

The development of autothermal microchannel reactor technology for hydrogen-based gas processing

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Thesis accepted in fulfilment of the requirements for the degree
Doctor of Philosophy in Engineering with Chemical Engineering
at the North West University

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Co-Promoter: Prof. Dmitri G Bessarabov

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Student number: 22800433

Hoe wonderlik is u gedagtes vir my, o God,

hoe magtig hulle almal!

~ Psalm 139:17

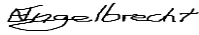
SOLEMN DECLARATION

I, Nicolaas Engelbrecht, declare herewith that the thesis entitled:

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

Signed at the North-West University (Potchefstroom Campus)



Nicolaas Engelbrecht

15/10/2021

Date

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ABSTRACT

Key challenges associated with the production, transport, storage and continuous use of hydrogen (H_2), generated from renewable energy, is the natural intermittency of some renewable resources such as solar photovoltaic and wind, and the physical properties of H_2 that complicates its handling in the industry, i.e. its low volumetric energy density and high flammability. The work presented in this thesis demonstrates the use of process intensifying microchannel reactor technology for the thermo-catalytic processing of renewable H_2 via attractive energy carriers: (i) the decomposition of ammonia (NH_3) to form H_2 , as well as (ii) the synthesis of methane (CH_4) using renewable H_2 as feedstock (CO_2 methanation).

Furthermore, these processes require heat management strategies for effective autothermal operation. The NH_3 decomposition reaction is endothermic and a coupled exothermic process (NH_3 oxidation) is demonstrated to provide the heating requirements for H_2 release. Conversely, the CO_2 methanation process is exothermic, and cooling is required to reach equilibrium favouring reaction temperatures that promote the conversion of H_2 and CO_2 towards CH_4 . Extensive experimental investigations were carried out into these thermally coupled processes, and reported on for NH_3 decomposition and for CO_2 methanation. Then an evaluation of a compact methanation demonstrator unit incorporating the microchannel-based reactor was carried out, followed by computational fluid dynamic (CFD) modelling to evaluate associated heat and mass transport properties in the microchannel reactor.

The scale of the microchannel reactors investigated here was such that NH_3 up to a flow rate of 6 NL min^{-1} was processible towards H_2 at a high conversion rate (99.8%), and corresponding to an equivalent H_2 fuel cell power of 0.71 kW_e , while total methanation flow rates of up to 7 NL min^{-1} were used to demonstrate CO_2 methanation (90.5% CO_2 conversion). Respective thermal efficiencies of 75.9% and 76.6% were obtained at the recommended steady-state operating points, which were close to thermodynamic equilibrium. These thermal efficiencies are deemed remarkable, considering the compact- and R&D-scale reactor technologies investigated herein. Overall, the work described in this thesis contributes to the development of micro-engineered reactors that are multifunctional catalytic conversion units and heat exchangers, and which support modular technologies for the processing of renewable H_2 .

Keywords: Microchannel reactor technology, process intensification, thermally self-sustained processes, power-to-X concept, renewable hydrogen, ammonia-to-hydrogen, CO_2 methanation

PREFACE

This thesis is presented in article-based format, as allowed for in rule 5.4.2 of the North-West University's General Academic Rules of 2017. Other academic rules that are applicable to the submission of a doctoral thesis as a series of original articles are rules 5.10.5, 5.10.8 and 5.10.9:

Rule **A.5.4.2** states: *“Faculty rules may provide that full or partial compliance with the research component of a doctoral degree may take the form of one or more publishable or published research articles in a specified field, taking into account the requirements of rules 5.10 and 5.12 and specifying the minimum number of research articles required in lieu of a thesis, mini-thesis or the research component of a professional doctoral degree.”*.

Rule **A.5.10.5** states: *“Where a candidate is allowed to submit the research product in the form of research articles, such research product must be presented for examination purposes as an integrated unit, supplemented with a problem statement, an introduction and a synoptic conclusion as prescribed by faculty rules and the manuscript submission guidelines, or the url link to the manuscript guidelines of the journal or journals concerned.”*.

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Rule **A.5.10.9** states: *“Where co-authors or co-inventors as contemplated in rule 5.10.8 were involved in the development of the research product, the candidate must mention this fact in the preface, and must include the statement of each co-author or co-inventor in the thesis, mini-thesis or research report immediately following the preface to the research product.”*.

Chapters 2, 3 and 4 presented herein have been published as original full-length articles. Numbering has been adapted for subsections, figures, tables and equations, to be consistent throughout the thesis. The references for these chapters follow the referencing style as stipulated by the journal in which the respective articles were published, while the referencing style for chapters 1, 5 and 6 follows the guidelines set out by the North-West University.

STATEMENT FROM CO-AUTHORS

This section summarises the statements of consent from the co-authors of the below mentioned journal papers, that Nicolaas Engelbrecht may submit these papers as chapters in his thesis, towards the fulfilment of the requirements for the degree *Doctor of Philosophy in Engineering with Chemical Engineering*.

- Engelbrecht, N., Everson, R.C., Bessarabov, D., Kolb, G. 2020. Microchannel reactor heat-exchangers: A review of design strategies for the effective thermal coupling of gas phase reactions. *Chemical Engineering and Processing - Process Intensification*, 157:108164.
- Engelbrecht, N., Chiuta, S., Bessarabov, D.G. 2018. A highly efficient autothermal microchannel reactor for ammonia decomposition: Analysis of hydrogen production in transient and steady-state regimes. *Journal of Power Sources*, 386:47–55.
- Engelbrecht, N., Everson, R.C., Bessarabov, D. 2020. Thermal management and methanation performance of a microchannel-based Sabatier reactor/heat exchanger utilising renewable hydrogen. *Fuel Processing Technology*, 208:106508.

I, Prof. Dmitri Bessarabov, director of HySA Infrastructure CoC, NWU, hereby grant Nicolaas Engelbrecht permission to submit the above-mentioned journal papers, of which I was a co-author, as chapters towards his doctoral thesis. My involvement was to allocate research funding towards all projects under the HySA Infrastructure program, acting as co-promoter to Nicolaas Engelbrecht's doctoral thesis, and proofreading the mentioned journal papers before publication.

Prof. Dmitri Bessarabov

Prof Dmitri
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16/03/2021

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I, Dr. Steven Chiuta, a previous employee and PhD graduate of HySA Infrastructure CoC, NWU, hereby grant Nicolaas Engelbrecht permission to submit the above-mentioned journal paper, of which I was a co-author, as a chapter towards his doctoral thesis. My involvement in

the research paper on the autothermal microchannel reactor for ammonia decomposition was the conceptualisation and initial correspondence with Fraunhofer IMM, which led to the design and development of the microchannel reactor used in that work, as well as proofreading the related journal paper before publication.

Dr. Steven Chiuta



Signature

15/02/2021

Date

I, Prof. Raymond Everson, Professor at the School of Chemical and Minerals Engineering, NWU, hereby grant Nicolaas Engelbrecht permission to submit the above-mentioned journal papers, two of which I was a co-author, as chapters towards his doctoral thesis. My involvement was to act as main promoter towards Nicolaas Engelbrecht's doctoral thesis, and the proofreading of the mentioned journal papers before publication.

Prof. Raymond Everson

Raymond
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I, Prof. Dr. Gunther Kolb, head of division Energy and Chemical Technology at Fraunhofer-IMM, hereby grant Nicolaas Engelbrecht permission to submit the above-mentioned review paper, of which I was a co-author, as a chapter towards his doctoral thesis. My involvement in the review paper was significant review and editing of the paper, as well as contributing the work of Fraunhofer-IMM towards the section: "thermal effects in experimental microchannel reactors demonstrated to date".

Prof. Dr. Gunther Kolb

Gunther Kolb

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NOMENCLATURE

		<i>SUBSCRIPTS & SUPERSSCRIPTS</i>	
C_{CO_2}	CO ₂ concentration, mol m ⁻³	0	Nominal value
C_p	Specific heat capacity, J kg ⁻¹ K ⁻¹	a	Absolute
d_1	Combustion channel size, m	atm	Atmosphere
d_2	Reforming channel size, m	cat	Catalyst
D_H	Hydraulic diameter, m	cool	Coolant flow
D_i	Diffusivity of species i , m ² s ⁻¹	D	External diffusion
D_{ij}	Binary diffusivity of species i in j , m ² s ⁻¹	decomp	Decomposition
d_z	Layer thickness, m	down	Out of plane, downward direction
E_a	Activation energy, J mol ⁻¹	e	Electric
H	Height, m	eff	Effective catalyst property
ΔH_{298K}	Enthalpy of reaction at 25°C, J mol ⁻¹	ext	External (boundary) temperature
ΔH_r	Enthalpy of reaction at real conditions, J mol ⁻¹	g	Gauge
L	Length, m	gas	Gas mixture
L_{comb}	Combustion catalyst offset from the channel inlet, m	h	Heat transfer coefficient, W m ⁻² K ⁻¹
LHV_i	Lower heating value of component i , MJ kg ⁻¹	i	Mixture component i
L_{ref}	Reforming catalyst offset from the channel inlet, m	in	Inlet
k	Thermal conductivity, W m ⁻¹ K ⁻¹	j	Mixture component j
$K(T)$	Temperature dependant equilibrium constant	max	Maximum
m_i	Mass flow of component i , kg s ⁻¹	meth	Methanation flow
n	Empirical factor	min	Minimum
n_i	Mole flow of component i , mol s ⁻¹	out	Outlet
n_T	Total mole flow, mol s ⁻¹	oxi	Oxidation
M_i	Molar mass of species i , g mol ⁻¹	P	Power
M_j	Molar mass of species j , g mol ⁻¹	PEM	Proton exchange membrane
P	Pressure, Pa	r	Reaction
P	Power, W	rec	Heat recovered in the H ₂ coolant stream
P_{atm}	Pressure, atm	s	Catalyst
ΔP	Pressure drop, Pa	stoic	Stoichiometric ratio
P_{eq}	Equivalent fuel cell power, W	th	Thermal
p_i	Partial pressure of species i , bar		

Q	Flow rate, $\text{m}^3 \text{s}^{-1}$	up	Out of plane, upward direction
q	Heat flow, W	w	Wall
Q_{oop}	Total out of plane heat transfer, W	x, y, z	Directional components
R	Flow resistance, Pa.s m^{-3}	<i>ABBREVIATIONS</i>	
R_{const}	Ideal gas constant, $\text{Pa.m}^3 \text{mol}^{-1} \text{K}^{-1}$	2D	Two dimensional
R_r	Reaction rate, $\text{mol kg}^{-1} \text{s}^{-1}$	CFD	Computational fluid dynamics
r_{Sabatier}	Sabatier reaction rate, $\text{mol m}^{-3} \text{s}^{-1}$	db	Dry basis
S_i	Selectivity of species i , %	DME	Dimethyl ether
t	Time, s	DSI	Department of Science and Innovation
T	Temperature, K	Exp.	Experimental
v	Fluid velocity directional	FC	Fuel cell
V	Fluid velocity vector	FT	Fischer–Tropsch
W	Width, m	GC	Gas chromatograph
X_i	Conversion of species i , %	GHSV	Gas hourly space velocity
y_i	Mole fraction of species i	HySA	Hydrogen South Africa
z	Axial coordinate, m	LHHW	Langmuir–Hinshelwood–Hougen–Watson
<i>GREEK SYMBOLS</i>		NL	Normal litre (at 20°C and 1 bar)
δ	Derivative	nlpm	Normal litre per minute (NL min^{-1})
δn	Derivative in normal direction	NTP	Normal temperature and pressure (20°C and 1 bar)
ε	Porosity	Nu	Nusselt number
ζ	Dimensionless axial coordinate	P&I	Piping and instrumentation
κ	Permeability, m^2	PCM	Phase change material
η	Thermal efficiency	PGM	Platinum group metal
Θ	Hydrogen utilization	PV	Photovoltaic
μ	Fluid viscosity, Pa.s	PtG	Power-to-gas
μ_{eff}	Effective Brinkman viscosity, Pa.s	Re	Reynolds number
Φ	Fuel-oxygen equivalence ratio	RWGS	Reverse water–gas shift
ρ	Fluid density, kg m^{-3}	SCR	Selective catalytic reduction
ω_i	Mass fraction of species i	SL	Standard litre (at 0°C and 1 atm)
v_i	Atomic diffusion volume of species i , $\text{cm}^3 \text{mol}^{-1}$	SNG	Synthetic natural gas
v_j	Atomic diffusion volume of species j , $\text{cm}^3 \text{mol}^{-1}$	vol.%	Volume percent
$\langle \rangle$	Porous catalyst property	wt.%	Weight percent

CHAPTER 1

INTRODUCTION

CHAPTER OVERVIEW

This chapter serves as an introduction to the scope of work that is undertaken in this thesis. The scene is set with some background on the rapid growth of renewable energy technologies since the turn of the 21st century, and associated challenges faced with the large-scale deployment of renewables. Hydrogen and other chemical energy carriers, e.g. NH_3 and CH_4 , certainly appear to be regenerative energy storage pathways, and their production could ease the fluctuations induced by solar photovoltaic and wind energy in electricity grids. Microchannel reactors as devices for effective chemical conversion are assessed, as could be applicable to the processing of renewable H_2 into- and from these chemical energy carriers, especially as microchannel reactor technology supports dynamic process operation (variable load), and excellent heat and mass transfer. The objectives of the thesis are presented—they are to evaluate autothermal microchannel reactor technology for two thermo-catalytic processes: (i) the decomposition of NH_3 for H_2 production, intended for fuel cell power applications, and (ii) the methanation (hydrogenation) of CO_2 , as a renewable energy storage and CO_2 sequestration technique.

1.1 BACKGROUND AND PROBLEM STATEMENT

Renewable energy generation technologies, particularly utilising solar and wind energy, have made significant inroads, since the turn of the 21st century, in the supply of GW-scale power worldwide. The International Energy Agency (IEA) expects renewables to be the world's largest source of electricity by 2025, supplying a third of the world's electricity demand, and surpassing coal as the main energy resource (IEA, 2020a:3). The fast growth of renewable energies was driven, initially, by the incorporation of cleaner energy generation technologies into national power grids, after the environmental issues associated with fossil-based energy resources were highlighted in the Paris Climate Change Agreement. Recently, the reduction in the installed cost of solar photovoltaic (PV) and onshore wind farms in favourable geographic locations has contributed to the deployment of renewables, which are able to supply electricity at the cheapest power purchase agreements for all new energy projects. The global average levelised cost of electricity for solar PV and onshore wind is projected to be as low as 0.039 and 0.043 USD/kWh, respectively, by 2021 (IRENA, 2019:12). These costs will surpass that of hydropower as the cheapest, although hydro is the largest deployed renewable energy resource, and will remain so at least until 2025 (IEA, 2020a:3).

The variability of solar and wind energy is arguably the one factor that limits its potential as a baseload power source (Matek and Gawell, 2015:105–107), which separates it from hydropower—a renewable energy source that can be used for baseload power or energy storage, particularly in water abundant regions such as the Nordic countries, Brazil, Canada and China. The fact that solar and wind energies are characterised by natural fluctuations means that electricity grids are put under enormous strain, especially those that integrate large percentages of these renewables, and with limited flexibility (e.g. the absence of hydro storage or open cycle gas turbines that can supply electricity at times of sudden power demand, or handle downturn). It seems therefore that smart grids will become vital as the renewable energy sector expands, as will also be the necessity to incorporate other methods of energy storage and supply that can ease the fluctuations that are induced by solar and wind energy technologies (IEA, 2020b:19).

In recent years, the production of environmentally friendly H₂ via water electrolysis (power-to-gas, PtG) has been one of the most promising technologies to convert and store renewable energy in a chemical energy carrier at MW-scale capacity. Renewable H₂ provides a pathway

for the storage of regenerative electric power—significant advancements have recently been made in the field of H₂-fuelled utility-scale gas turbines and fuel cell (FC) technologies (Nejat Veziroglu, 2012:655–656). Renewable H₂ has been widely recognised by governments and policy makers, industry, and academia as a future clean energy carrier with multiple end-use applications. At the moment, large-scale and far reaching H₂ infrastructure is not yet established across industries and in the transport sector (Brey *et al.*, 2018:2893). In a recent IEA report (IEA, 2019:16), seven recommendations, summarised in Figure 1.1, were underlined that could stimulate future growth towards H₂ economies worldwide. Collectively, these avenues to establish H₂ technologies target research and development across the H₂ technology spectrum, policy support for sustainable energy solutions, promoting large-scale demand for renewable H₂, as well as the technologies benefitting existing industries, shipping ports and the transport sector.

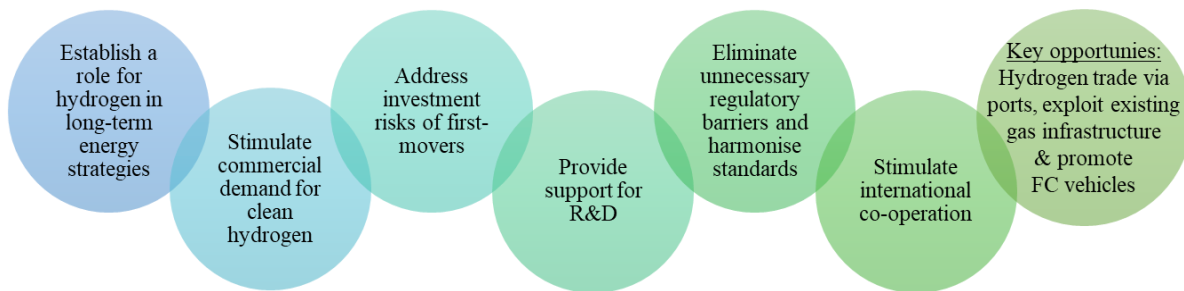


Figure 1.1: The International Energy Agency’s seven recommendations to establish H₂ technology at a global scale (IEA, 2019:16).

The storage and transport of H₂ faces a number of barriers due to its low density (0.082 kg.m⁻³ at NTP). Either significant compression or liquification (at cost) is required to ensure that the handling of pure H₂ is practically feasible. At 700 bar and 20°C, compressed H₂ has a density of 42.2 kg.m⁻³, while at 1 bar and -252.9°C, liquid H₂ has a density of 70.8 kg.m⁻³. In a recent study by Fraunhofer ISE that analysed future potential energy export technologies (Hank *et al.*, 2020:2271), it was estimated that, due to liquid hydrogen’s inevitable boil-off properties, it becomes more economically feasible to transport H₂-containing chemicals such as NH₃ and methanol, across shipping distances of more than ~7000 km (from renewable-abundant regions such as Africa, to space limited-regions such as Europe). In addition, the safety aspect that comes with handling a highly flammable compressed gas or liquid is of great importance—a factor that is not simplified by hydrogen’s small molecule size and its ability to leak much easier from pipelines and storage equipment. Since the inception of the PtG concept, PtG has

expanded to include the production of fuels and chemicals such as NH_3 , CH_4 and CH_3OH . Without exception, these chemical energy carriers have various applications: for renewable energy storage and the regeneration of power, energy export in future global energy markets, use as chemical building blocks in industry, and as potential automotive fuels (Figure 1.2). Ammonia is easily liquified at low pressure (8.6 bar_a), while methanol is already in the liquid state at ambient conditions (subsequent H_2 densities of 108.5 and 100.0 kg $\text{H}_2 \text{ m}^{-3}$, respectively). Although CH_4 (~90% constituent of natural gas) is rarely liquified other than for long-distance ship transport, gaseous and compressed CH_4 has GWh-scale energy storage capacity in natural gas networks. Renewable H_2 blending in natural gas networks is feasible, but limited to low percentages due to equipment material and end-user restrictions (Altfeld & Pinchbeck, 2013:5–10). For the sake of brevity, these limitations are not discussed further.

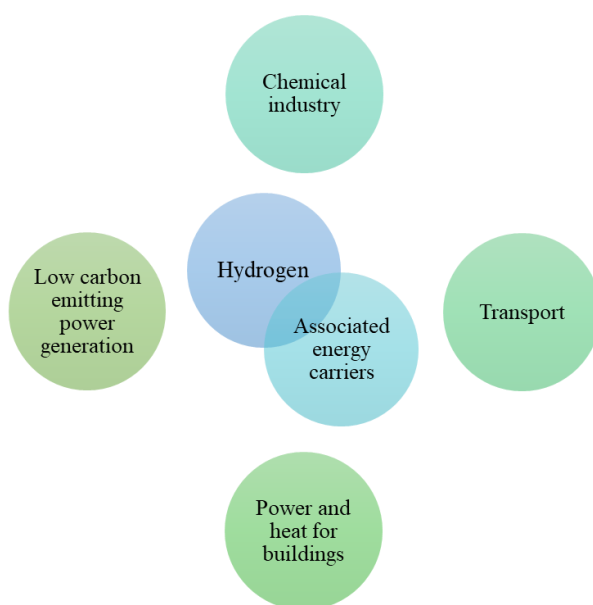


Figure 1.2: Prospects of renewable power-to-hydrogen and associated power-to-X technology in the future energy industry. Inspired by IEA (2019:89–122).

1.2 MOTIVATION

In this work, two catalytic processes will be investigated for the production and conversion of renewable H_2 :

- I. The first process is the decomposition of NH_3 for H_2 production, intended for FC power applications.

The recent ‘green drive’ has seen NH_3 being included as a likely future carbon-free energy vector that may have origin from renewable energy sources. Ammonia has a

current global annual production volume of ~170 million metric tonnes (Soloveichik, 2019:377)—albeit near exclusively from fossil-based origin—and is traded by ship, rail, road and pipeline, for application in the chemical and agricultural industries. To generate power from NH_3 (especially in off-grid and mobile applications), one pathway is the decomposition of NH_3 to produce H_2 , and to subsequently feed commercial proton exchange membrane or alkaline FCs with the H_2 fuel. This conversion process is slightly endothermic and requires a high quality heat source ($>600^\circ\text{C}$).

- II. The second process is the methanation (hydrogenation) of CO_2 , as a renewable energy storage and CO_2 sequestration technique.

