calculations. *International Journal of Hydrogen Energy*, 43(52), 23523-23537.

As Head Expert at «All-Russian Research Institute for Nuclear Power Plants Operation» JSC ("VNIIAES JSC"), Moscow, Russia, I am responsible for manuscript reviewing, revising, and editing.

This statement satisfies Rule 5.4.2.8 and Rule 5.4.2.9 of the General Academic Rules 2015 of the North-West University.

Signed at Obninsk on 11 day of November 2021

Signature: 

Statement of consent: D.Y. Koshmanov

To whom it may concern

I, DMITRI Y. KOSHMANOV, declare that I have read this consent form and give my permission to ALEXANDER A. MALAKHOV to use the publication listed below, of which I am co-author, in the thesis entitled "**Mitigation strategies for hydrogen safety in the confined environment: CFD modelling and validation**". The thesis is submitted for the degree *Doctor of Philosophy in Engineering with Chemical Engineering* at the Potchefstroom campus of the North-West University, South Africa:

1. Avdeenkov, A. V., Sergeev, V. V., Stepanov, A. V., Malakhov, A. A., Koshmanov, D. Y., Soloviev, S. L., Bessarabov, D. G. (2018). Math hydrogen catalytic recombiner: Engineering model for dynamic full-scale calculations. *International Journal of Hydrogen Energy*, 43(52), 23523-23537.

As Director at Investment Scientific-Production Company "Russian Energy Technologies" (RET), Moscow, Russia, I am responsible for manuscript reviewing, revising, and editing.

This statement satisfies Rule 5.4.2.8 and Rule 5.4.2.9 of the General Academic Rules 2015 of the North-West University.

Signed at KOSUMANOVD.E on 04 day of NOVEMBER 2021

Signature: _____



Statement of consent: S.L. Soloviev

To whom it may concern

I, SERGEY L. SOLOVIEV, declare that I have read this consent form and give my permission to ALEXANDER A. MALAKHOV to use the publication listed below, of which I am co-author, in the thesis entitled **"Mitigation strategies for hydrogen safety in the confined environment: CFD modelling and validation"**. The thesis is submitted for the degree *Doctor of Philosophy in Engineering with Chemical Engineering* at the Potchefstroom campus of the North-West University, South Africa:

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As D.Sc. in Engineering and Supervisor of the OJSC at «All-Russian Research Institute for Nuclear Power Plants Operation» JSC ("VNIIAES JSC"), Moscow, Russia, I am responsible for manuscript reviewing, revising, and editing.

This statement satisfies Rule 5.4.2.8 and Rule 5.4.2.9 of the General Academic Rules 2015 of the North-West University.

Signed at Moscow on 12 day of November 2021

Signature: S Soloviev

Statement of consent: Ms. Alina E. Kozhukhova

To whom it may concern

I, ALINA E. KOZHUKHOVA, declare that I have read this consent form and give my permission to ALEXANDER A. MALAKHOV to use the publication listed below, of which I am co-author, in the thesis entitled **"Mitigation strategies for hydrogen safety in the confined environment: CFD modelling and validation"**. The thesis is submitted for the degree *Doctor of Philosophy in Engineering with Chemical Engineering* at Potchefstroom campus of North-West University, South Africa:

1. Kozhukhova, A. E., du Preez, S. P., Malakhov, A. A., Bessarabov, D. G. (2021). A Thermally Conductive Pt/AAO Catalyst for Hydrogen Passive Autocatalytic Recombination. *Catalysts*, 11(4), 491.

As Postdoctoral student at North-West University (Potchefstroom Campus), Faculty of Engineering, HySA Infrastructure (CoC), South Africa, I am responsible for manuscript reviewing, revising, and editing.

This statement satisfies Rule 5.4.2.8 and Rule 5.4.2.9 of the General Academic Rules 2015 of the North-West University.

Signed at Potchefstroom on 03 day of November 2021

Signature:  _____

APPENDIX E: RANGE OF EXPERIMENTAL ERRORS AND CALIBRATION DATA

Infra-red camera calibration

Temperature distribution throughout the catalyst surface was determined by an IR camera (M100hd, Telops, Canada). The camera was fitted with an optional lens designated to capture thermal data in the temperature range 0–325 °C and 147–600 °C.

The calibration files applied to the camera output were set by selecting the calibration collection. The optical path selection was made by selecting the appropriate collection because each collection is associated with a specific lens. The Radiometric Temperature (RT) calibration mode was set for the data output from the camera. The RT mode effectively represents for each pixel the temperature of a perfect blackbody that would create the signal measured by that particular pixel. As this is done on a pixel-by-pixel basis, RT performs non-uniformity correction and expresses the results in units of temperature.

The Non-uniformity Correction (NUC) data uses the information contained in a calibration block to apply a gain and offset correction to the RAW data on a pixel-by-pixel basis. This is done so that a uniform scene like a blackbody should give a uniform digital level measurement. As a count-based quantity, NUC measurements are typically proportional to exposure time for a constant scene.

Base calibration accuracy and uniformity was performed by Telops 17.03.2017. The RT error map and radiometric calibration block summary are presented in Figures A-3 and A-4, respectively.