The CO_2 methanation reaction was founded and published by French chemist, Paul Sabatier, in 1913. Methane, the combustible constituent of natural gas (i) offers the ability to store and transport, at large-scale, renewable energy through natural gas networks, (ii) has application in power generation cycles with existing gas turbine technology, and acts as a regenerative power source to balance power grids with large percentages of variable renewables, (iii) is a heat source for commercial and residential buildings via industrial-scale boiler technology, and (iv) provides lower carbon and particulate emissions compared to gasoline and diesel fuels when burned in internal combustion engines (Wilson & Styring, 2017:8). The methanation of CO_2 is an exothermic process, and produces ~18% of the lower heating potential of the reacted H_2 as heat.

In both these processes, a reactor is required with load following capabilities. For H_2 production from NH_3 , the demand-side power requirement governs the rate of H_2 produced (reactor throughput). On the other hand, the process of converting H_2 and CO_2 into CH_4 is susceptible to the availability of excess renewable energy (and H_2), whether it is solar- or wind energy based. Conventional reactors such as fixed beds are well known for gas phase reactions, but are generally intended for continuous operation, with start-up times and thermal cycles in the order of hours or even days (Eigenberger, 1992:229).

Microchannel reactor technology is a typical example of process intensifying equipment for application in the chemical process industry. One of the first groups to coin the term “*process intensification*” is the group of Stankiewicz & Moulijn, (2000:23). A simple definition of this term is quoted from the group, as follows:

“Process intensification consists of the development of novel apparatuses and techniques that, compared to those commonly used today, are expected to bring dramatic improvements in manufacturing and processing, substantially decreasing equipment-size/production-capacity ratio, energy consumption, or waste production, and ultimately resulting in cheaper, sustainable technologies.”

Microchannel reactors are designed as multifunctional reactor/heat exchanger devices that can sustain dynamic process operation and control, boasting effective heat and mass transfer which eases variable load operation (Men *et al.*, 2007:82). There exists a necessity to demonstrate micro-engineered reactors that are able to produce and convert renewable H₂ at increased throughput rates, compared to the rates achieved to date (Deshmukh *et al.*, 2010:10883). In order to do so, microchannel reactor technology that is scaled up for these processes need to be operated autothermally—in essence, processes being able to sustain their own thermal requirement via the utilisation of reaction heat.

1.3 RESEARCH HYPOTHESIS

Microchannel reactor technology, with process intensifying transport properties (improved heat and mass transfer), offers suitable processing equipment for the thermo-catalytic conversion of H₂ into- and from chemical energy storage media. Moreover, this also involves renewable H₂ processing that is subject to fluctuating supply and demand (as a result of local demands for H₂ FC power, or variable renewable energy supply).

1.4 AIM AND OBJECTIVES

Hydrogen energy is widely considered as one of the clean energy vectors of the future. The overall objective of this work is to develop microchannel reactor technology for the processing of H₂, and examine the performance of the reactor for two catalytic processes: (i) NH₃ decomposition for H₂ production, and (ii) CO₂ methanation (Sabatier process) to produce synthetic CH₄. Important operational parameters of a bench-scale microchannel reactor, capable of autothermal (thermally self-sustained) operation, will be investigated. To a large extent, this thesis focuses on improved thermal management, i.e. heating with an indirect, yet thermally coupled, exothermic reaction in the case of the endothermic NH₃ decomposition process, and cooling provided to the exothermic CO₂ methanation reaction. The specific objectives of the thesis, and research questions to be answered, are the following:

- I. To assess the relevant literature on the thermal coupling of exothermic and endothermic reactions in microchannel reactors—that has been investigated experimentally, as well as computationally. The review focusses on the indirect thermal coupling of reactions in microchannel reactors with spatial segregation achieved through heat conductive reactor walls. What reactor designs and operating strategies are typically the most effective for the transfer of heat in such micro-structured devices?
- II. To experimentally evaluate the NH_3 decomposition process in a microchannel reactor for H_2 FC applications. In order to achieve self-sustained operation, the thermal coupling with the NH_3 oxidation reaction will be realised. Is a microchannel reactor suitable for dynamic (start-up) and steady-state production of high purity H_2 from NH_3 , and what thermal efficiency can be obtained for the ammonia-to-hydrogen process?
- III. To assess a bench-scale experimental microchannel reactor for the CO_2 methanation process. This investigation will evaluate the possibility of improved thermal efficiency of the microchannel reactor, by incorporating a cooling medium to recuperate reaction heat from the exothermic CO_2 methanation process. What is the effect of the cooling medium's flow direction on the reactor temperature profile, and does the resultant temperature gradient improve reaction equilibrium? Is the CH_4 that is produced of such purity that it can be directly stored/blended, for instance, in natural gas networks?
- IV. To use the operational knowledge gained on the autothermal microchannel reactor for CO_2 methanation (in the bench-top investigation) and integrate the reactor and balance of plant into a compact and portable technology demonstrator. Performance-wise, does certain process simplifications affect, or even improve, the reactor's thermal and methanation performance, and does the reactor perform well during extended dynamic operation, and at recommended (high-throughput H_2) scenarios?
- V. To use an advanced CFD modelling tool to characterise other thermal effects and kinetic rates in the CO_2 methanation demonstrator, which is not possible through the experimental assessments alone. Using a literature obtained kinetic rate law, is the experimental reactor accurately described by computations? Does any model assumptions possibly limit the applicability of CFD models when describing thermally coupled microchannel reactors for H_2 processing?

1.5 LAYOUT OF THE THESIS

This introductory chapter (Chapter 1) provides an overview of renewable H_2 production and processing, as motivation for this thesis. Subsequent chapters cover the following:

Chapter 2 presents a literature overview of the topic, already published as a review article [Engelbrecht, N., Everson, R.C., Bessarabov, D., Kolb, G. 2020. Microchannel reactor heat-exchangers: A review of design strategies for the effective thermal coupling of gas phase reactions. *Chemical Engineering and Processing - Process Intensification*, 157:108164], detailing various reactor designs, flow configurations and operational characteristics of model-based and experimental autothermal microchannel reactors for the processing of H_2 .

Chapter 3 presents an ‘experimental chapter’, published as a research article [Engelbrecht, N., Chiuta, S., Bessarabov, D.G. 2018. A highly efficient autothermal microchannel reactor for ammonia decomposition: Analysis of hydrogen production in transient and steady-state regimes. *Journal of Power Sources*, 386:47–55], describing an autothermal microchannel reactor for NH_3 decomposition, to be used in H_2 FC power applications. This chapter reports the reactor’s dynamic (start-up) and steady-state performance to produce H_2 from NH_3 .

Chapter 4 presents another ‘experimental chapter’, published as a research article [Engelbrecht, N., Everson, R.C., Bessarabov, D. 2020. Thermal management and methanation performance of a microchannel-based Sabatier reactor/heat exchanger utilising renewable hydrogen. *Fuel Processing Technology*, 208:106508], describing an autothermal microchannel reactor for the CO_2 hydrogenation (methanation) process, to be used in renewable energy storage applications. The reactor’s performance is assessed on thermal aspects as well as CO_2 methanation performance, and subsequently compared to other microchannel reactors for CO_2 methanation in the literature.

Chapter 5 presents a combined ‘experimental and modelling chapter’, devoted to the design, development and assessment of a compact and portable CO_2 methanation demonstrator—incorporating microchannel reactor technology—for the self-sustained production of CH_4 from renewable H_2 . This chapter presents the validation of the CO_2 methanation demonstrator’s steady-state performance to that discussed in Chapter 4 (bench-top evaluation), presents reactor dynamics attained during an extended dynamic test, and describes the development and experimental validation of a full, two dimensional CFD model based on the microchannel reactor.

Chapter 6 presents the conclusions to the work described in this thesis, as well as recommendations for the further development of autothermal microchannel reactor technology for H₂-based gas processing.

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CHAPTER 2

MICROCHANNEL REACTOR HEAT-EXCHANGERS: A REVIEW OF DESIGN STRATEGIES FOR THE EFFECTIVE THERMAL COUPLING OF GAS PHASE REACTIONS

CHAPTER OVERVIEW (ABSTRACT)

The thermal coupling of endothermic and exothermic reactions is an important pathway for integrated thermal management within chemical reactors, which supports process intensification. Microchannel reactors are unique in the sense that they provide various design and operational characteristics that benefit high throughput and millisecond contact time chemical conversions. These include high microchannel aspect ratios, improved heat transfer (via thin and thermally conductive reactor substrates), and enhanced mass transfer (due to limited diffusional effects). In this review of experimental and simulated microchannel reactors, focus is put on improved designs and operating strategies to support thermal conduction across microchannel walls, yet keep chemical products from the respective reactions separate using spatially segregated reaction chambers. Three common flow configurations (counter-current, co-current and cross-flow designs) are critically discussed as a result of their abilities to distribute – and in some cases recirculate – reaction heat, the steady-state temperature profiles established within them as a result of flow direction, and reactant conversions/product yields as a result of their thermal characteristics. Special attention is devoted to microchannel design aspects, including wall thermal conductivity, channel dimensions, catalyst positioning and other design strategies (distribution manifolds and heat recirculative reactor designs) to improve heat and mass flows within microchannel reactors.

Engelbrecht, N., Everson, R.C., Bessarabov, D., Kolb, G. 2020. Microchannel reactor heat-exchangers: A review of design strategies for the effective thermal coupling of gas phase reactions. *Chemical Engineering and Processing - Process Intensification*, 157:108164.

2.1 INTRODUCTION

The natural intermittency of renewable energy sources have led to the exploration of various energy storage methods, including chemical energy storage. Compressed gas and liquid fuels (e.g. hydrogen, methane, ammonia, methanol and ethanol) have a superior energy density and storage capacity compared to battery, fly-wheel and compressed air energy storage systems. Stationary power generators based on chemical fuel conversion (e.g. fuel reformers coupled with fuel cells or alternatively gas turbines) can operate continuously, while mobile units (e.g. automobiles) can be refuelled within minutes. Moreover, the combination of fuel processors and fuel cells intended for on-board/mobile applications eliminate the need for on-board hydrogen storage vessels [1]. Perhaps the biggest restriction of chemical energy storage methods are their relatively low round-trip energy efficiencies and high initial capital cost [2]. Power-to-power efficiencies are generally in the order of 33–45% for methane and methanol fuels [3]. The biggest energy loss can be ascribed to the electrolyser and fuel cell [4], while the fuel processors can have efficiencies above 90% when incorporating combined-heat and power systems.

Traditionally, fuel processing is performed for two reasons: (i) for power generation purposes, and (ii) the processing thereof towards chemicals of higher monetary value. Both these processes can benefit from micro-engineered reactor technologies (e.g. microchannels or monoliths), which in essence supports the concept of *process intensification* [5]. In the case of steam reforming, a portion of the fuel that is being reformed, is combusted to provide heat for the endothermic heat requirements [6], while cooling is applicable for reforming through partial oxidation and synthesis reactions. These reactions are thermally coupled in spatially segregated microchannels to provide intimate heat transfer, resulting in a plate heat-exchanger like design. These reactors support increased catalytic productivity compared to similar-sized conventional fixed-bed or fluidised-bed reactors. This is a result of catalyst surface-to-volume ratios in the order of 10–100 m²/m³ higher compared to their conventional counterparts [1,7–10]. They are also modular based and can be scaled to design capacities by simply externally “numbering-up” processors in parallel [11,12] or better internally numbering-up by increasing the length and number of channels [13]. The intimate heat transfer characteristics are a result of reactions taking place on, or near, highly conductive (in most cases metallic) reactor walls (e.g. wall-separated microchannels with deposited catalysts) [14–16]. Heat recovery from exothermic

reactions, or heat supply to endothermic reactions can therefore be very efficient, yet heat loss minimisation also becomes imperative as a result of the intensified thermal properties [17].

Microchannel fuel processors were subject to investigation from the mid-1990s by companies and institutions including American-based Batelle, PNNL, DuPont, MIT and Georgia Tech, German-based Fraunhofer IMM and KIT, and UK-based University of Newcastle [17,18] to name just a few. This has led to the development of industrial-scale FT synthesis reactors (Velocys, Inc.), modular synthetic methane and FT reactor units (INERATEC GmbH) and multi-kilowatt fuel-to-H₂ reformers (Fraunhofer IMM). Arguably, the greatest industrial expedient of microchannel technology to date is the American-based company Velocys, Inc., which developed a microchannel reactor to produce synthetic fuels from biomass-derived syngas. Microchannel reactor technology sits at the core of their modular-based FT synthesis reactors, with nominal capacity of 36 bpd for each microchannel stack (0.6 × 0.6 × 0.6 m) [19]. The plant, situated in Oklahoma City, and operated by ENVIA Energy, has since been under financial restructuring.

The application of microchannel reactors are ideal for fast chemical reactions, and supports the inhibition of mass transfer limitations, making kinetic measurements at isothermal conditions possible [20]. Applicable reactions extend – but are not limited to – hetero/homogeneous combustion, chemicals synthesis, fuel reforming, methanation, shift reactions and purification systems. The multi-functionality of microchannel reactors not only extends towards acting as chemical reactor/heat exchangers; they are essentially micro-mixers [11], and they can incorporate multiple reaction steps in one device [21]. For instance, the establishment of a specific temperature profile within the reactor can enhance the performance of equilibrium limited processes (e.g. methanation and water-gas shift processes) [21,22].

Regarding safety in microchannel reactors, the structured flow paths ensure in many cases that flame combustion is suppressed as a result of narrow channel dimensions (<1000 µm) and high gas velocities through them [1]. This becomes important in highly reactive processes such as ethylene oxide synthesis [23,24].

A fundamental advantage of using microchannel reactors for fuel processing is their load following capabilities. The reforming of fuels for hydrogen production (and ultimately power generation) is subject to the power demand. Similarly, in the light of converting renewable energy towards fuels for energy storage applications, the natural intermittency of the renewable

source determines the reactor throughput. To an extent, storage buffers (e.g. hydrogen storage) can be used to alleviate the degree of load changes on the reactor. The sub-second contact times within micro-engineered reactors allow them to adjust quickly to these process demands. On the contrary, conventional reactors are more suited for continuous and steady-state processing, due to their large sizes and limits with respect to ramp rate (dynamics).

Conventional fixed-bed reactors often suffer from thermal resistances, detrimental to achieving high thermal efficiencies [25,26]. For instance, the methane steam reforming reaction takes place at roughly 900°C, yet sufficient heat has to be conveyed to the reaction zone using a thermally coupled combustion reaction [15]. To transfer heat to the reforming reaction, a temperature gradient is required across the gas-tube-gas boundary [14]. The larger the thermal resistance associated with this boundary, the steeper the temperature gradient necessary, and the less efficient the process becomes. Generally, the flame heating of industrial reformers also leads to the production of nitrogen oxides, as a result of high flame temperatures [9,14].

In addition to structural stability at high temperature, cost considerations and manufacturability, the selection of a suitable reactor wall material depends on its thermal conductivity, as it acts as the heat transfer medium between reaction chambers. Common materials used for reactor substrates include low conductivity materials (~1–3 W/m/K), e.g. silica and cordierite, medium conductivity materials (~15–50 W/m/K), e.g. alumina and stainless steels, and high conductivity materials (~80–400 W/m/K), e.g. aluminium, copper and silicon carbide [17,27–29]. Typically, for a certain reactor design, there exists an optimum wall conductivity that allows sufficient heat recirculation to ensure thermal stability, yet convey enough heat to the heat sink (endothermic reaction or cooling fluid) to contribute to thermal efficiency within the device and minimise hot spots attained in the microchannels [30]. Generally, high conductivity materials contribute to lower reactor temperatures, while low conductivity materials delay heat transfer and results in excessive reactor temperatures. The optimum wall material varies for different fuels, flow rates and channel dimensions. It is therefore sufficient to say that a certain wall material will not necessarily be compatible for different reaction systems [30], however there exist operating windows that allow satisfactory performance for different wall materials, flow rates and geometric properties. In this review paper, important design considerations – with respect to these operating windows of microchannel reactor technology – are critically discussed. The scope of this work is narrowed

to multifunctional reactor/heat-exchanger devices, which couple endothermic/exothermic reactions and exothermic/cooling processes.

In recent years, the fuel processing in intensified reactor technologies has attained ample consideration. For instance, an early review by Holladay et al. [31] described fabrication techniques and small-scale experimental microreactors associated with hydrogen production via reforming for portable fuel cell applications. Kiwi-Minsker and Renken [32] described experimental microreactors with different designs for homogeneous and multiphase reactions. Önsan and Avci [33] have reviewed reactor and catalyst design strategies for processes such as hydrocarbon steam reforming, partial oxidation and CO removal units. Among others, reactor designs employing fixed-beds, monoliths, microchannels and integrated reactors (e.g. membranes) were critically discussed. Rebrov et al. [34] provided a detailed review of the design strategies for equal flow distribution in microchannel systems. In addition, heat transfer effects with respect to fluid-phase convection and microchannel wall conductivity were conferred. Kolb [35] provided a comprehensive overview of experimental microreactors demonstrated to date. The review details microreactors of the smallest (sub-watt) scale to the design, control and demonstration of integrated reactors for the processing of fuels towards H₂ production, and the synthesis of renewable carbon-based energy carriers. Delparish and Avci [36] provided an overview of microchannel, monolith and foam reactors for the reforming of renewable/bio-based fuels, and the synthesis of FT products; describing both experimental and modelling efforts.

On the contrary, this review specifically focusses on the design aspects of microchannel flow configurations (counter-, co- and cross-flow designs), material selection and the effect of wall thermal conductivity on heat transfer, catalyst positioning within microchannels, and the distribution of feed gas to improve flow uniformity and thermal dispersion in these microchannel systems. Throughout this review, the benefits of these aspects, and in some cases the limitations, are conferred.

2.2 THERMAL EFFECTS IN DIFFERENT FLOW CONFIGURATIONS OF SELF-SUSTAINED MICROCHANNEL REACTORS

In this section, a selection of papers are discussed to outline the heat transfer between exothermic and endothermic reactions in spatially segregated microchannels, according to three flow configurations (counter-, co- and cross-flow). These works are a combination of

experimental evaluations as well as computational fluid dynamic (CFD) modelling, due to its ability to characterise and quantify heat and mass transfer in the dynamic space of coupled microchannel systems.

2.2.1 Counter- and co-current flow configuration

Venkataraman and co-workers [14] developed an experimental concentric-type quartz reactor for ethane steam reforming. The reforming reaction was carried out homogeneously in an inner quartz tube, with a 4 mm diameter. The outer and inner tubes formed an annulus of 1 mm, with a 5 wt.% Pt/Al₂O₃ catalyst washcoat applied to the outer surface of the inner tube (thickness of 10 µm). Methane/air combustion (in a ratio of 1:10) over this catalyst served as heat source.

The effect of a variation in the methane flow rate on the reformat temperature is shown in Figure 2.1. Ethane, steam and nitrogen feed flow rates of 0.3, 0.3 and 0.15 SL/min were applied. In the case of a counter-current flow configuration (Figure 2.1a), a substantial temperature peak developed at the start of the combustion catalyst (~4 cm). With the increase in methane flow rate from 0.1 SL/min to 0.3 SL/min, the maximum temperature increased from ~800°C to ~1100°C. In addition, the temperature peak shifted slightly downstream to the ~6 cm position. An ethane conversion of 82% and selectivity towards ethylene of 77% was obtained for the 0.3 SL/min methane case.

For the co-current flow configuration, the heat generated by the combustion reaction caused a rapid temperature rise at the reactor inlet (Figure 2.1b). For the methane fuel condition of 0.3 SL/min, a maximum temperature of ~810°C was reached, while the ethane conversion was low (47%) due to slow kinetics (yet a high selectivity towards ethylene, 96%). The maximum temperature recorded was substantially lower than for the counter-current flow configuration. Moreover, the downstream temperature decline was not as significant as that observed for the counter-current case. This was mainly due to the difference in directional flow of sensible heat between the two reactions. However, missing heat-exchangers for pre-heating the reactor feed (with product gas) impair the results of this work.

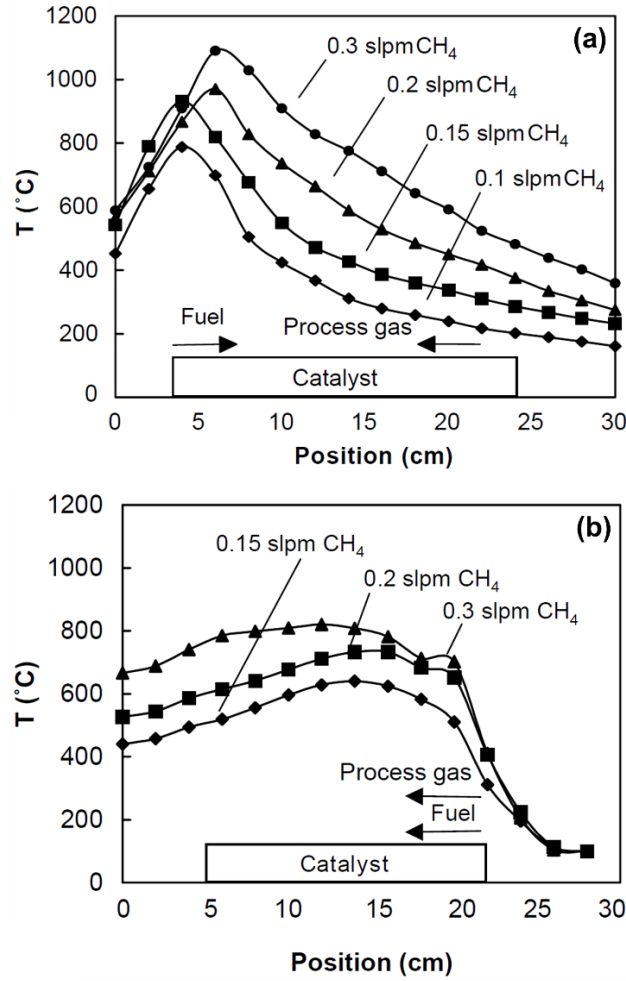


Figure 2.1: Temperature profiles of variable methane fuel flow rates to the combustion annulus of a concentric-type quartz reactor for (a) counter-current and (b) co-current flow arrangements. The reforming feed correspond to ethane, steam and nitrogen flow rates of 0.3, 0.3 and 0.15 SL/min, respectively. Renumbered from [14] with permission from Elsevier.

Consider the CFD modelling work by Deshmukh and Vlachos [27] using homogeneous propane/air combustion as heat source to the catalytic ammonia decomposition reaction. The half-height of microchannels was modelled for model simplification (total height of 600 μm for the combustion reaction and 300 μm for the reforming reaction), with a conductive wall separating the channels (300 μm). A reactor length of 1 cm was used. Two cases for the thermal conductivity of the separating wall (7.5 and 200 W/m/K), and a variable linear inlet velocity of ammonia were used to determine the thermal effects on parameters including the wall and gas centreline temperatures, species conversion, hydrogen power produced and exit gas temperatures, for both flow configurations. In Figure 2.2, the two flow configurations are compared for linear inlet velocities for ammonia of 0.3 m/s, and for propane/air of 0.5 m/s.

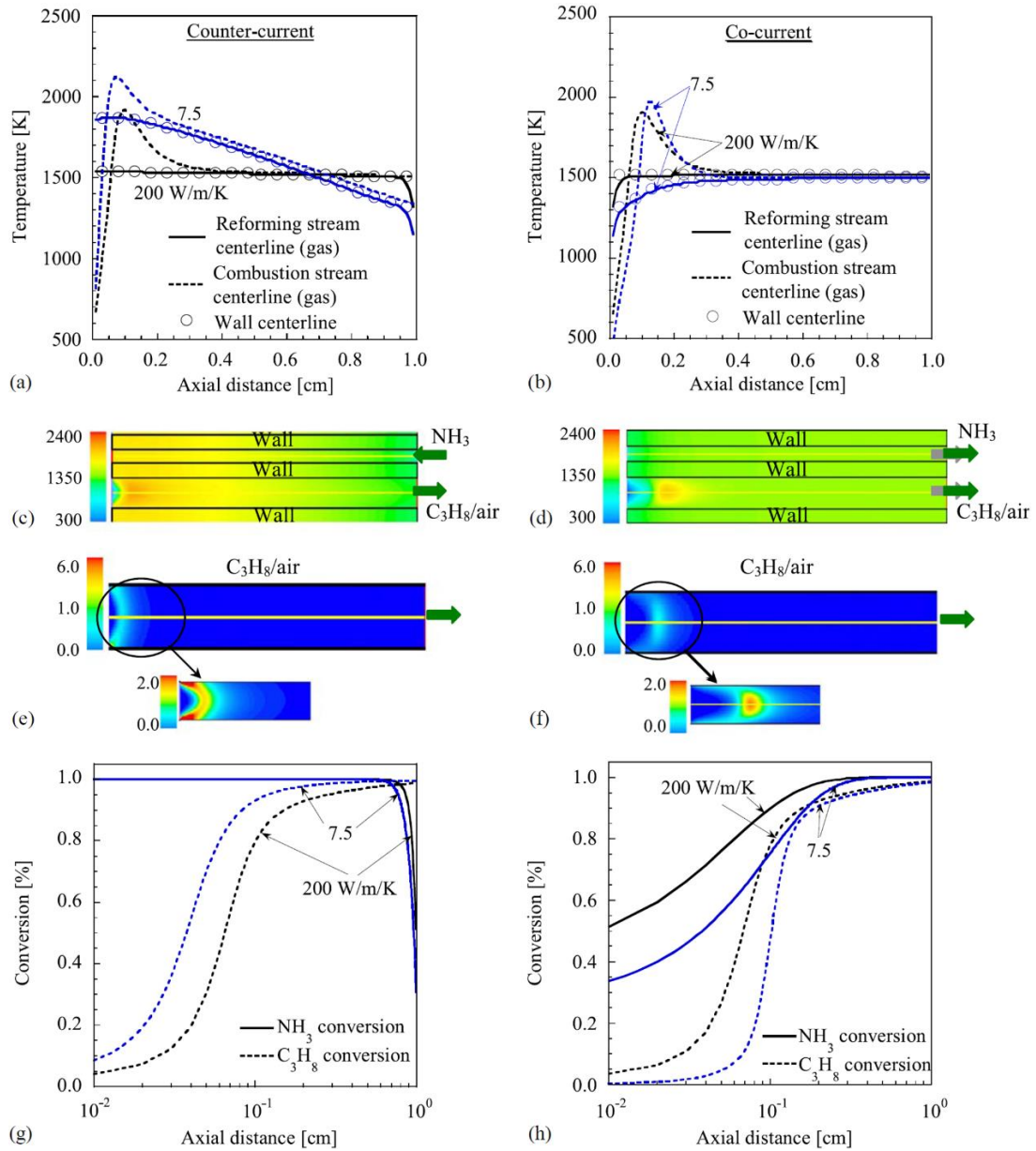


Figure 2.2: Reforming, combustion and conductive wall centreline temperatures (K) for (a) counter-current and (b) co-current flow configurations. Results are plotted for wall thermal conductivities of 7.5 and 200 W/m/K. Two-dimensional plots for temperature (c and d) and propane combustion rate (e and f), illustrated for counter-current and co-current configurations, respectively. A wall thermal conductivity of 7.5 W/m/K is used, and the combustion rate expressed in a unit of kmol/m³/s. Ammonia and propane conversion for (g) counter-current and (h) co-current flow configurations for the 7.5 and 200 W/m/K wall thermal conductivities. All the results are plotted against the axial distance from the propane/air inlet, and for a linear velocity of ammonia (0.3 m/s) and propane/air (0.5 m/s) at the respective channel entrances. Reprinted from [27] with permission from Elsevier.

Firstly, it was observed that the wall centreline temperature for the two flow conditions was near identical and isothermal (~ 1500 K) for the high wall thermal conductivity (200 W/m/K) condition (Figure 2.2(a,b)). Rapid heat distribution was achieved from the combustion zone along the axial direction of the wall, and independent of the flow configuration. In all the cases presented, the wall acted as a heat source for the incoming cold ammonia flow, and heated the reforming stream within 0.05 cm from the channel inlets to the temperature of the wall. Further along the channels, the reforming stream temperatures remained interconnected and close to the local wall temperature.

Conversely, when a wall thermal conductivity of 7.5 W/m/K was used for the counter-current flow configuration, the spatially segregated heat generation near the combustion inlet, and heat sink near the reforming inlet caused a significant wall temperature gradient (Figure 2.2a). Extreme temperatures for the wall (~ 1900 K) and combustion stream (~ 2100 K) approximately 0.1 cm from the combustion inlet was deemed inappropriately high for the stability of the catalyst and the wall. This observation was also conferred in previous work by these authors, discussing the counter-current flow arrangement in detail [37]. At the reforming inlet, the ammonia stream was heated rapidly to the temperature of the wall (~ 1300 K), and followed the increasing wall temperature towards the hotter combustion inlet (~ 1900 K). For the short microchannel length investigated (1 cm), a substantial temperature gradient of approximately 600 K was obtained, which is of course rather a theoretical value disregarding heat losses and radiation effects.

For the co-current flow arrangement and the low thermal conductivity (7.5 W/m/K), the cold ammonia stream inlet kept the wall temperature low initially, before the wall temperature asymptotically neared 1500 K approximately 0.3 cm from the inlet. Subsequently, it was concluded that slow axial heat distribution in the wall was achieved from the region where the combustion flame stabilised towards the inlet of the reactor. From the 0.3 cm point and onwards, the heat transfer across the wall dominates slower reaction rates in both channels, and evident in the stabilisation of both gas and wall temperatures at 1500 K. As concluded by the authors [27], the flame in the combustion channel stabilised farther down the channel (Figure 2.2d), and evident in the rate of propane consumption (unit of $\text{kmol/m}^3/\text{s}$) in Figure 2.2f. Importantly, this was a result of the overlapping of reaction regimes, and the heat sink posed by the reforming reaction.

For the counter-current flow arrangement, the flame could stabilise much closer to the inlet of the combustion channel (Figure 2.2c); this is also evident in the consumption rate of propane/air (Figure 2.2e). Notably, this is for the 7.5 W/m/K wall thermal conductivity condition. As stated by the authors [27], there was little effects on the region where propane combustion occur for the 200 W/m/K wall thermal conductivity, comparing the two flow configurations (Figure 2.2(g,h)).

This paper can serve as first indication, that obviously a co-current flow arrangement has significant advantages when coupling exothermic and endothermic reactions concerning the temperature distribution within the reactor.

Zanfiri and Gavrilidis [38] evaluated the counter- and co-current flow arrangement for methane steam reforming and methane/air combustion. Both reactions were considered via catalytic conversion. The channels were modelled with a length of 30 cm and a half height of 1 mm, wall thickness of 500 μm , catalyst layer thicknesses of 20 μm and wall thermal conductivity of 25 W/m/K. Importantly, it was assumed that both reaction mixtures enter the microchannels at a temperature of 793 K. Realistically, the inflow of gas would be pre-heated by (1) either the opposite exhaust gas (counter-current) or (2) regressive heat flux from the microchannel reactor (co-current), both assumptions lacking in the paper of Venkataraman et al. [14] as mentioned above.

For the reforming and combustion streams, inlet velocities of 4 m/s and 3.2 m/s were chosen, respectively, and temperature profiles were plotted (not shown in this review). The wall centreline temperature in the case of the co-current flow configuration is 769 K at the inlet, and 914 K at the outlet. For the majority of the reactor length (4.5 cm from the inlet–outlet), both reforming and combustion centreline temperatures were slightly lower than the wall temperature, due to the fact that the combustion reaction generated heat on the surface of the wall, as opposed to flame combustion in the bulk gas phase [27]. As a result, the combustion gas temperature spike caused by the flame in Ref. [27] was not observed for the catalytic combustion in Ref. [38].

The heat flux generated and consumed by the respective combustion and reforming reactions are plotted for the co-current configuration in Figure 2.3a, while the respective methane conversions are shown in Figure 2.3b, as a function of the dimensionless axial coordinate (ζ) from the reforming inlet. The moderate heat generated/consumed in the co-current

configuration is characteristic of the overlapping of reaction zones (12 and 7 kW/m², respectively for combustion and reforming at the outlet). In this instance, the entire length of microchannels were utilised for methane conversion by both reactions (Figure 2.3b). The initial decrease in heat consumed by the reforming reaction was due to the gas inlet with a higher temperature (793 K) than the minimum obtained (771 K) at axial coordinate $\zeta = 0.15$.

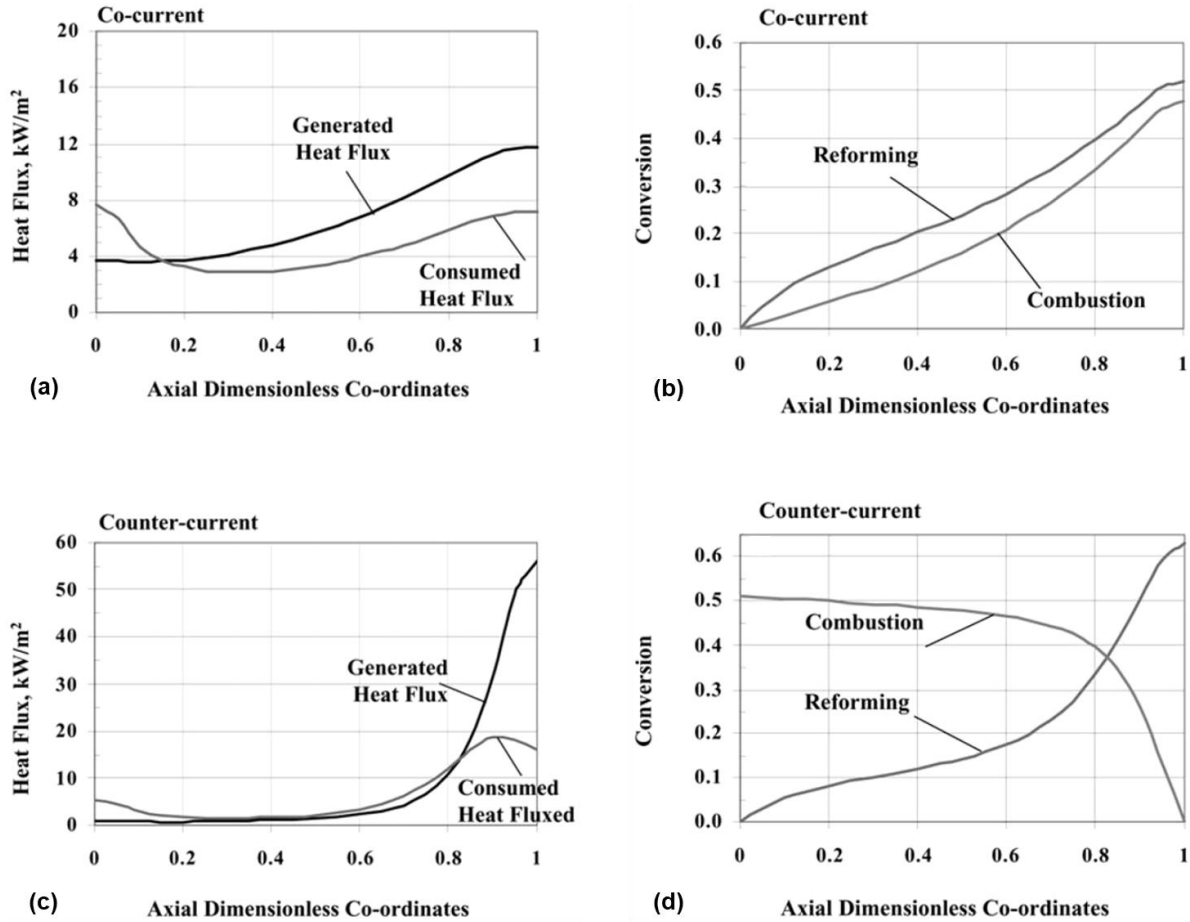


Figure 2.3: (a) Heat flux generated/consumed and (b) methane conversions for the combustion and reforming reactions in the co-current flow configuration, plotted against the axial coordinate from the reforming channel inlet. Comparable heat flux (c) and methane conversions (d) for the reactions in the counter-current flow configuration. Renumbered from [38] with permission from Elsevier.

In the case of the counter-current flow configuration, more pronounced temperature differences in the gas and wall centreline temperatures were observed. Close to the combustion channel inlet ($\zeta = 0.85$), the gas centreline temperature peaked at 1021 K, after entering the microchannel at 793 K. The wall temperature reached a maximum value (1103 K) at the inlet

of the combustion channel, due to axial heat conduction and the effect of reaction heat generated on the surface of the wall. The centreline temperature of the reforming gas stream also reached a maximum (~ 1060 K) at the combustion inlet.

The local maximum heat flux generated by the combustion reaction in counter-flow mode (Figure 2.3c) was close to 5 times higher (55 kW/m^2) compared to the maximum for the co-current configuration in Figure 2.3a (12 kW/m^2). Notably, for the counter-current configuration this heat was generated near the combustion channel inlet, while for the co-current configuration, the maximum was achieved at the combustion outlet. For the counter-flow scenario, the low heat flux, due to low gas and wall temperatures near the inlet of the reforming channel ($\zeta = 0-0.6$), led to the majority of methane being reformed, also in the region of rapid methane combustion ($\zeta = 0.6-1$ in Figure 2.3d). Nevertheless, the final methane reforming conversion was found to be higher for counter-flow (62.8%) compared to co-current flow (52%), but this depends on reactor design and flow rates chosen. In a practical system, full conversion needs to be achieved in both cases.

In follow-up work, Zanzir et al. [39] doubled the pre-exponential constant of the first order kinetic rate for catalytic methane combustion (from 2×10^8 to $4 \times 10^8 \text{ s}^{-1}$). The activation energy of 90 kJ mol^{-1} was unchanged for methane combustion, and again the LHHW kinetics derived by Xu and Froment [40] was used for methane steam reforming. All other geometric and boundary parameters were the same as described in Ref. [38].

Firstly, for the co-current flow configuration, the wall temperature increased to a maximum of 1058 K in the latter half of the reactor (Figure 2.4a). This maximum is mainly due to the near complete methane combustion (98%) as a result of the faster kinetics, compared to the original work in Ref. [38]. The maximum heat flux generated/consumed increases in magnitude (26 and 15 kW/m^2 , respectively for combustion and reforming) and is located at the $\zeta = 0.35$ coordinate. As the corresponding combustion and reforming maximums were achieved at the same axial location, it leads to believe that the thermal coupling between the reactions is efficient and negligible heat transfer delays exist through the conductive wall [39]. Although these maximums were achieved at a given axial location, practically the entire length of microchannels were utilised for both reaction conversions (Figure 2.4a). The reforming conversion at the reactor outlet was 95%.

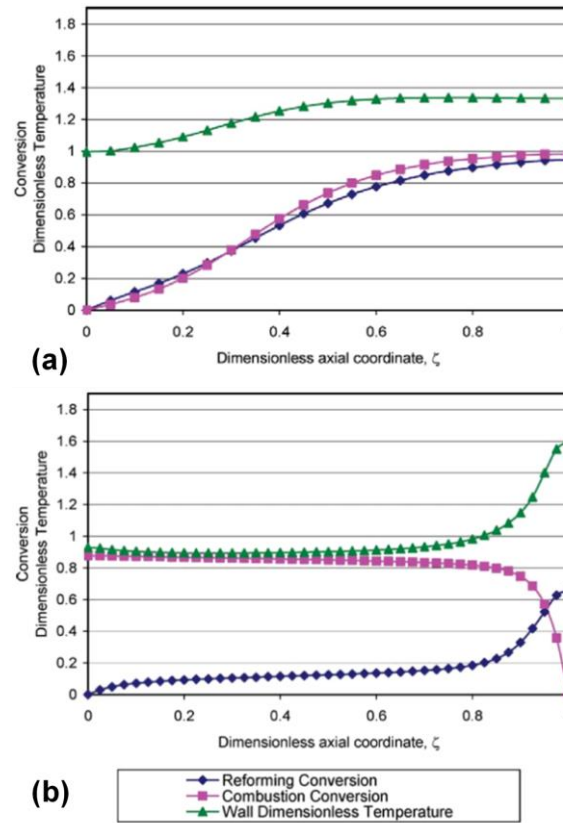


Figure 2.4: A plot of dimensionless wall temperature (793 K reference), methane reforming and combustion conversions against the axial dimensionless coordinate (ζ) from the reforming inlet, for (a) co-current and (b) counter-current flow configurations. Renumbered from [39] with permission from John Wiley & Sons, Inc.

In the counter-current flow configuration (Figure 2.4b), a spatially limited reaction zone occurred, as methane combustion was apparent exclusively near the combustion inlet ($\zeta = 0.9$ – 1). A significant wall temperature spike (1270 K) accompanied this local heat generation. Subsequently, the downstream combustion channel ($\zeta = 0$ – 0.8) does not support sufficient heat for the reforming reaction to occur, and the methane is not combusted fully at the channel exit ($\sim 87\%$). A two-fold increase in the combustion rate therefore does not necessarily favour higher reforming conversions (62% [39] vs 62.8% [38]), as the excessive heat generated is not effectively transferred to the reforming channel in the short region near the combustion inlet [39]. A maximum heat generation of $\sim 72 \text{ kW/m}^2$ accompanied the temperature spike. The combination of sustained heat release and the region where it occurs therefore seems crucial.

Increased thermal efficiencies will be achieved if reactor systems are scaled-up. In essence as the reactor volume to outer surface ratio increases, the extent of heat generated versus heat lost

through the outer surface intensifies significantly. The required rate of combustion fuel per unit reactor volume (to supply the same reforming performance) is reduced and leads to a greater efficiency [41].

Summarizing the results of the work of Zanzir et al. [38,39], the strong dependency of the applicability of simulation results from the quality of the kinetic expressions chosen gets obvious. The doubling of the rate constant can easily occur when comparing different catalysts and they change the result completely. However, the advantages of the co-current flow arrangement are even more pronounced compared to the former case [38].

Arzamendi et al. [42] investigated the steam reforming of methanol, with methanol combustion as heat source, which takes place at much lower reaction rates owing to the several hundred K lower reaction temperature. Both reactions were modelled as catalytic with CFD. A comparison of counter-current, co-current and cross flow arrangements was performed in a plate reactor with 10 channels each for reforming and combustion. Square microchannels with 700 μm sides and 20 mm in length were used as base case. The methanol/steam mixture was fed in an equimolar ratio to the reactor, while the combustible mixture consisted of 2 vol.% methanol in air.

For reforming and combustion space velocities of 28 224 1/h and 75 263 1/h, respectively, reactor configurations had block temperature differences of 4°C (co-current), 19°C (counter-current) and 7°C (cross-flow), as illustrated in Figure 2.5. In a simplified co-current model with 2 channels each for reforming and combustion, Arzamendi et al. [42] noted that if complete conversion is achieved well before the microchannels exit, the relatively high temperatures associated with this region initiates the reverse water-gas shift reaction, producing undesired CO and reduces the yield of H_2 . It is therefore essential to choose flow rates carefully, firstly to achieve the desired temperature with the combustion reaction, but also to utilise the entire length of the microchannels to achieve full conversion of the reforming reaction [42]. This, however, depends largely on the catalyst technology applied. While conventional catalyst technology such as Cu/ZnO shows high activity for reverse water-gas shift as soon as the methanol is consumed completely, this is not the case for novel, highly active formulations such as Pd/ In_2O_3 / Al_2O_3 or Pt/ In_2O_3 / Al_2O_3 [43–48]. As a conclusion, the much lower reaction rates of methanol steam reforming lead to much lower temperature gradients in the reactor, while heat conductivity effects of the walls obviously get much more dominant.