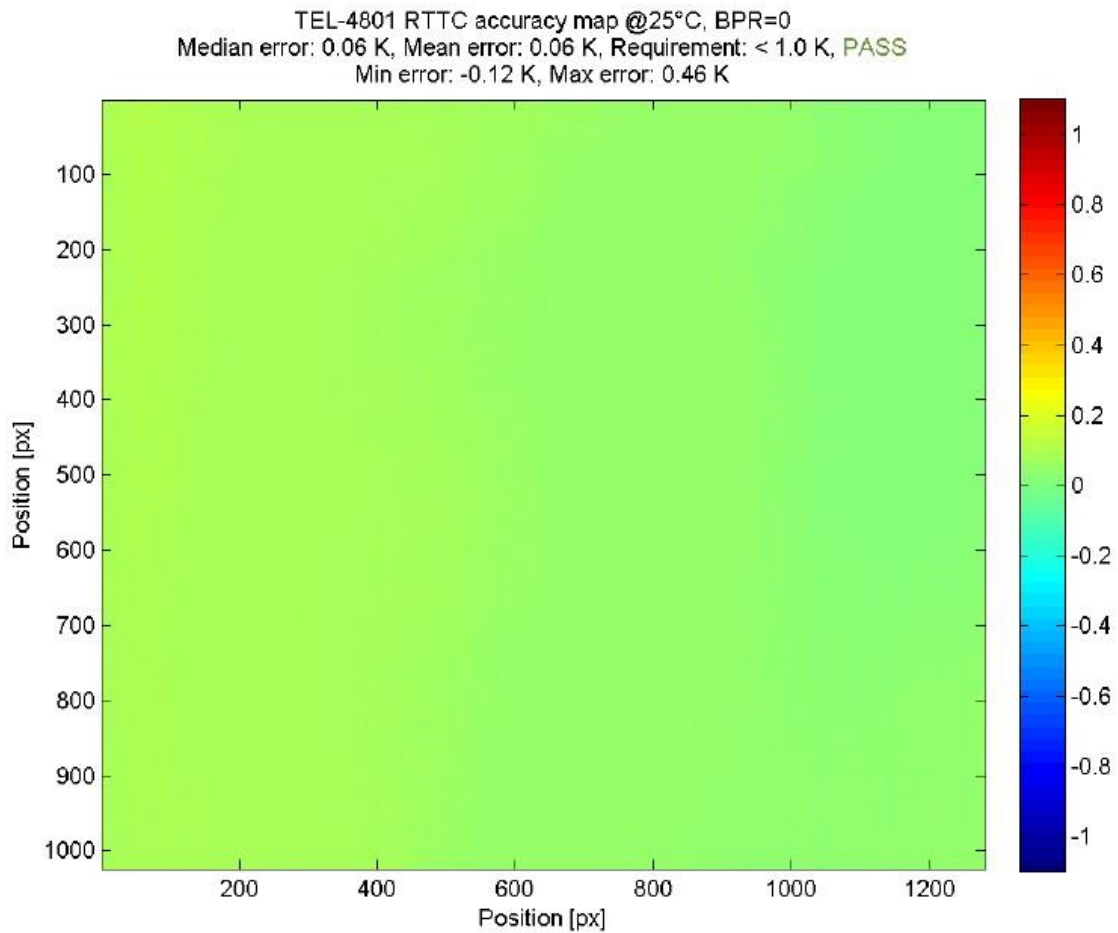


Figure A-3: Radiometric temperature error map.

Collection		Lens	FW	NDF	MF	ET	Temp range	Validation BB Temp	RT error	NUC unif	Status
#	POSIXtime					[μs]	[°C]	[°C]	[°C]	[%]	
Requirement									<1°C/1%	<2%	
0	1489699640	#1	1	N/A	N/A	1741	[0 325]	75	0.07	0.22	Pass
2	1490639441	#1	2	N/A	N/A	277	[147 600]	450	-0.2	0.25	Pass

Legend: FW: filter wheel position; NDF: AEC+ neutral density filter position; MF: manual filter; ET: exposure time for multi-point blocks; Temp range: recommended temperature range to use the calibration block; Validation BB Temp: black body temperature used to measure the block's performances; RT error: median temperature error; NUC unif: standard deviation of the NUC image.

Figure A-4: Calibration block summary.

Therefore, the error of temperature distribution measurements was taken as <1%.

Hydrogen concentration

Hydrogen concentration before and after the recombination reaction in the recombiner section testing station was measured using hydrogen sensors (XEN-5320, The Netherlands). Before evaluation of the hydrogen content, hydrogen sensors were calibrated using certified hydrogen/nitrogen gas mixtures (2 and 4 vol% of hydrogen) (Afrox, South Africa). The calibration was performed in the custom calibration curve measurement mode. In the hydrogen measurement mode, inaccuracy was estimated to be 1–3 %.

APPENDIX F: MATHEMATICAL FORMULATION OF THE CFD MODEL

BOUNDARY CONDITIONS DESCRIBED IN CHAPTER 3

The boundary conditions at the hydrogen release point were set as a pressure outlet. The pressure outlet boundary is an outflow condition which imposes the working pressure. The boundary conditions at the open side of facility were set as stagnation boundary. Stagnation boundary is allowing to provide outgoing flow (released hydrogen) from the domain.

For a pressure outlet as well as for stagnation boundary, STAR-CCM+ computes the following values at the boundary faces, depending on the flow situation: v – face velocity, P_{in} – specified pressure, T_{in} – initial temperature. In order for pressure outlet:

$$v = v_{in} * n, \quad (1)$$

$$P_{in} = P_{in}, \quad (2)$$

$$T_{in} = T_{ref}, \quad (3)$$

where n is normal to the face area, T_{ref} - reference temperature of domain. The boundary face velocity (v) is extrapolated from the interior of the domain. $T_{in} = 300K$, during simulation is extrapolated from the interior of the domain.

As long as the process assumed isothermal, the pressure and velocity for stagnation boundary is calculated from the Bernoulli equation:

$$P_{in} = P_t - \rho/2 * |v|^2, \quad (4) \quad 1$$

$$|v| = v, \quad (5)$$

where, P_t = total pressure, v - the boundary velocity magnitude is extrapolated from the interior of the domain.

The domain wall was assumed adiabatic.