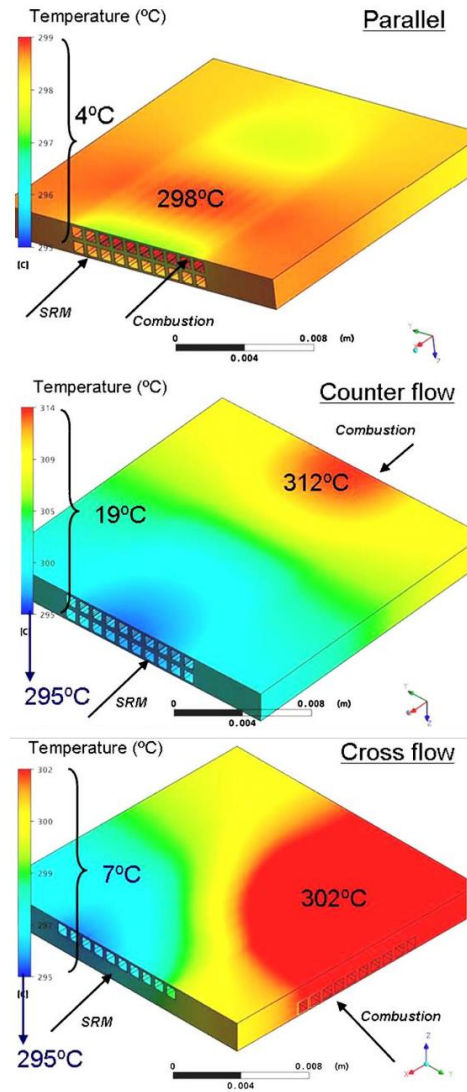


Figure 2.5: Co-current (top), counter-current (middle) and cross-flow (bottom) designs investigated for the thermally coupled methanol steam reforming and methanol/air combustion reactions at respective space velocities of 28 224 1/h and 75 263 1/h. Reprinted from [42] with permission from Elsevier.

Blakeley and Sullivan [49] experimentally evaluated and modelled a ceramic microchannel reactor for the processing of methane. Steam reforming ($S/C = 2.5$), autothermal reforming ($S/C = 2.5$, $O/C = 1.0$) and catalytic partial oxidation ($O/C = 1.0$) were considered, and the reactor performance compared. A counter-current flow strategy was implemented, with pre-heated nitrogen sustaining the high temperatures within the reactor. Two plates with reactive microchannels and three plates with heating microchannels (10 channels each of $W = 3.14$ mm, $H = 740$ μm and $L = \sim 72$ mm) were sandwiched in an alternating fashion, with alumina wall thickness of 740 μm .

The experimental reactor achieved up to 90% CH₄ conversion during autothermal reforming at high throughput (75 000 1/h). Typically, the H₂ and CO selectivities varied considerably as they are strongly dependent on the S/C and O/C ratios. The CFD model developed to describe the reactor was very accurate in predicting experimental performance across the spectrum of parameters varied.

From the model, it is evident that in the exothermic case of catalytic partial oxidation, heat was generated at the microchannel inlet region (Figure 2.6a) and resulted in a high microchannel wall temperature ($\sim 640^\circ\text{C}$) at the inlet (Figure 2.6c). A significantly lower temperature of $\sim 550^\circ\text{C}$ was obtained for the steam reforming case at the microchannel inlet. However, the pre-heated nitrogen, which supplied heat for the reforming, also caused an increasing temperature gradient towards the reforming channel outlet. The authors noted that the heat producing reactions might be more economically feasible due to reduced energy requirements compared to methane steam reforming, although they produce lower hydrogen yields within the syngas. These observations however are reactor and scale specific, and require further economic assessment.

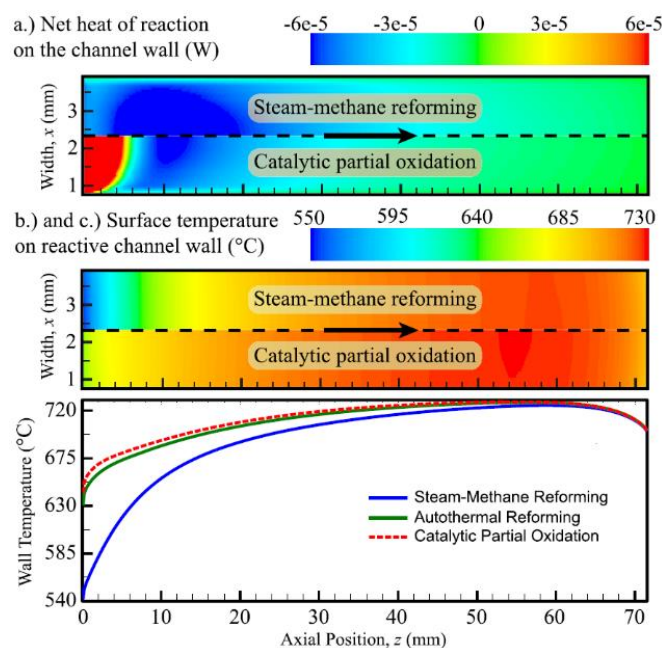


Figure 2.6: 2D CFD modelling plots for (a) heat consumption/generation and (b) surface temperature at the channel wall for steam methane reforming and catalytic partial oxidation, plotted against the axial microchannel length. (c) Wall centreline temperature plotted against the axial length for all three reactions investigated. Reprinted from [49] with permission from Elsevier.

Ozturk and Avci [50] evaluated dimethyl ether (DME) synthesis in a counter-current microchannel reactor using air as coolant medium. The half-height of an adjacent synthesis and cooling microchannel was modelled, with dimensions of: $W = 600\ \mu\text{m}$, $H = 300\ \mu\text{m}$ and $L = 7.5\ \text{cm}$. The synthesis microchannel was coated with a $\text{Cu-ZnO/Al}_2\text{O}_3 + \gamma\text{-Al}_2\text{O}_3$ catalyst with a washcoat thickness of $50\ \mu\text{m}$. A stainless steel wall with thickness of $100\ \mu\text{m}$ and thermal conductivity of $15\ \text{W/m/K}$ separated the reaction and cooling microchannel. The model accounted for the kinetic rates of the equilibrium hydrogenation of CO (MS1 in Figure 2.7c) and CO_2 (MS2 in Figure 2.7c) to form methanol, and for the dehydration of methanol to form DME. Reference conditions included: reaction pressure of 50 bar, H_2/CO ratio of 2.5, H_2/CO_2 ratio of 10, syngas inlet velocity of $0.01\ \text{m/s}$ and air inlet velocity of $10\ \text{m/s}$.

The effects of varying H_2/CO feed ratio (2.5–4.0) were investigated (H_2 feed assumed constant and CO balanced with N_2 for the different cases), and is presented for a number of reaction parameters in Figure 2.7. While the inlet temperature of the synthesis gas was assumed as 508 K, temperature increases were observed to 515–517 K near the inlet region of the microchannel (Figure 2.7a). In the three cases of varying H_2/CO ratios, the outlet temperature of the synthesis stream was subject to the inlet temperature (508 K) of the counter-current flow of air. The CO conversion (Figure 2.7b) was recorded as high as ~55% for the CO lean syngas feed ratio (H_2/CO of 4.0) at the microchannel outlet.

The CO hydrogenation rates (Figure 2.7c) presented for H_2/CO ratios of 2.5 and 4.0 asymptotically decrease towards equilibrium methanol formation (rates $\approx 0\ \text{kmol/m}^3/\text{s}$). On the other hand, the rates of CO_2 hydrogenation for the two cases presented shows the influence of the equilibrium WGS reaction, as local minima were obtained at axial position $\sim 1.0\ \text{cm}$. Due to the low CO_2 content in the syngas feed (and subsequently its sensitivity to equilibrium WGS), these effects are only clearly apparent in the CO_2 hydrogenation rate. Steam, which is a by-product of CO_2 hydrogenation, thus showed local maximum yields at the same axial position (up to 5.3% for the H_2/CO ratio of 4.0, Figure 2.7d), while being consumed downstream via WGS. The occurrence of the decreasing temperature profile across the length of the reactor, albeit a few degrees K, affects the interplay between the hydrogenation and WGS reactions (equilibrium phenomenon). The methanol yield was recorded at the microchannel outlet as high as ~60% for the syngas ratios of 3.5 and 4.0 (Figure 2.7e). On the other hand, a syngas ratio of 2.5 appears to have improved methanol dehydration towards DME by ~10% compared to the H_2/CO ratio of 4.0 (Figure 2.7f). This is largely due to the suppressed steam

formation via CO₂ hydrogenation, which allowed the dehydration reaction to proceed better at the H₂/CO ratio of 2.5.

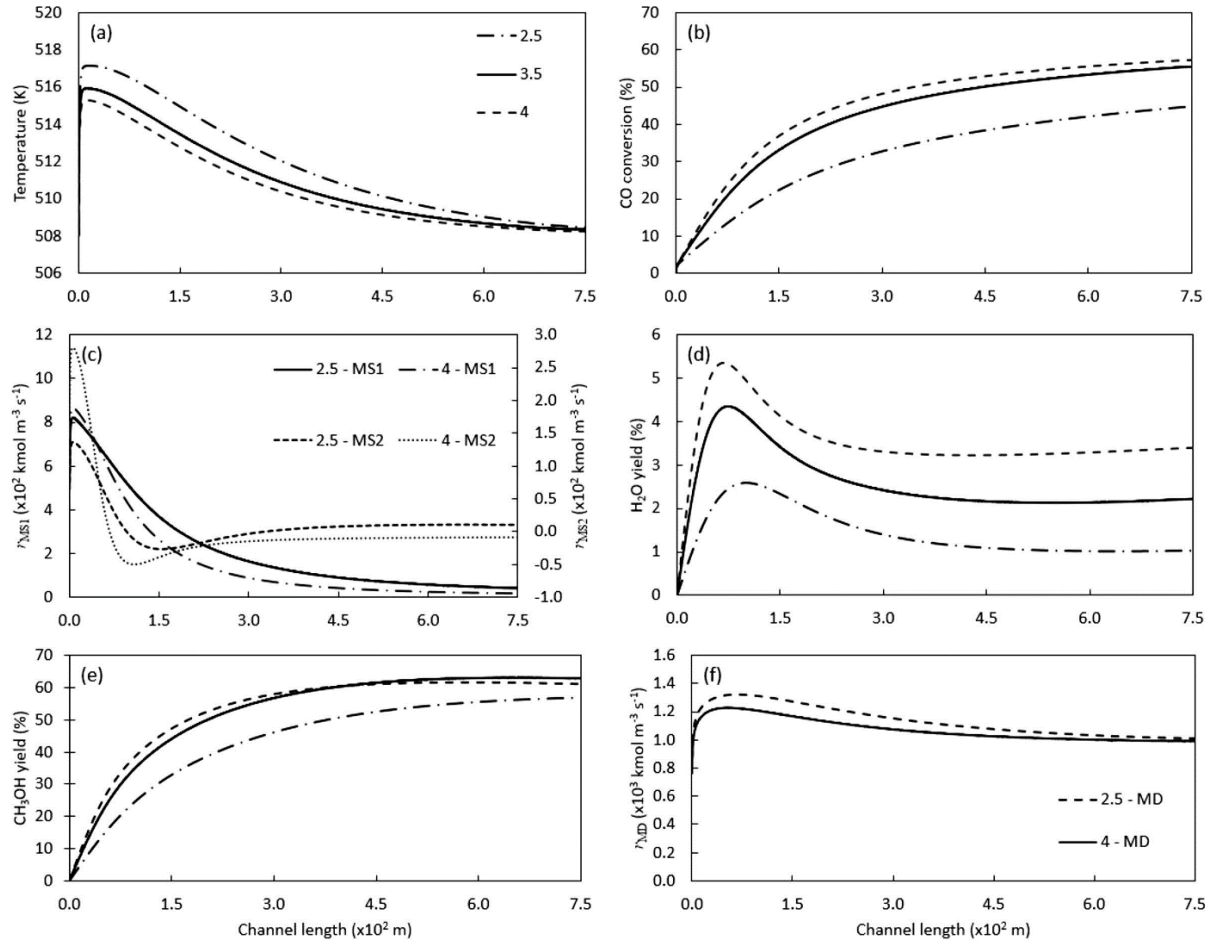


Figure 2.7: The influence of H₂/CO feed ratio (2.5, 3.5, 4.0) during DME synthesis in a wall coated microchannel reactor/heat exchanger on the (a) synthesis gas temperature, (b) CO conversion, (c) CO and CO₂ hydrogenation rates expressed as MD1 and MD2, respectively, (d) H₂O yield, (e) methanol yield, and (f) methanol dehydration rate to form DME. The legend expressed in (a) applies to (b), (d) and (e). Reprinted from [50] with permission from Elsevier.

The exothermic CO₂ methanation process, which could benefit from equilibrium favouring temperature profiles, was investigated in both co- and counter-current flow configurations by Engelbrecht et al. [51]. An experimental microchannel reactor, which was designed as a stack of catalytic plates, contained 1800 microchannels in total for both methanation and coolant flows; each microchannel with dimensions of: W = 500 μm, H = 250 μm and L = 10 cm. The reactor was fabricated from stainless steel (SS316Ti). A 5 wt.% Ru/Al₂O₃ catalyst was washcoated on the inner walls of the methanation microchannels with a coating thickness of

45 μm . Hydrogen, a common heat transfer fluid, was used as coolant medium to the methanation process in order to achieve steady-state temperatures in the range of 400–450°C. Methanation flow rates of 4–7 NL/min (at a stoichiometric 4:1, $\text{H}_2\text{:CO}_2$ ratio) and coolant flows of 0.8–5.6 NL/min were used to characterise the thermal behaviour and methanation performance of both flow configurations at a reaction pressure up to 10 bar_g.

The obtained steady-state temperature profiles for methanation are illustrated in Figure 2.8, with the convention of the methanation flow inlet at axial location 1 for both flow configurations. For the low methanation flows (4 NL/min), the thermal effects between co- and counter-current flow configurations were not clearly apparent, due to the low flow rates applied for the coolant medium (1.2 NL/min for co-current, and 1.4 NL/min for counter-current flow). Both flow configurations showed temperature maximums of 414–414.8°C in the middle of the reactor. CO_2 conversions of ~91% were achieved.

When the microchannel reactor was operated at full-load (7 NL/min methanation flow), significant differences in the temperature profiles were observed, comparing the two flow scenarios (Figure 2.8). In the co-current case, a coolant flow rate of 3.2 NL/min was feasible, and a general trend of heat flux towards the exit of the reactor (axial location 10) was observed (induced by both streams flowing towards the reactor exit). The reactor inlet and outlet temperatures were measured as 409.2°C and 431.8°C, respectively. When the counter-current flow configuration was applied, the coolant stream, at a flow rate of 5.2 NL/min, now entered the reactor at axial location 10. The effect of the coolant entering axial location 10 is clearly apparent, as the temperature was measured as 415.2°C in this region. A much higher methanation inlet temperature (435.5°C) indicates that heat was transported by the coolant stream from the hottest section in the reactor center towards the inlet region. It is envisioned that the main reaction zone is also located closer to the methanation inlet. For this condition, a CO_2 conversion of 90.5% was achieved, with a CH_4 content of 63.9 vol.%. Due to the lower outlet temperature, this performance was better than the co-current case, which yielded only 89.1% CO_2 conversion. Overall, counter-current flow supported better heat utilisation with higher flows of the coolant stream, and showed lower reactor outlet temperatures which improved methanation equilibrium. Nonetheless, it was observed that the methanation equilibrium still limits CH_4 product content in a single microchannel reactor. To improve methane quality, Neuberg et al. [52] coupled an adiabatic reactor to a downstream counter-current cooled reactor operated at lower temperatures, while Chwoła et al. [53] carried out

methanation in two isothermal reactors in series; the second reactor at a lower temperature to the first.

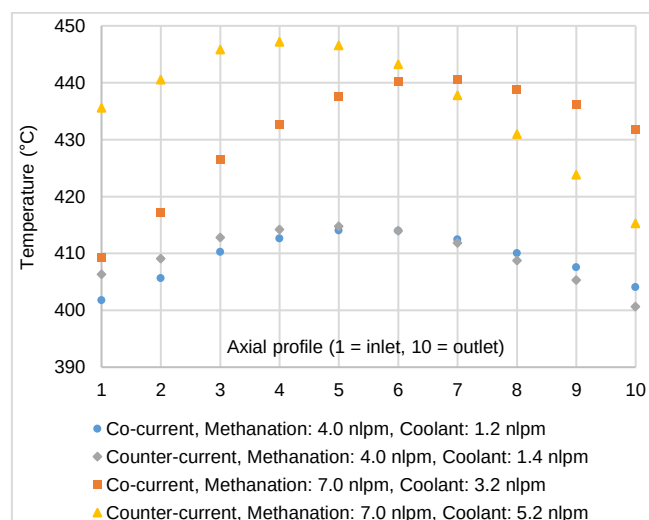


Figure 2.8: Steady-state axial temperature profiles in an experimental microchannel reactor/heat exchanger for CO₂ methanation in co- and counter-current flow configurations. The methanation flow inlet is located at axial position 1 for both flow configurations. Conditions correspond to part-load (4 NL/min) and full-load (7 NL/min) methanation scenarios at a reaction pressure of 10 barg. For each case, the coolant flow was adjusted to reach steady-state temperatures in the range of 400–450°C. Adapted from [51] with permission from Elsevier.

2.2.1.1 A summary of respective flow configuration advantages

a. Counter-current flow

Although excessive temperatures could be obtained in the counter-current flow configuration for low conductivity wall materials, the use of high conductivity materials possibly allows high conversions of exothermic reactions such as water-gas shift and methanation at increased reactor throughput in specific cases. For reforming combined with combustion, the spatial segregation between the respective combustion and reforming reaction zones provides reaction stability, but also bears danger of catalyst damage through heat excursions [54]. Therefore, the applicability of counter-flow operation may well be limited to homogeneous reactions and highly heat resistant construction materials.

However, of interest is the advantage that a declining temperature gradient along microchannels could pose for an exothermic reaction such as water-gas shift [55,56] or CO₂

methanation [51,52]. Typically, the majority of reactants are converted in the high temperature region, while the lower temperature near the reactor outlet acts as a conditioning stage to reach favourable conversions (improved equilibrium) [51,54,57,58]. A similar observation was made by Kolios et al. [59,60], in which the lower downstream temperature was utilised as a water-gas shift stage to condition methanol steam reforming products. This is possible, because highly active reforming catalysts also generate equilibrium for methanation and water-gas shift reactions.

b. Co-current flow

Co-current reformer reactor operation has shown to lower device temperatures at comparable wall thermal conductivity, combustion and reforming flow rates, due to the overlap of local reaction zones along the axial direction of microchannels [27]. Typically, the endothermic reforming reaction's inflow acts as a heat sink, thus pushing the maximum heat released by the exothermic reaction further from the inlet downstream of the microchannel, compared to counter-current flow and is therefore the preferable operating mode.

The overlap of endothermic and exothermic reaction zones ensures that it is possible to utilise the entire axial dimension of microchannels for the reaction to take place [39]. Heat generation and consumption is more moderate than for counter-flow operation, and the transverse heat balance depends mainly on the respective reaction zones. Heat transfer limitations are possible only when fixed catalyst beds are applied in the heat-exchanger reactor, while the heat transfer from one catalyst layer on a coated plate to the other side (also coated) is negligible.

The formation of hot spots and large temperature gradients is minimised, permitting minimal thermal stresses being imposed on reactor bodies [42].

Lower device temperatures allow for more stable catalyst operation and longevity, and opens up a larger variety of construction materials for microchannel reactors [17]. However, the operational flow rates should be carefully chosen, because insufficient temperatures in the main steam reforming reaction zone of the device will result in undesirable conversions of the endothermic reaction [14,26].

2.2.1.2 A summary of respective flow configuration limitations

a. Counter-current flow

For the combination of steam reforming and combustion in counter-current flow operation, reactors are susceptible to excessively high temperatures (hot spots), especially in cases where low conductivity wall materials or imbalanced flow rates (too high combustion or too low reforming flow rates) are used.

The high temperatures obtained in the counter-current design, when aiming for optimal productivity, could result in the combustible reactants being subject to homogeneous combustion (combined hetero/homogeneous combustion is not discussed further).

The high exit gas temperature of the reforming stream, however lead to a certain reduction in product selectivity, e.g. the CO content is higher during hydrocarbon reforming, which is not an advantage when hydrogen production is targeted for low temperature PEM fuel cell application. In the case of high temperature SOFCs, CO, which is the primary product of steam reforming, should not be an issue.

If too high wall thermal conductivities are applied, the effectivity of the heat-exchanger concept is lost as a result of axial heat recirculation [28,61,62].

Temperature gradients often encountered in counter-current reactors bear significant advantages for exothermic equilibrium reactions such as water-gas shift and methanation, as discussed above.

b. Co-current flow

The co-current configuration leads to lower reaction rates for the reforming reaction compared to counter-current flow, at comparable reaction rates of the combustion reaction. However, it might easily happen, that the endothermic zone experiences a “thermal collapse”, e.g. the reaction temperature drops too far to reach significant conversion.

Should too high reforming/cooling flow rates be implemented, a dynamic temperature wave will propagate down the length of the reactor, and ultimately lead to the thermal collapse. This can often be the case when thermodynamically limited exothermic reactions (e.g. methanation) are heat sources. The entire length of microchannels are used for the reaction, and a typical hot spot near the inlet is marginal. For combustion reactions (which happen fast), the hot spot can

only be controlled through the feed flow rate or composition (air surplus), cooling flow rate or designing the reactor with higher wall conductivity materials.

2.2.2 Cross-flow configuration

Pan and Wang [63] evaluated an experimental plate-fin reformer for the self-sustained steam reforming of methanol (Figure 2.9). Heat was provided through combustion of a mixture of hydrogen and a fraction of the reformat in a cross-flow arrangement, the reaction being catalysed by 1 mm Pt/Al₂O₃ pellets filled in the channels. The reforming channels contained 0.442–0.681 mm particles of Cu/ZnO/Al₂O₃. In addition, the methanol/water feed was vaporised in two outer chambers to the combustion channels (Figure 2.9). Fifteen thermocouples (numbered #1–15 in Figure 2.9) were used to measure temperatures at various depths of the methanol/steam vaporisation, reforming and combustion sections.

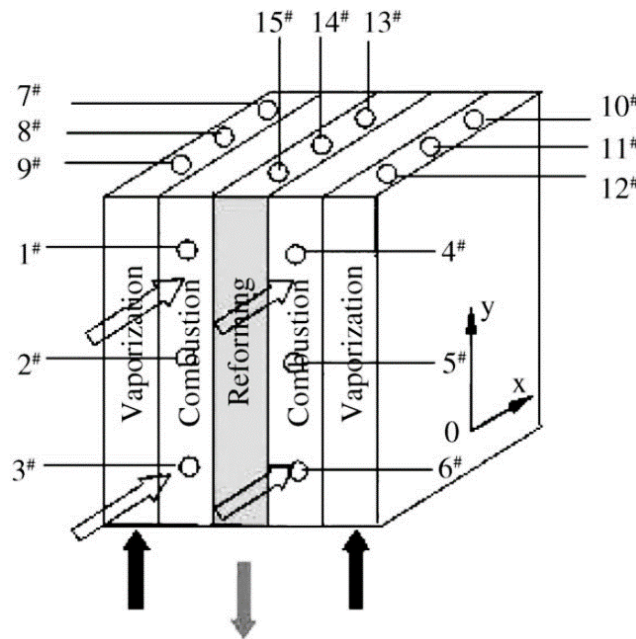


Figure 2.9: A plate-fin methanol steam reformer. A cross-flow arrangement of combustion channels supporting the thermal coupling of a model anode off-gas. Reprinted from [63] with permission from Elsevier.

The extreme temperature gradient for “Combustion 1” (Figure 2.10) was attributed to an uneven flow distribution [63]. However, a contributing factor is the location of this thermocouple. The measurement was taken near the reforming chamber inlet, and after the feed was vaporised (Figure 2.9). This region will naturally be hotter and not as good a heat sink as the inlet region of the vaporisation chamber (“Combustion 3”). The temperature distribution in

the reforming channels were more uniform (not shown), with a slightly decreasing temperature gradient from the inlet to the outlet. In later work, Pan and Wang [64] showed via modelling of the plate-fin reformer that the cross-flow arrangement indeed causes a diagonal temperature gradient across the reformer, contributing to undesired CO formation in the hotter channels of the reformer [35].

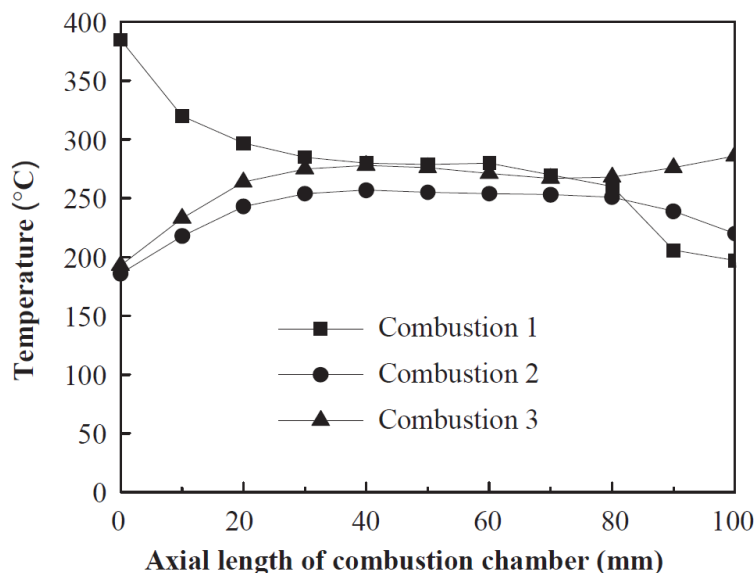


Figure 2.10: Combustion temperature profile in a cross-flow plate-fin reformer. “Combustion 1” and “Combustion 3” were measured near the reforming outlet and inlet, respectively. Reprinted from [63] with permission from Elsevier.

Arzamendi et al. [42], who modelled the methanol steam reforming and methanol/air combustion discussed earlier, also recognised that a temperature gradient established across the diagonal of a cross-flow plate reactor, however only with a 7°C difference (Figure 2.5). The major advantages of the cross-flow design, which are the simple construction and spatial segregation of the gas inlets and outlets, especially at the small-scale, contributed to this design being chosen for the lab-scale fabrication of the microchannel reactor.

Deshmukh et al. [65] reported the temperature distribution of a high-throughput (GHSV = 290 ms) pilot-scale cross-flow microchannel reactor for FT synthesis (Figure 2.11). This work formed part of Velocys, Inc.’s scale-up of microchannel reactor technology towards commercialization. A partial water/steam evaporative technique was used as cooling mechanism. Despite the significant heat release from the FT synthesis process (-165 kJ/mol CO [65]), the reactor was controlled to within $\pm 2^\circ\text{C}$ of the average temperature.

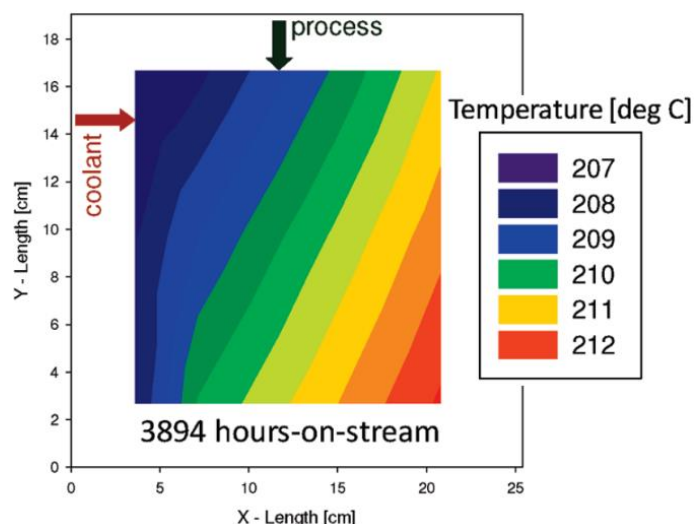


Figure 2.11: Temperature distribution in a cross-flow microchannel reactor for FT synthesis. Adapted with permission from [65]. Copyright (2010) American Chemical Society.

Regatte and Kaisare [66] investigated with modelling, the cross-flow coupling of ammonia decomposition and propane/air combustion (Figure 2.12), with both reactions taking place catalytically (on Ru and Pt, respectively). The reforming microchannels had dimensions of $W = 300 \mu\text{m}$, $H = 300 \mu\text{m}$ and $L = 10 \text{ mm}$ and the combustion microchannels with $W = 400 \mu\text{m}$, $H = 400 \mu\text{m}$ and $L = 3 \text{ mm}$. An ammonia flow rate of 0.225 mL/s , propane/air flow rate of 2.4 mL/s , wall thermal conductivity of 15 W/m/K , wall thickness of $250 \mu\text{m}$ and fuel/air equivalence ratio of 0.85 was used in the reference case.

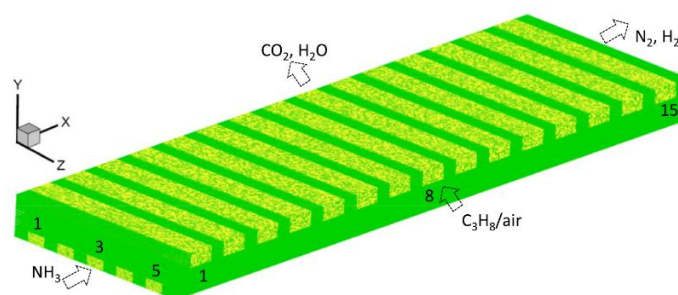


Figure 2.12: Cross-flow microchannel design for the coupling of ammonia decomposition and propane/air combustion. Reprinted from [66] with permission from Elsevier.

It is evident that the individual combustion channels in the cross-flow arrangement had significantly different temperature profiles (Figure 2.13a). Near the outlet of the combustion microchannels, a large temperature difference (223.5 K) was observed between the first and the last channel. For combustion Channel-1, which flowed across the inlet of the ammonia

decomposition channels, the heat consumption was extensive due to fast decomposition rates of ammonia (Figure 2.13b). Combustion Channel-1 therefore had the lowest overall temperature profile. The hottest channel (Channel-15) flowed across the outlet of the decomposition channels, and the insignificant decomposition reaction rates was the cause of the high temperature observed in this channel. A slight difference in the propane mass fraction ($\sim 8\%$) was noticed between Channel-1 and Channel-15 in the region where the two temperature extremes established, roughly midway down the axial length of the combustion channels (Figure 2.13a).

The temperature and the ammonia mass fraction profiles were near identical for all five endothermic microchannels (Figure 2.13b). At the inlet of these microchannels, the temperature rose rapidly to the downstream temperature of combustion Channel-1 (Figure 2.13a). A flexi-point was obtained, and thereafter the axial temperature of the endothermic channels steadily increased as the temperature was dominated by the subsequent combustion channels (Figure 2.12). The temperature of the reforming channels at their outlet corresponded to that of combustion Channel-15. It is therefore apparent that the localised heat transfer (coupling of the reactions) is adequate in a cross-flow arrangement. However, due to the nature of the cross-flow design, the reactor is exposed to significant thermal stresses that arise on the global scale. A considerable temperature gradient established from the reforming inlet to the outlet.

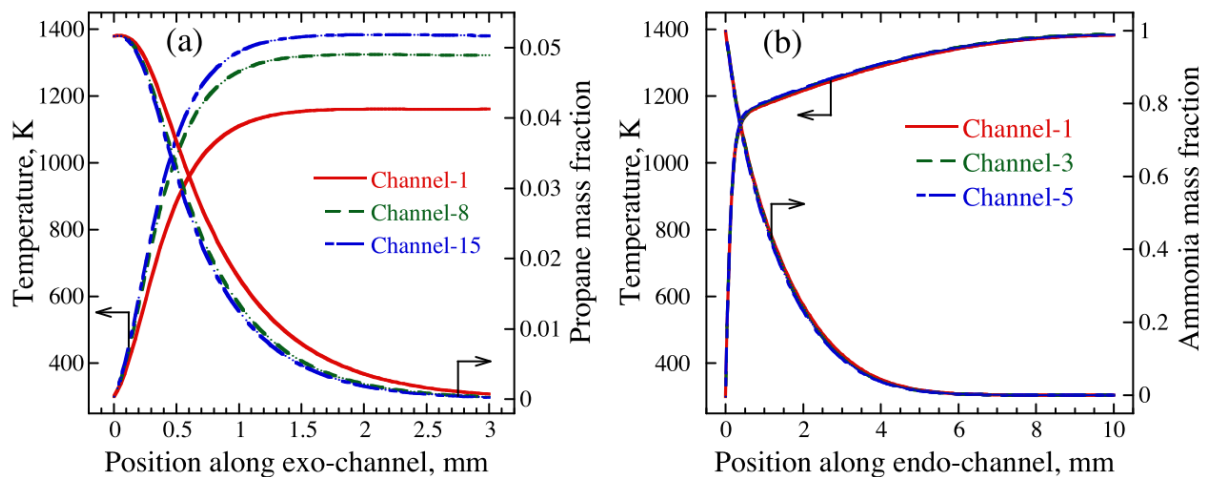


Figure 2.13: Axial temperature and mass fractions for (a) the exothermic microchannels (propane/air combustion) and (b) the endothermic microchannels (ammonia decomposition). The results are plotted for the first, middle and last microchannels for each reaction. Reprinted from [66] with permission from Elsevier.

Son and co-workers [67] investigated a cross-flow design for the oxidative coupling and steam reforming of methane. Instead of channel-based catalysts, thin but broad catalytic beds were positioned in an alternating, cross-flow design (Figure 2.14b). Thermal observations and gas conversions/yields from an experimental reactor was validated with a full 3D CFD model. As base case, catalyst bed thicknesses of 3 mm were used, with space velocities of 0.5 and 3.8 L CH₄/g_{cat}/h, respectively, for steam reforming and oxidative coupling. For the steam reforming of methane, the feed of CH₄/H₂O/N₂ varied accordingly (1/2.5/0.7–2.7) to influence the maximum temperature attained in the catalyst bed, while the feed for the oxidative coupling reaction was constant at 3/1/5 (CH₄/O₂/N₂).

For the CFD model, the temperature profile for steam reforming (in the direction of oxidative flow) was seen to have a low point near the oxidative inlet (Figure 2.14a) due to the domination of fast reaction rates of the endothermic reforming reaction. From the reforming inlet to the outlet, a temperature increase of approximately 150°C was obtained. Experimentally, the temperature difference was much more gentle (20°C), probably due to non-ideal measurement conditions. The oxidative coupling catalyst bed showed a maximum temperature halfway down the length of the bed (30 cm). Often for co-current and cross-flow designs, a maximum temperature is achieved in this region when a mildly exothermic reaction is coupled with a highly endothermic reaction. For the experimental reactor, equilibrium reforming of methane was attained (99% conversion) for all the scenarios of N₂ dilution, while the oxidative coupling yielded methane conversions of 22.9–35.7% and C₂ yields of 10.4–14.3%.

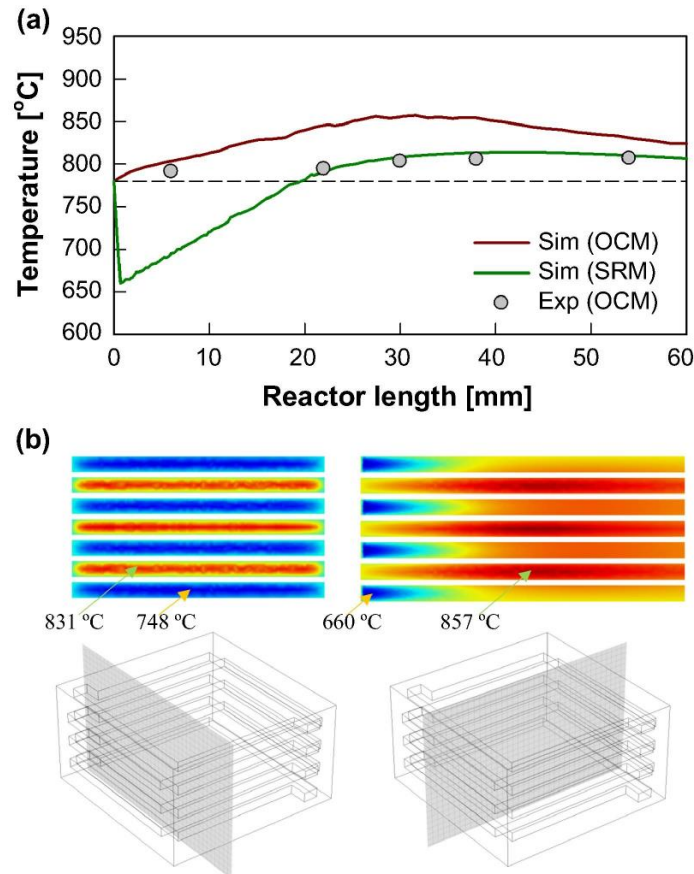


Figure 2.14: (a) Simulated and experimental axial temperatures in the directional flow of oxidative coupling of methane. (b) Simulated temperatures in the reactor's respective cross-sections: (left) the directional flow of methane steam reforming (at location $z = 15$ mm from the oxidative inlet) and (right) the directional flow of oxidative coupling of methane (middle of the reactor (Figure 2.14a)). Reprinted from [67] with permission from Elsevier.

2.2.2.1 A summary of cross-flow configuration advantages

On a practical note, the nature of a cross-flow design simplifies the feed and exit manifolds, to distribute gas flow to and from the reactor [42]. Separation is achieved by perpendicular flow angles to the reactor. This effect becomes important in small-scale reactor applications where spacial limitation is an important design parameter. Nevertheless, the cross-flow design remains simple and manufacturable at low cost with the addition of these manifolds.

For moderate and high wall thermal conductivities, a cross-flow arrangement can support reduced temperature gradients, and operate at low endothermic flow rates [66].

2.2.2.2 A summary of cross-flow configuration limitations

In some cases (wrongly designed flow rates or in the case of low wall thermal conductivity) hot spots form, leading to undesired reaction products and reduced selectivity. Typically a hotspot is obtained at the inlet of the combustion channels and near the reforming outlet, where little heat is consumed [35].

2.3 ALTERNATIVE STRATEGIES FOR IMPROVED THERMAL COUPLING

2.3.1 Reactor wall thermal conductivity

In this section, examples of variable wall thermal conductivity on the thermal effects within microchannel reactors are conferred. These effects however are flow configuration dependent. Firstly, the simulations by Deshmukh and Vlachos [27] are used to evaluate wall conductivity effects in counter-current and co-current flow configurations. Then, the cross-flow arrangement of Regatte and Kaisare [66] is considered. Both studies considered coupled propane/air combustion and ammonia decomposition, although the combustion reaction was considered homogeneously [27] and catalytically [66].

Deshmukh and Vlachos [27] delineated regions of variable ammonia flow velocity and wall thermal conductivities, in which the counter- and co-current configurations, reported in section 2.2.2.1, are feasible (Figure 2.15). For co-current flow and low thermal conductivity materials (e.g. Al_2O_3), the region where high rates of ammonia decomposition take place (near-inlet) undermines the flame structure of the co-current linked propane/air flame. This is evident in the delayed propane conversion in Figure 2.2(h). Ultimately, only lower ammonia flow rates are feasible for these materials. With higher thermal conductivity materials, improved heat transfer causes the flame structure to stabilise closer to the inlet of the channels (Figure 2.2b), and subsequently the coupled reactor can tolerate increased ammonia flows. Generally, the co-current flow configuration allows a wider selection of wall materials compared to counter-current flow.

As highlighted with numerous examples, the counter-current configuration is rarely feasible with low wall thermal conductivity materials (0.1–10 W/m/K), as extreme temperatures are obtained near the combustion inlet in the presence of too high combustion or too low decomposition flow rates. As illustrated by Deshmukh and Vlachos [27], the shaded region indicating the feasible operating space for counter-current flow is narrower than that of co-current flow (Figure 2.15). On the other hand, the counter-current configuration allows higher

ammonia flow rates to be used at medium-to-high wall thermal conductivities (50–200 W/m/K). The cold and hot reaction zones in the reactor are separated (Figure 2.2a), allowing for its stabilisation with an increased heat sink (higher ammonia flow).

Both configurations behave practically the same for wall thermal conductivities in excess of 200 W/m/K (e.g. aluminium). This is evident in the isothermal wall temperature illustrated for the two configurations (Figure 2.2a,b). Although the example by Deshmukh and Vlachos [27] is reaction specific (catalytic ammonia decomposition and homogeneous propane/air combustion), the principle of heat transfer in these configurations remain the same. For instance, traditional counter-current reactors will remain prone to high temperatures when using low conductivity wall materials.

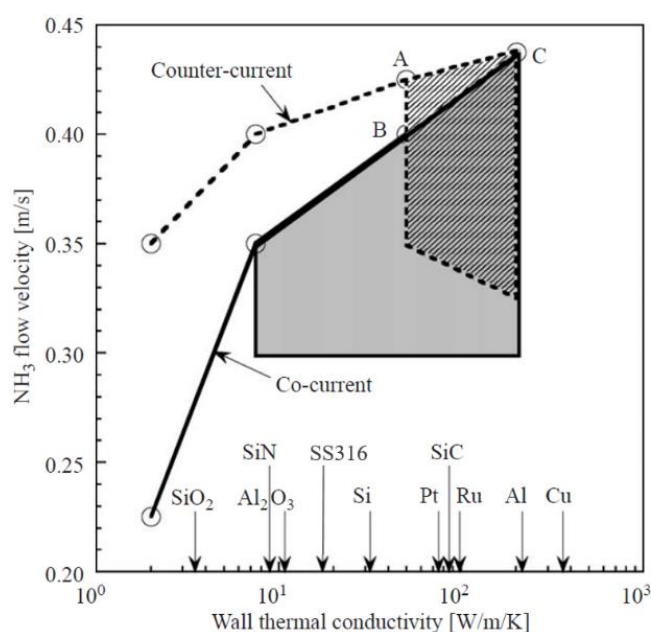


Figure 2.15: Feasible operating regimes with respect to endothermic ammonia decomposition flow velocities for counter- and co-current flow configurations at different wall thermal conductivities. Adapted from [27] with permission from Elsevier.

The effect of a variable reactor wall thermal conductivity was also investigated by Regatte and Kaisare [66] on the cross-flow microchannel reactor described in section 2.2.2 for the coupling of propane/air combustion and ammonia decomposition reactions. An ammonia flow rate of 0.225 mL/s, propane/air flow rate of 2.4 mL/s, wall thickness of 250 μm and fuel/air equivalence ratio of 0.85 was used. The temperature distribution obtained within the cross-flow microchannel reactor is illustrated in Figure 2.16 for wall thermal conductivities of 1, 15 and 100 W/m/K.

For a wall thermal conductivity of 1 W/m/K, a significant and increasing temperature profile existed in the direction of ammonia flow (Figure 2.16b: top). This gradient was also observed on the propane side, with the first propane/air channel losing significant heat to the cold and incoming ammonia flow (Figure 2.16a: top). In this channel, only 97% propane conversion was achieved. A maximum temperature difference in the order of 745 K was observed between the first and the last propane/air microchannel, rendering this scenario not feasible due to high device temperatures in excess of 1500 K at the ammonia outlet. The first ammonia channel near the propane-air inlet was slightly hotter than the downstream ammonia channels, at any given axial location (Figure 2.16b: top).

As expected, a high wall thermal conductivity of 100 W/m/K was seen to create near isothermal conditions, especially comparing the ammonia microchannels (Figure 2.16b: bottom). In the case of the propane/air microchannels, a slight temperature gradient exists and the channel that is located near the ammonia inlet is cooler than the channel at the ammonia outlet (Figure 2.16a: bottom). A difference of 33 K was noted between their respective maximums.

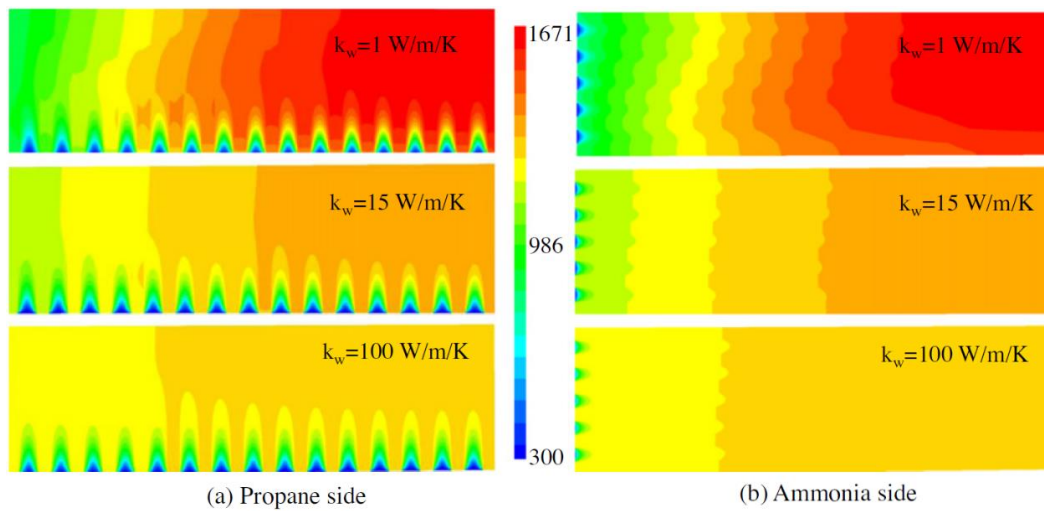


Figure 2.16: The effects of wall thermal conductivities of 1, 15 and 100 W/m/K on (a) temperature of propane/air microchannels and (b) temperature of ammonia decomposition microchannels, in a coupled cross-flow configuration. An ammonia flow rate of 0.225 mL/s, propane/air flow rate of 2.4 mL/s, wall thickness of 250 μ m and fuel/air equivalence ratio of 0.85 was used. Reprinted from [66] with permission from Elsevier.

Hosukoglu et al. [68] modelled a counter-current microchannel reactor/heat exchanger for the hydrocracking of FT waxes with a wide hydrocarbon distribution of C_{5-70} components [69] and according to a kinetic model [70] described elsewhere. The half-height of hydrocracking and

cooling microchannels was modelled, with the hydrocracking microchannel having dimensions of: $W = 500 \mu\text{m}$, $H = 500 \mu\text{m}$ and $L = 10 \text{ cm}$. The hydrocracking microchannel was coated with a $\text{Pt/SiO}_2/\text{Al}_2\text{O}_3$ catalyst with a washcoat thickness of $50 \mu\text{m}$. The cooling channel was slightly larger ($W = 600 \mu\text{m}$ and $H = 600 \mu\text{m}$). A separating wall with thickness of $300 \mu\text{m}$ and thermal conductivity of 44.5 W/m/K (AISI steel) was applied. Reference conditions included: hydrocracking inlet temperature of 460°C , pressure of 53.75 bar , WHSV of $160 \text{ kg}_{\text{wax}}/\text{kg}_{\text{cat}}/\text{h}$, and H_2/wax ratio ($\text{kg H}_2/\text{kg wax}$) of 0.1275 . Steam was used as coolant, with an inlet temperature of 390°C and linear velocity of 0.05 m/s .

The heavy hydrocarbons (C_{22+}) were noticed to decrease from an initial molar fraction of 0.3 to 0.2 at the outlet of the microchannel reactor (Figure 2.17). The majority of products from the cracking process fall within the jet fuel cut (C_{11-18}), as its fraction increased from 0.43 to 0.48 . The fraction of the diesel cut decreased from 0.135 to 0.125 . It was reported that the high inlet temperature of 460°C favours the production of jet fuel derivatives, while diesel products increase slightly at a lower inlet temperature of 440°C (not shown), especially at a WHSV of $160\text{--}180 \text{ kg}_{\text{wax}}/\text{kg}_{\text{cat}}/\text{h}$ and coolant inlet temperature of 390°C . However, it was observed that C_{22+} hydrocarbon conversions above 95% were only possible at the 460°C inlet temperature.

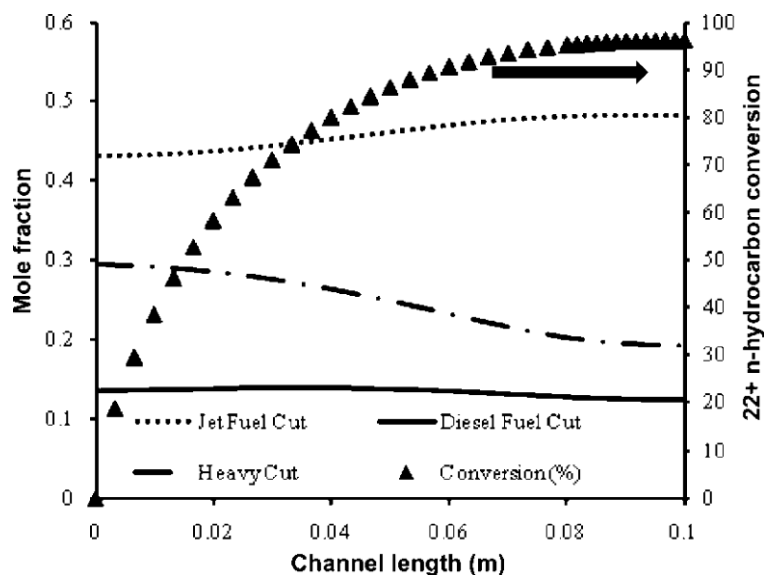


Figure 2.17: Modelled product distribution and C_{22+} hydrocarbon conversion during FT hydrocracking in a microchannel reactor. Reprinted with permission from [68]. Copyright (2004) American Chemical Society.

Furthermore, the effects of three wall materials were investigated using alumina, steel and SiC , with thermal conductivities assumed as 27 , 44.5 and 87 W/m/K , respectively, on the resultant

temperature profiles within the reactor (Figure 2.18). It was observed that the two inlet temperatures (460°C for the H₂/FT waxes and 390°C for the coolant) of the counter-currently operated reactor provided thermal stability to the inlet and outlet extremes of the reactor. However, for the lower conductivity alumina material, the temperature was seen to increase to 470°C at axial position 8 cm. Temperature excursions are detrimental to processes sensitive to product selectivity, especially FT wax hydrocracking [68]. Alternatively, the highly conductive SiC dissipated heat via axial heat conduction between the reactant stream and the coolant.

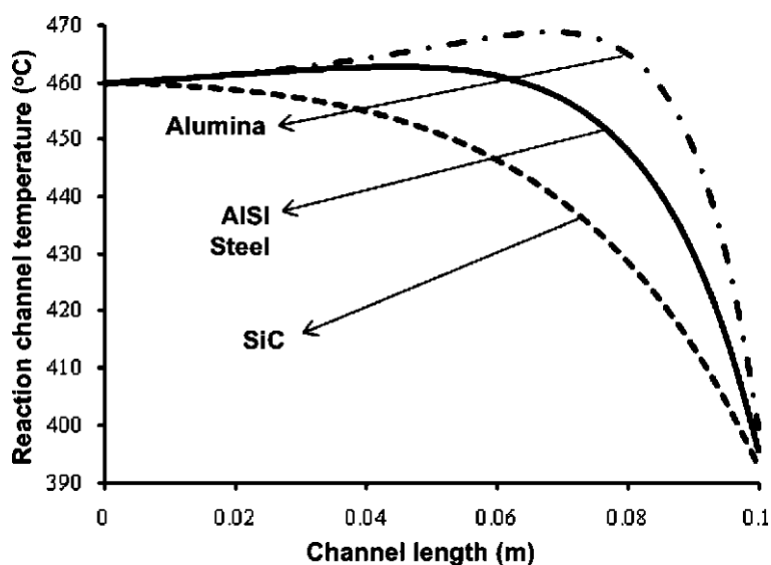


Figure 2.18: Hydrocracking temperature profile as a function of three wall materials (alumina, steel and SiC) across the 10 cm-long microchannel reactor length. Reprinted with permission from [68]. Copyright (2004) American Chemical Society.

2.3.2 Channel dimensions

Stefanidis and Vlachos [26] investigated with modelling, a co-current strategy for thermally coupled high and low temperature steam reforming, by using methane and methanol fuels, respectively. The half-height of microchannels was modelled for simplification (total height of 600 μm for the combustion channel and 400 μm for the reforming channel). The nominal wall conductivity was 100 W/m/K, with a wall thickness of 750 μm and microchannels length of 10 cm. For the nominal cases, combustible inlet velocities of 3 m/s and reforming inlet velocities of 9.75 m/s were applied. Although the authors discussed variations in wall conductivity, it will not be reviewed herein for brevity.

In the methane case, both methane combustion and methane reforming showed quick reaction rates (as a result of high temperature operation), and neared reaction completion within 1 cm

of the inlets of the co-current microchannels, at nominal microchannel dimensions and flow rates. The reaction zones overlapped well, and resulted in a near-isothermal wall temperature (~ 1063 K) at the high wall conductivity. For lower temperature operation (650–700 K), methanol combustion was also quick to completion, however the reforming of methanol (which could not be operated at such temperatures when regular Cu/ZnO catalyst would be applied) was reaction controlled and spanned the entire length of the microchannel. This created a slightly decreasing temperature gradient (50 K) along the length of the microchannel, as a result of the gradual heat consumption via reforming.

The effect of increasing the microchannel size from the nominal value was investigated. Firstly, the combustion channel size was increased according to a ratio of d_1/d_1^0 (d_1^0 being the nominal value). The feed flow rate of the combustion side was kept constant, which resulted in an increasing fluid residence time within the microchannel. For all the channel sizes investigated, the methane and methanol combustion residence times were sufficiently long to ensure conversions greater than 99% for the two feed flow rates under investigation (3 m/s and 6 m/s). The effects on the reforming conversion (Figure 2.19a) and maximum wall temperature (Figure 2.19b) are illustrated for both the fuels. The methane reforming conversion was resistant towards the changes in the combustion channel size, due to sufficiently fast rates of the reforming reaction. However, methanol reforming showed some incomplete conversion at a $d_1/d_1^0 = 6$ ratio and 6 m/s gas velocity in the combustion channels (Figure 2.19a), as the majority of combustion heat was provided farther from the inlet of the microchannels (which was attributed to mass transfer limitation), and keeping in mind that the methanol reforming reaction was already close to incompleteness (reaction controlled) at the nominal values. Essentially, longer microchannels or increased reforming residence times are then required to better utilise the combustion heat released. On the contrary, the methanol combustion and reforming reaction zones actually overlapped better at the $d_1/d_1^0 = 6$ ratio, and lower maximum reactor temperatures were obtained (Figure 2.19b), at the expense of the incomplete conversion of the reformat.

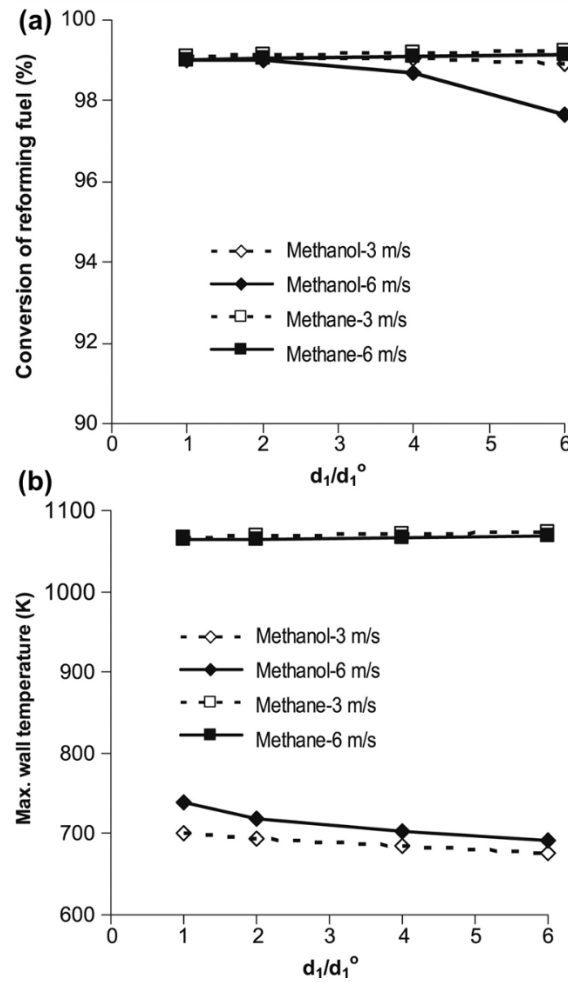


Figure 2.19: The effect of increased combustion channel size (d_1), relative to the nominal half-height size (d_1^0) of 300 μm on (a) reforming fuel conversion and (b) maximum wall temperature. Channel size increases meant that increased combustion residence times were obtained for fixed methane and methanol combustion flows of 3 m/s and 6 m/s. Renumbered from [26] with permission from Elsevier.

When the reforming channel size was increased according to a ratio of d_2/d_2^0 (d_2^0 being the nominal value), methane and methanol combustion was unaffected, and remained complete for all channel sizes and combustion flows. It was observed that some reductions in the methane reforming conversion occur for larger channel sizes ($d_2/d_2^0 = 4-6$) and low combustion flow rate (3 m/s) (Figure 2.20a). This could be attributed to slightly lower reactor temperatures (compared to the 6 m/s combustion flow), and the fact that the methane reforming reaction became more diffusion controlled, due to larger channel sizes. The methanol reforming conversion decreased linearly with increasing reforming channel size (Figure 2.20a), due to the same diffusional effects hampering the reaction. With the same combustion heat provided at

the microchannels inlet, maximum wall temperatures increased with the same linearity (Figure 2.20b). Similar observations were made by the same authors, coupling catalytic reactions of propane combustion and methane steam reforming also in a co-current strategy [71].

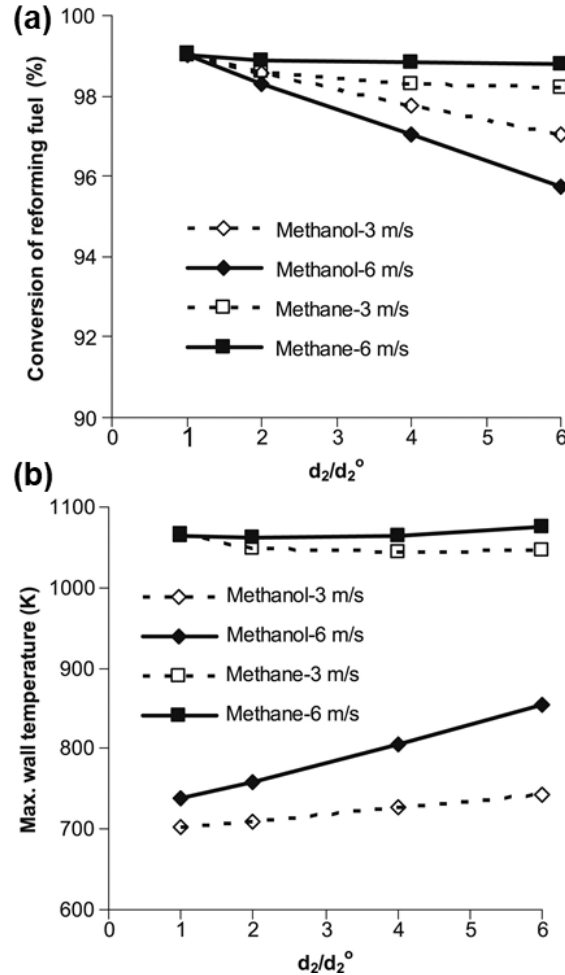


Figure 2.20: The effect of increased reforming channel size (d_2), relative to the nominal half-height size (d_2^0) of 200 μm on (a) reforming fuel conversion and (b) maximum wall temperature. Channel size increases meant that increased reforming residence times were obtained. Plotted for methane and methanol combustion flows of 3 m/s and 6 m/s. Renumbered from [26] with permission from Elsevier.

2.3.3 Catalyst positioning

As a measure of limiting temperature extremes in the counter-current flow configuration, Zanfiri and Gavrilidis [38] imposed catalyst distribution functions on the combustion catalyst (methane/air), as a function of the axial dimensionless coordinate (ζ) from the methane steam reforming inlet (Table 2.1). The rate of the combustion reaction was factored by three

distribution functions; (1) uniformly, (2) linear and (3) a parabolic function. Differences in the wall centreline temperature, methane reforming and combustion conversions were observed, with the total amount of catalyst being kept constant between the scenarios.

Table 2.1: The effect of combustion catalyst distribution on coupled, counter-current methane steam reforming and methane/air combustion. Adapted from [38] with permission from Elsevier.

	Distribution type	Distribution function $f(\zeta)$	$T_{\min}$ (K)	$T_{\max}$ (K)	Reforming conversion (%)	Combustion conversion (%)
1	Uniform	1	732	1103	62.9	51.0
2	Linear	$1.5 - \zeta$	749	966	61.2	43.6
3	Parabolic	$0.5 + 1.128(\zeta - 1.1)^2$	757	948	60.5	43.0

As a result of the linear and parabolic catalyst distributions, the temperature of the wall near the combustion inlet ($\zeta = 1$) was significantly reduced in these cases. It is illustrated in Figure 2.21 with the dimensionless wall temperature, using 793 K as reference temperature (feed inlet temperatures). The maximum temperature recorded near the combustion channel inlet was 966 K (linear) and 948 K (parabolic), compared to the 1103 K for the base case (uniform distribution). At the inlet of the reforming channel, the minimum wall temperature was seen to increase by up to 25 K (parabolic distribution).

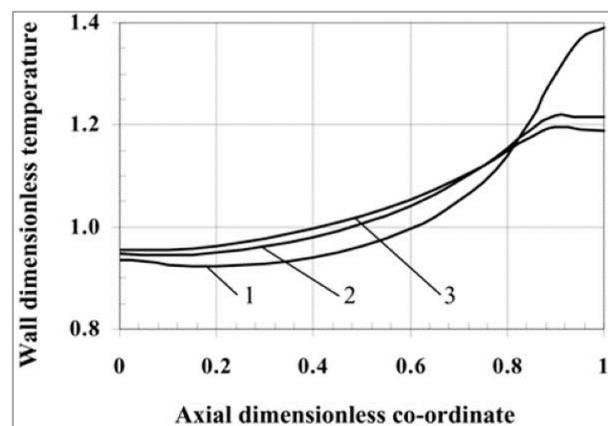


Figure 2.21: The effect of combustion catalyst distribution on coupled, counter-current methane steam reforming and methane/air combustion. A plot of dimensionless wall temperature (793 K reference) against the axial dimensionless coordinate from the reforming inlet, for (1) uniform, (2) linear and (3) parabolic distributions. Reprinted from [38] with permission from Elsevier.

The maximum heat flux generated at the combustion channel inlet reduced considerably, from 55 kW/m^2 (uniform) to 20 kW/m^2 (linear) and 16 kW/m^2 (parabolic) (Figure 2.22). Although in the cases of the linear and parabolic distributions, the combustion channel has an increasing catalyst loading towards the reforming inlet, the degree of heat consumed by the reforming reaction still acted as a heat sink, and subsequently caused the lowest temperature obtained at the reforming inlet (Figure 2.21).

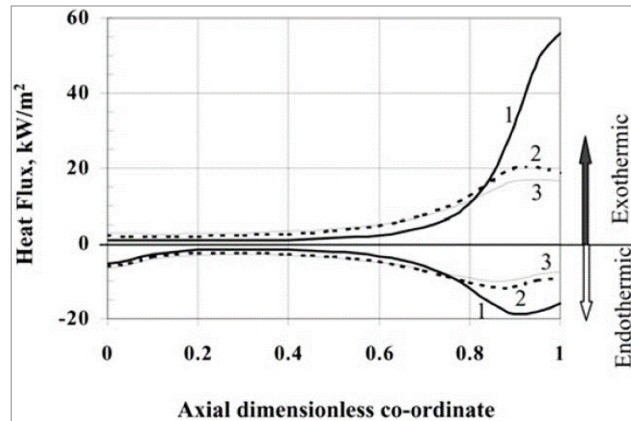


Figure 2.22: The effect of combustion catalyst distribution on coupled, counter-current methane steam reforming and methane/air combustion. A plot of heat flux generated/consumed by the reactions against the axial dimensionless coordinate from the reforming inlet, for (1) uniform, (2) linear and (3) parabolic distributions. Reprinted from [38] with permission from Elsevier.

There was found that the modification of the catalyst distribution had a marginal effect on the reforming conversion (62.9% for the uniform and 60.5% for the parabolic distribution), yet the combustion conversion dropped by as much as 8% for the parabolic distribution (Table 2.1). In this case, the separation distance between the regions of main reforming and combustion reactions were reduced, and together with the decline in the extreme temperature spike at the combustion inlet, a lower combustion conversion was observed.

In subsequent work, Zanfiri et al. [39] designed an optimisation problem, which maximises the sum of methane reforming and combustion conversions, subject to the confinement of the centreline wall temperature (1000–1500 K) for the entire length of the reactor. A counter-current flow configuration was used due to its notorious low and high temperature extremes at the respective reforming and combustion inlets. In order to achieve an optimal design, the channel length was variable (maximum allowable limit of 0.6 m), and both reforming and

combustion catalysts could be offset so that the coverage of catalyst could start some distance into the channels (L_{ref} and L_{comb} in Figure 2.23). Two cases were modelled; the first with only catalytic combustion kinetics (Figure 2.24a), and the second accounted for both catalytic and homogeneous combustion kinetics (Figure 2.24b). In both cases, the maximum microchannel length allowed in the model contributed to optimal results.

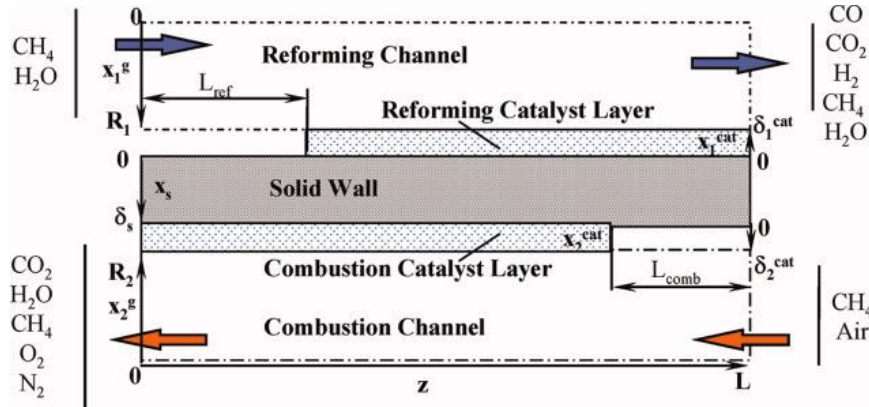


Figure 2.23: Counter-current flow geometry depicting methane steam reforming and methane combustion channels, with respective L_{ref} and L_{comb} catalyst offsets. Reprinted from [39] with permission from John Wiley & Sons, Inc.

In the case of catalytic combustion only (Figure 2.24a), the wall temperature peak shifted to the region where the combustion catalyst starts (L_{comb} of 0.2652 m). A reforming catalyst offset of $L_{\text{ref}} = 0.0135$ m was obtained. For a uniform distribution of catalyst, the wall temperature peak was obtained at the inlet of the combustion channel (Figure 2.4b). In the offset case, the majority of heat is released close to the middle of the reactor, hence the sensible heat from the downstream reforming gas is recirculated by the incoming combustion stream ($\zeta = 0.558-1$). This phenomenon contributes to the extreme temperature peak attained (1484 K).

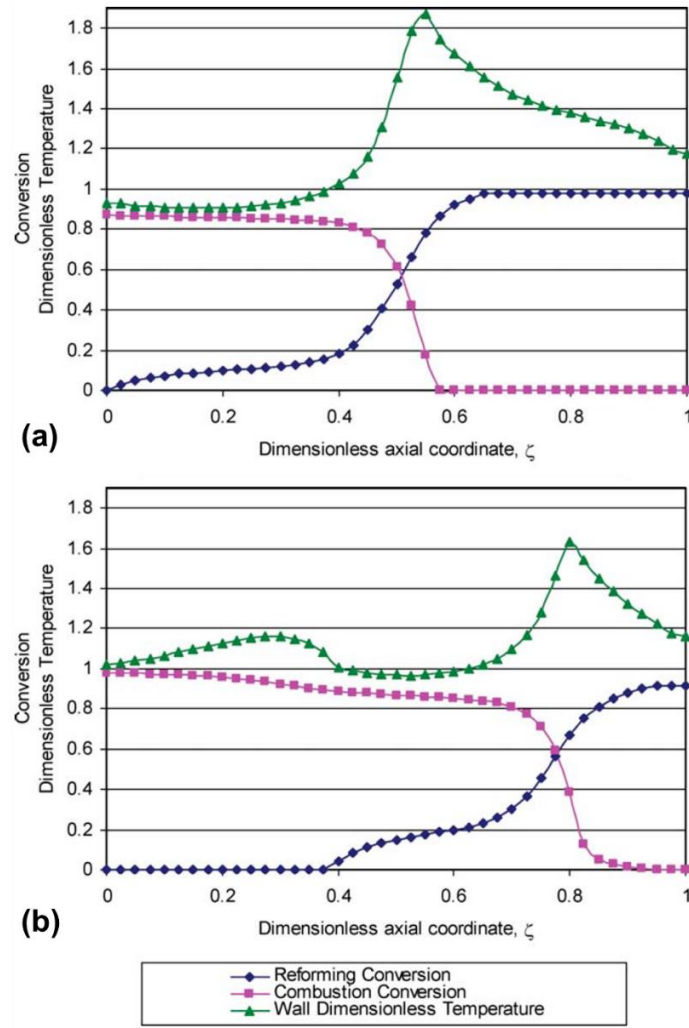


Figure 2.24: A plot of dimensionless wall temperature (793 K reference), methane reforming and combustion conversions against the axial dimensionless coordinate (ζ) from the reforming inlet, for optimised catalyst offsets. (a) Catalytic combustion and (b) catalytic and homogeneous combustion is considered in a counter-current flow configuration. Renumbered from [39] with permission from John Wiley & Sons, Inc.

With the inclusion of homogeneous combustion kinetics, the catalyst offsets were found to be $L_{\text{ref}} = 0.225$ m and $L_{\text{comb}} = 0.104$ m, and the total length of channels still at a maximum value of 0.6 m. The combustion of methane was reported to occur upon entering the microchannel due to the homogeneous combustion (Figure 2.24b). The maximum temperature spike was lower (1293 K), compared to the catalytic combustion-only case (1484 K). A lower reforming conversion was obtained (91.7%), as a result of the methane combustion propagation towards the inlet of the combustion channel. A shorter distance of the reforming channel was exposed to sufficiently high temperatures to achieve a reforming conversion as was observed in the

former case (99%). Near the inlet of the reforming channel ($\zeta = 0-0.375$), a local temperature maximum was obtained due to the catalytic combustion and the absence of heat consumed by the reforming reaction.

Although the reduction of extreme temperature peaks can be achieved by adjusting the offset of the combustion catalyst, and even if the reactor temperature is below the maximum temperature limit, the occurrence of local maxima can have damaging effects on the reactor. For instance during dynamic reactor operation (fluctuating temperature peaks), unnecessary mechanical stress will be induced on the reactor substrate and catalyst due to the different thermal expansion coefficients of these materials. More even reactor temperature distributions supports the added benefit of its operation being sustainable, i.e. handling fluctuations in reactor feed better. Whereas isolated temperature peaks might disappear with varying flow rates, and subsequently lead to thermal extinction. Similar approaches to overcome the disadvantages of the counter-current flow design were conducted by simulation and experiment by the group of Eigenberger in the same period of time, which will be discussed below.

Pattison and Baldea [72] demonstrated an improvement in a counter-current reactor's temperature distribution by incorporating a segmented combustion catalyst and a phase change material (PCM) layer confined between two conductive walls. The modelling of both catalytic methane steam reforming and methane combustion was undertaken from previous works [39,73–75]. In a base case model, the offset of the reforming and combustion catalysts were optimised (Figure 2.25a). A second strategy implemented was the segmentation of the combustion catalyst, while the offset of the reforming catalyst was also included (not shown). It was determined that more than four segments of the combustion catalyst provided insignificant improvements in the temperature distribution, and as a result the model was limited in this sense [72,75]. The determination of the segmentation parameters (including the catalyst location, segmentation length and number of segments) was delineated by Pattison et al. [75]. Lastly, the PCM layer (500 μm thickness) was added within two cover plates (250 μm thickness) of the reactor wall, as well as combustion catalyst segmentation and reforming catalyst offset (Figure 2.25b). This layer was implemented to dissipate excessive heat using the latent melting of the layer, when temperature extremes are present. Thermal properties of the PCM layer was selected as that of a high thermal conductivity material (a typical copper alloy) to minimise heat transfer lags through the combined wall. Importantly, the melting point of the PCM layer was selected as 1166 K.

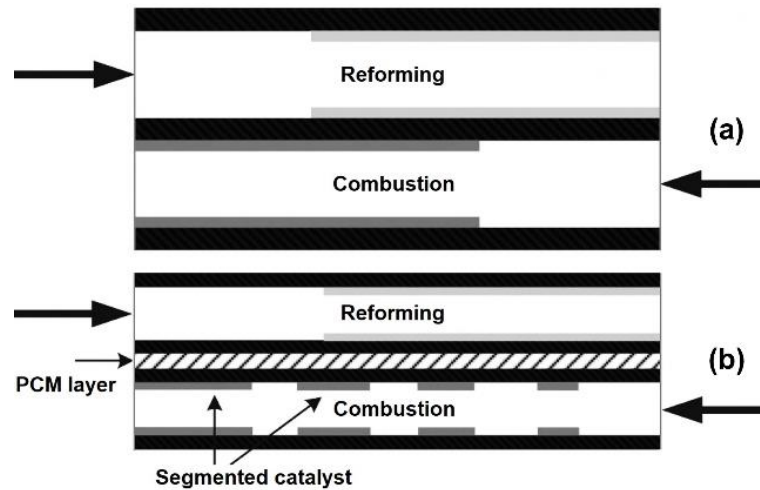


Figure 2.25: Coupled catalytic methane steam reforming and methane combustion microchannels in counter-current configuration for (a) offset reforming and combustion catalysts and (b) offset reforming catalyst, phase change material (PCM) layer and segmented combustion catalyst positioning. Adapted from [72] with permission from Elsevier.

For the base case (Figure 2.26a), a substantial temperature peak established close to the start of the combustion catalyst. A temperature maximum of 1310 K was obtained. A similar temperature profile was also noted by Zafir et al. [39] (Figure 2.24a). With the segregation of the combustion catalyst (Figure 2.26b), three smaller temperature peaks were obtained; in essence forming a temperature plateau near the middle of the reactor. The maximum temperature recorded was reduced to 1200 K, while the methane reforming conversion increased to 98% (compared to the baseline 96%). With the inclusion of the PCM layer, the temperature maximum was only 1132 K. Although the melting temperature of the layer was not reached (1166 K), the increased conductivity of the wall distributed heat more effectively in the axial direction of the wall [72]. The methane reforming conversion at the outlet was once more 98%.

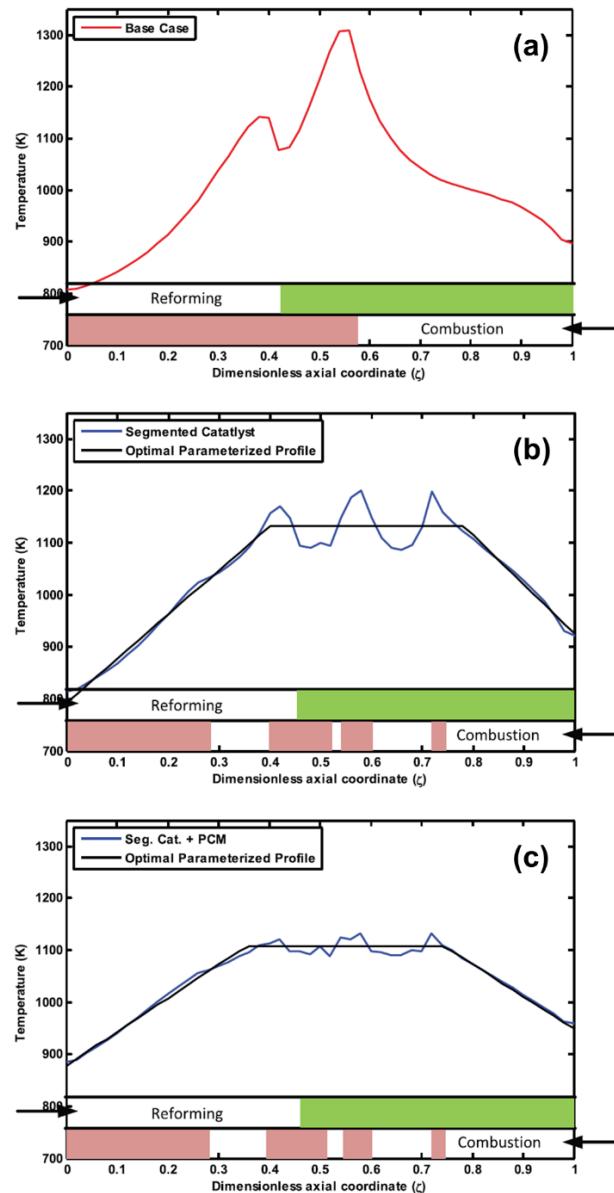


Figure 2.26: Optimal reactor centreline temperature for a coupled counter-current design with (a) reforming and combustion catalyst offsets (Figure 2.25a), (b) a reforming catalyst offset, with segmented combustion catalyst and (c) a PCM layer confined between two walls, a reforming catalyst offset, with segmented combustion catalyst (Figure 2.25b). Results are plotted against the axial dimensionless coordinate (ζ) from the reforming inlet. Reprinted from [72] with permission from Elsevier.

Even in a co-current flow strategy, the formation of hotspots is inevitable, but less pronounced in most cases. The work of Jeon et al. [76] showed that increasing the number of segmentations of combustion catalyst significantly reduced the temperature and reaction rate of methane/air combustion, coupled to catalytic methane steam reforming. For a 2D optimised segmentation

model, the microchannels had a length of 50 mm, heights of 500 μm , a separating wall of 500 μm and catalyst thicknesses of 100 μm . The wall material supported a thermal conductivity of 20 W/m/K. A requirement for the optimisation method was that the reforming outlet conformed to a 90% methane conversion. A Box–Behnken design method was employed to determine to optimal combustion catalyst length (1.06 mm), segmentation (1.19 mm) and number of catalyst sections (10). The maximum temperature was limited to 978 K (Figure 2.27), and the rate of catalytic combustion was reduced by an order of close to six times, compared to a uniform catalyst distribution. Downstream of the segmented region the combustion catalyst was modelled as being uniform, as low reaction rates dominate in this region (Figure 2.27).

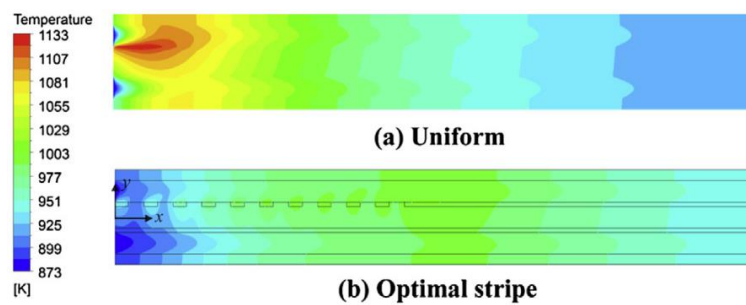


Figure 2.27: Centreline temperature for (a) uniform and (b) evenly spaced segmentation catalyst for methane/air combustion. Both cases include a uniform methane steam reforming catalyst. Conditions correspond to a reforming inlet velocity of 4 m/s (S/C ratio of 3.0) and a combustion inlet velocity of 3.1 m/s (9 vol.% methane/air). Reprinted from [76] with permission from Elsevier.

Herdem et al. [77] evaluated the effect of combustion and reforming catalyst segmentations according to four configurations (Table 2.2), for co-current methanol steam reforming and methanol/air combustion. Specifically in the reforming channel of the 2D model, there was accounted for methanol steam reforming, methanol decomposition and water-gas shift reactions. For the reforming reaction a S/C ratio of 1.5 was used, while the O/C ratio was 3.25 for combustion. Both the feed gas inlet temperatures were set as 150°C. The microchannel dimensions for the reaction coupled system are defined in Table 2.2, while Figure 2.28 illustrates the four catalyst configurations.

Table 2.2: Microchannel dimensions and combustion/reforming catalyst segmentation configurations for methanol steam reforming and methanol/air combustion. A co-current flow configuration was used. Adapted from [77] with permission from Elsevier.

Variable	Combustion	Reforming
Channel length	10 cm	10 cm
Channel width	700 μm	700 μm
Channel height	500 μm	700 μm
Catalyst thickness	16 μm	30, 35, 40, 45, 50 μm
Catalyst configuration		
1 (Figure 2.28a)	Continuous	Continuous
2 (Figure 2.28b)	Segmented (35 active segments)	Continuous
3 (Figure 2.28c)	Segmented (35 active segments)	Segmented (34 active segments)
4 (Figure 2.28d)	Segmented (35 active segments)	Segmented (two active segments)

In configuration 1, both the combustion and reforming catalysts were continuously coated in the microchannels (Figure 2.28a). For configurations 2, 3 and 4, the combustion catalyst were segmented with 34 evenly spaced blank regions of 2 mm length (Figure 2.28b,c,d). The reforming catalyst was continuous in configuration 2 (Figure 2.28b), segmented with 33 evenly spaced blank regions of 1 mm length in configuration 3 (Figure 2.28c), while for configuration 4, one large inactive region of 20 mm in the central part of the reforming channel separated two catalytic segments (Figure 2.28d).

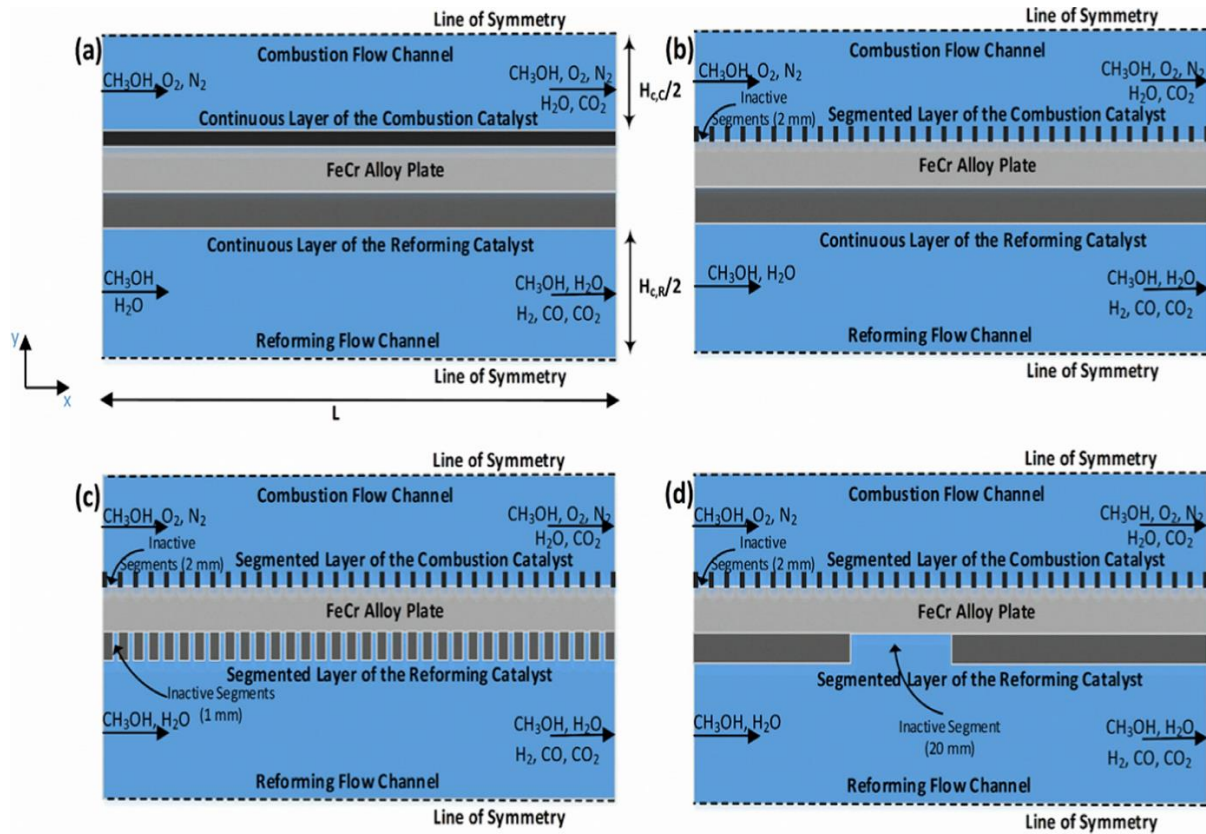


Figure 2.28: Coupled methanol steam reforming and methanol/air combustion in a co-current flow arrangement, for four combustion and reforming catalyst configurations defined in Table 2.2. Reprinted from [77] with permission from Elsevier.

The average reforming stream temperature is illustrated in Figure 2.29 for the four catalyst segmentation cases presented. For the continuous combustion and reforming catalyst (configuration 1), a characteristic temperature peak developed near the reactor inlet. Yet the maximum temperature recorded ($\sim 306^\circ\text{C}$) was not as high as other configurations to be discussed later, as a result of the overlap of local reaction zones. Moreover, the temperature peak was narrow and only provided a small region in which rapid conversion of reformat was obtained (Figure 2.30). An unsatisfactory conversion (60%) was obtained at the reforming channel's outlet. Typically, feed pre-heating can be achieved to a temperature much higher than the 150°C inlet temperature presented in this case. Nonetheless, higher feed inlet temperatures (Figure 2.29) of the reforming stream will result in improved reforming conversions, and lead to better utilisation of the microchannel inlet region (Figure 2.30) for reaction to take place. Configuration 2, with the segmented combustion catalyst and continuous reforming catalyst, provided the lowest temperature peak ($\sim 303^\circ\text{C}$) of the four configurations.

However, the temperature peak was broader than in configuration 1, and subsequently meant that the conversion of methanol ($\sim 75\%$) was much higher at the microchannel outlet.

The inclusion of inactive reforming catalyst segments (configuration 3) effectively meant that the temperature maximum was even higher ($\sim 314^\circ\text{C}$). A slightly lower reforming conversion could be achieved as that in the continuous catalyst case (configuration 2), as the catalyst surface area was reduced. With the inclusion of a large inactive segment in the reforming catalyst (configuration 4), two temperature peaks were obtained. Firstly, a small peak ($\sim 303^\circ\text{C}$) near the reforming inlet developed, which corresponds to configuration 2. Secondly, a large temperature extreme ($\sim 331^\circ\text{C}$) was obtained in the absence of the heat consumption by the reforming reaction, near the middle of the microchannel. As soon as the reforming catalyst is present again, a sharp decrease in temperature and increase in the reforming conversion was seen. At the reforming channel outlet, 77.5% methanol conversion was obtained. However, because methanol combustion normally happens instantaneously at such high reaction temperatures, it could be questioned, if the kinetic expressions applied reflect the performance of the combustion reaction properly.

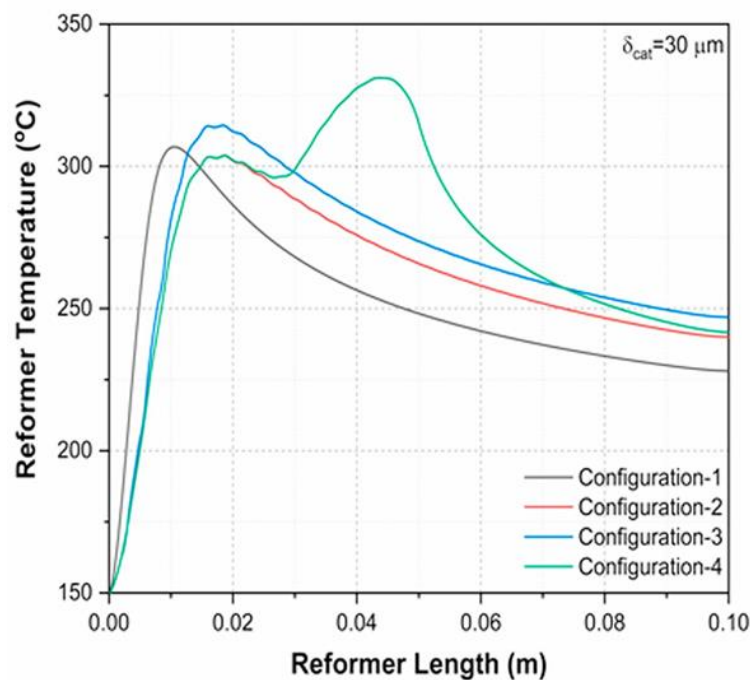


Figure 2.29: Average reforming channel temperature for the catalyst configurations defined in Table 2.2, against the axial length from the reactor inlet. A co-current flow configuration was used, with a reforming catalyst thickness of $30\ \mu\text{m}$. Reprinted from [77] with permission from Elsevier.

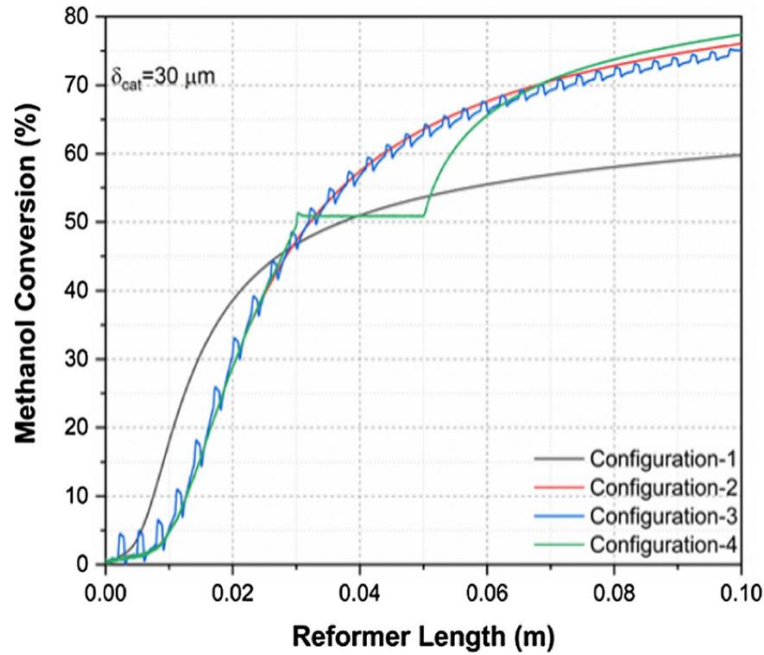


Figure 2.30: Methanol reforming conversion for the catalyst configurations defined in Table 2.2, against the axial length from the reactor inlet. A co-current flow configuration was used, with a reforming catalyst thickness of 30 μm . Reprinted from [77] with permission from Elsevier.

2.3.4 Feed gas distribution

2.3.4.1 Even flow distribution within manifolds

As in any heterogeneous reaction chamber, the immediate thermal effects, caused by the production or consumption of reaction heat, are governed by reactant flow to the areas within the reactor containing the active catalyst. The even distribution of reactant flow is therefore mandatory to attain satisfactory conversion and heat generation within an array of microchannels [78,79]. In saying this, other important considerations are compact manifold and microchannel systems, and reasonable pressure drop across the network of channels [80]. This is important during the scale-up of microchannel reactors for large-scale production capacities [79,81].

Uneven flow profiles are one of main reasons for thermal distributions that may cause low reactant conversions, poor utilisation of reactor volume, irreversible catalyst sintering and adverse material stresses and embrittlement. This section is devoted to the effective design of the flow paths/manifolds that distribute the fluid to the catalytic microchannels. Common manifold designs, often used for microchannel reactors, are presented in Figure 2.31.

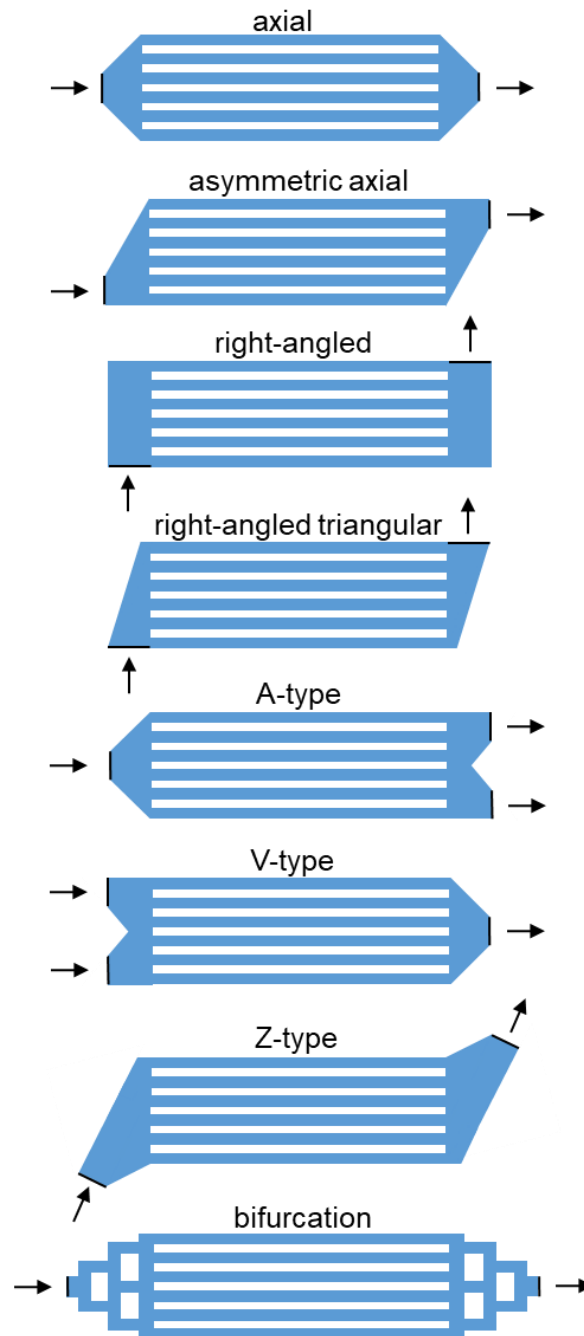


Figure 2.31: Common microchannel manifold designs. These designs are for illustration purposes only, and are subject to geometric modifications. The list is unexhausted, and the designs might be referred to with different titles in published literature. Inspired by [82–84].

Tomomura et al. [85] modelled the flow distribution of water within microchannels ($W = H = 100 \mu\text{m}$) with right-angled inlet and outlet manifolds. Importantly, assumptions of laminar flow and the no-slip boundary condition on channel and manifold walls was made. Microchannel length improved flow uniformity significantly, as a result of the increased pressure drop within

microchannels, compared to that of manifold contributions. With a larger outlet manifold area (with the addition of vertical manifold spacing), improved flow uniformity was attained between microchannels, as a result of reduced dynamic pressure differences at the outlet region of the channels (Figure 2.32). However, during more detailed simulations, a dead volume was observed in the top-right corner of the larger outlet manifold. Subsequently, an optimisation procedure was followed, which resulted in the design of triangular-shaped inlet/outlet manifolds.

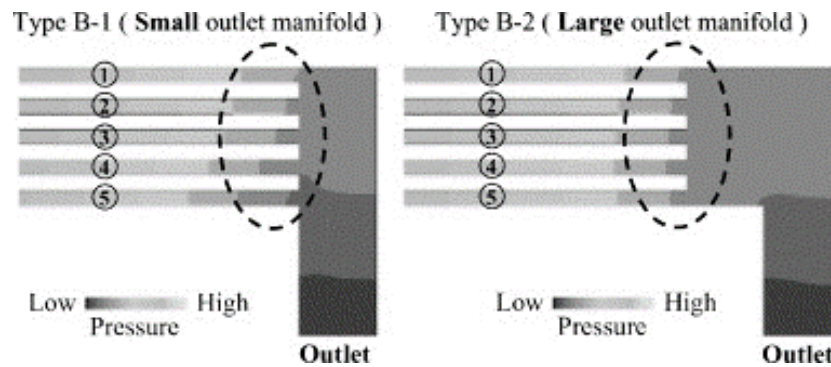


Figure 2.32: Reduction of dynamic pressure difference between microchannels, as a result of larger outlet manifold area. Reprinted from [85] with permission from Elsevier.

Mohammadi et al. [86] investigated with modelling, variable geometric parameters of triangular manifolds to optimise flow distribution, albeit for water as working fluid at low Reynolds numbers ($5 < Re < 25$) in a microchannel heat exchanger. Probably the most surprising observation by Mohammadi et al. [86] is that vertical corner spacings added to inlet (E_{in} , Figure 2.33: left) and outlet (E_{out} , Figure 2.33: left) triangular manifolds showed significant improvements in flow uniformity due to the reduction of shear stresses on the triangle hypotenuse. The standard deviation of the normalised channel velocities for 20 microchannels are illustrated in Figure 2.33: (right). For small corner spacings (E_{in} , $E_{out} = 250 \mu\text{m}$), the optimal corner angle was noted to be smaller ($\sim 9^\circ$), while for larger manifolds induced by larger spacings (1 mm), the angle increased to $\sim 18^\circ$, at comparable channel dimensions ($W = 500 \mu\text{m}$, $H = 200 \mu\text{m}$, $L = 2 \text{ cm}$) and flow conditions (Re number = 7.11).

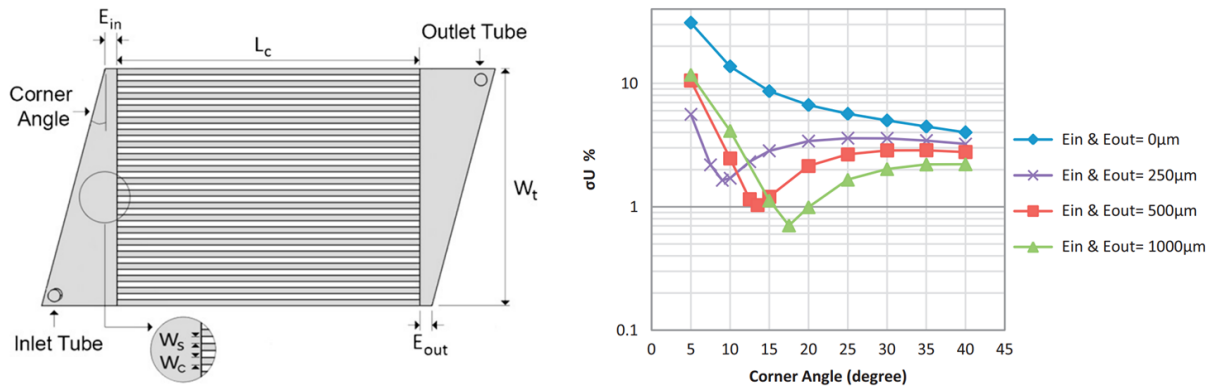


Figure 2.33: (left) The effect of triangular manifold design with a variation in corner angle and vertical spacings of E_{in} and E_{out} . (right) Standard deviation of normalised channel velocities for 20 microchannels with dimensions: $W = 500 \mu\text{m}$, $H = 200 \mu\text{m}$, $L = 2 \text{ cm}$, and water flow at a Re number of 7.11. Reprinted from [86] with permission from Elsevier.

Pan et al. [87] investigated the design of a complex right-angled triangular manifold, in which the triangle hypotenuse is curved for optimal flow distribution. The fluid flow was modelled as equivalent flow and electric resistances, in the inlet manifold, respective channels and the outlet manifold. The individual pressure drops was subsequently calculated according to Ohm's law ($\Delta P = RQ$). An optimisation procedure was generated to find the optimal inlet and outlet manifold geometries at distinct microchannel widths and depths. It was noted that the channels width is the parameter that most affects the curvature of the outlet manifold geometry.

Mei et al. [82] developed an equivalent electric resistance model for flow estimations, and found that higher microchannel aspect ratios (increase in channel length and decrease in width) improved the flow distribution within microchannels. Generally, a symmetric A-type microchannel configuration that was geometrically optimised produced a more even flow distribution compared to a Z-type layout.

In a comprehensive CFD model, Jang et al. [88] preferred a square A-type microchannel reactor, above an asymmetric axial design for the steam reforming of methanol. Two distribution posts within the respective inlet and two outlets of the A-type design improved the flow distribution, to- and from the microchannels. Ultimately, the methanol conversion increased from 83% to 99% using the A-type design.

In different work, Balaji and Lakshminarayanan [89] found that the symmetric nature of the A-type design provides good flow distribution and allows for ease-of-design, with an inlet and two outlets in both flow directions of a counter-current configuration. For gas velocities of 2–

4 m/s within the distribution manifold and microchannels, low Reynolds numbers (<200) indicated complete laminar flow within the heat exchanger.

Griffini and Gavriilidis [90] modelled a Z-type inlet/outlet distribution manifold as a base case, and the effects of design parameters on flow uniformity. It was observed, with numerous 2D and 3D simulations, that increased channel length, larger vertical spacing of the inlet/outlet manifolds, decrease in plate width (consequently lower throughput at constant inlet velocity) and shape of the manifolds (an oval-shaped inlet/outlet produced better flow distributions) contributed to improved flow uniformity between the channels.

In an instance where square micro posts (200 μm) are used to bring uniformity to fluid flow distributions, Regatte and Kaisare [91] demonstrated that triangular inlets and outlets (Figure 2.34c), with cross-flow across the posts improved fluid distribution, vs right-angled cross-flow posts (Figure 2.34b) at a moderate total inlet flow rate (3.9 L/min). This was demonstrated using CFD modelling for the propane/air combustion reaction, with the catalyst coated on the side walls of the posts. The triangular cross-flow posts also supported the lowest pressure drop, and similar propane conversions to axial posts (Figure 2.34a) below 4 L/min. At flows above 4 L/min, the propane conversion within the triangular cross-flow posts deviated from the higher conversions obtained within the axial configuration, due to reactant blowout near the reactor exit. This leads to believe that triangular inlets and outlets, with cross-flow posts, are ideally suited for lower flow rate regimes.

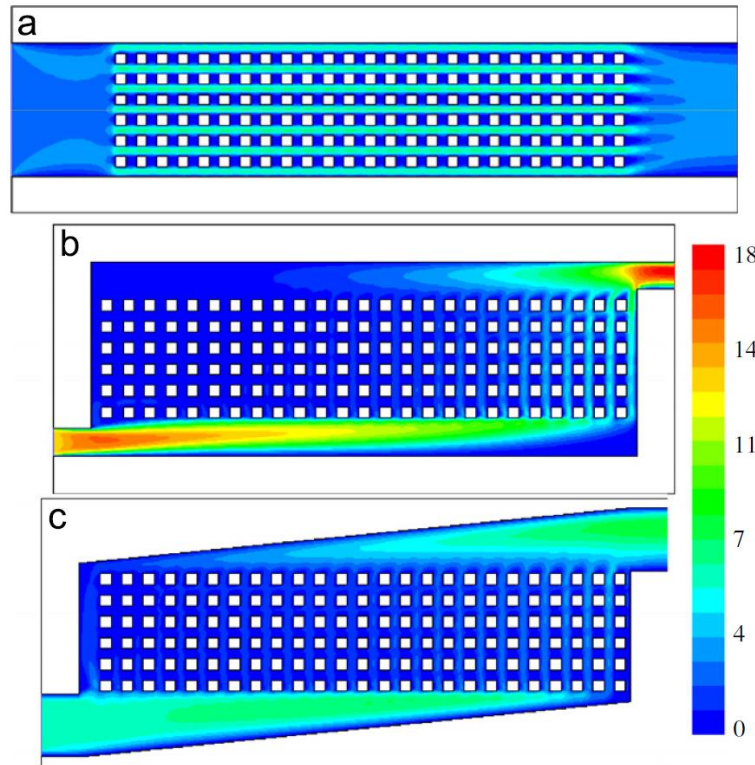


Figure 2.34: Velocity distribution (m/s) in a posted microchannel reactor for propane/air combustion (3.9 L/min feed flow) with (a) axial posts, (b) right-angled inlet and outlets with cross posts, and (c) 5.766° tapered (triangular) inlet and outlets with cross posts. The “cross” configuration refers to the transverse fluid flow vs the inlet/outlet direction. Reprinted from [91] with permission from Elsevier.

Delsman et al. [83] concluded using CFD modelling that flow distributions within microchannel reactors are flow rate dependent, in the sense that there exists (i) a range of low flow rates that are associated with wall friction effects, and (ii) flow rates higher than this range which causes inertia-controlled flow distributions. The transition zone between the two regions of flows is reactor specific (aspect ratio, channels vs posts, flow velocities, fluid properties etc.), and a manifold design for satisfactory flow distribution is not always obvious. Griffini and Gavrilidis [90] also noted this transition zone within a Z-type microchannel plate design discussed previously, and quantified this transition with the Re number (12.83), below which the fluid distribution is independent of flow rate.

Amador et al. [84] noted that equal flow distribution can be achieved by (i) either ensuring that the pressure drop effects of inlet and outlet distribution manifolds is minimal (i.e. similarity of pressure drops within parallel reaction channels creates flow uniformity), or (ii) with detailed

simulations of manifolds in the case of asymmetric manifolds. Manufacturing tolerances and some variations in total flow rate is not as crucial for Case (i), while Case (ii) relies on precise microchannel fabrication and coating techniques, and exact flow rates and fluid densities (i.e. Re number) to achieve flow uniformity. On the other hand, a symmetric bifurcation approach generally provides equal flow distribution, even at high Re numbers, but is prone to larger pressure drops due to the several flow separations/junctions and fluid directional changes [84].

2.3.4.2 Multiple axial inlet points

Kolios et al. [92] investigated the even distribution of methane/air as fuel along the axial length of a modelled combustion channel, coupled to a methane steam reforming channel. A counter-current strategy was followed. This model is a simplification of that first proposed by Frauhammer et al. [93]. Previously, extreme temperature excursions were noticed at the start of the combustion catalyst, when the fuel was fed exclusively to the inlet of the channel [94]. This strategy resulted in a significant temperature spike, similarly observed in other studies. For the distributed feed case (Figure 2.35a), the axial profile of temperature (Figure 2.35b), reforming conversion (Figure 2.35c) and concentration of methane in the combustion channel (Figure 2.35d) was indicative of good thermal coupling between the channels. Virtually the entire length of the microchannel was utilised for the reforming of methane (according to Xu & Froment kinetics [40]).

Of note is the efficient pre-heating of the opposite and incoming cold reactant gas for both reforming and combustion streams (Figure 2.35b). The temperatures of both the reforming and combustion streams seem well linked, and revealing of good thermal coupling. The authors [92,93] did not specify the thermal conductivity of the wall, which is a determining factor of the immediate heat transfer (and ultimately temperature difference) between the microchannels in the pre-heating zones.

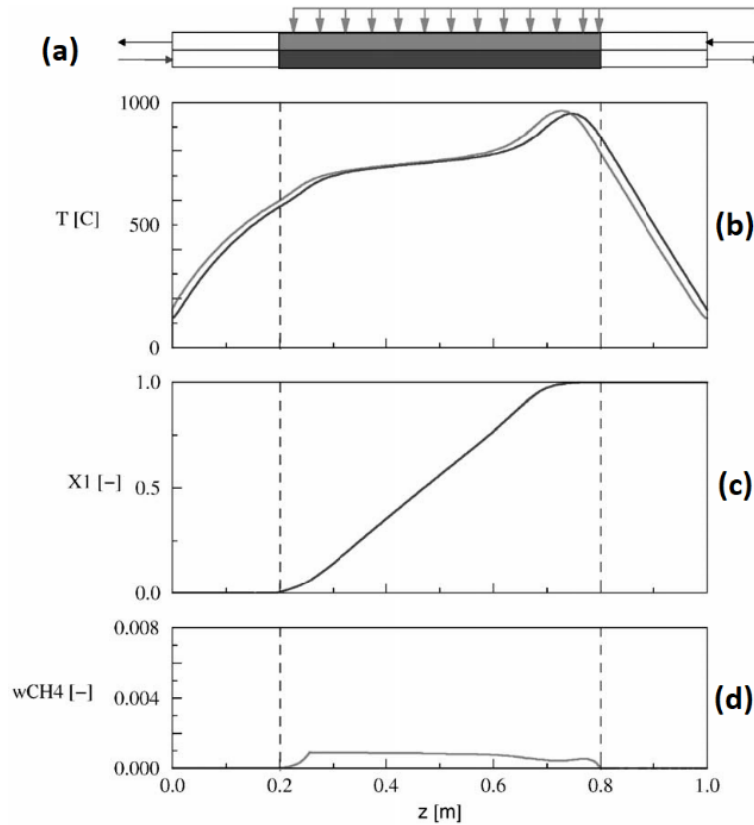


Figure 2.35: (a) Even axial distribution of combustion feed for a counter-current methane steam reforming and methane combustion reactor. Axial profiles for (b) reforming (black line) and combustion (grey line) centreline temperatures, (c) methane reforming conversion and (d) methane concentration in the combustion channel. The methane steam reforming feed is located at axial position $z = 0$ m. Renumbered from [92] with permission from Elsevier.

Pattison et al. [75] investigated both the distribution of combustion and reforming feed gas along the axial coordinate of coupled, counter-current microchannels. This work is a continuation of that previously reported [39] for off-set catalyst distributions (section 2.3.3). Similarly to the effect that segregated catalyst positioning has, the distribution of feed gas allows for selective heat generation and consumption along the axial channel coordinate [75]. With accurate implementation, feed gas distribution reduces the likely occurrence of temperature extremes. The combustion and reforming feeds were introduced at four and three axial locations, respectively (Table 2.3).

Table 2.3: Optimal distributed feed reactor design for coupled counter-current methane steam reforming and methane combustion. Adapted with permission from [75]. Copyright (2004) American Chemical Society.

Variable	Length	Flow fraction
Total reactor length	63.4 cm	-
Combustion feed points	23.8 cm	6.0%
	30.9 cm	58.0%
	35.9 cm	32.8%
	63.4 cm	3.2%
Reforming feed points	0 cm	28.9%
	23.8 cm	61.1%
	30.9 cm	10.0%
Max temperature	915°C (1188 K)	
Reforming conversion	98.8%	
Combustion conversion	99.7%	

The optimised modelling results presented for the distributed gas feed were compared to that of the segregated combustion catalyst (Ref. [72,75]). For the feed distribution case, a temperature maximum of 1188 K was recorded, as well as a respectable temperature plateau established from $\zeta = 0.25$ –1 of the axial coordinate (Figure 2.36). At the inlet of the combustion channel ($\zeta = 1$), the small fraction of combustible mixture fed at the inlet (3.2%) caused a significantly higher temperature (~ 1125 K), compared to the case of the segregated catalyst (~ 925 K), which did not support a combustion catalyst segment at the inlet. As a result, the plateau is more prolonged in the feed distribution case. On the other hand, Pattison et al. [75] concluded that the thermal efficiency of the reactor would be lower in the feed distribution case, as some sensible heat is lost via the reforming gas outlet. However, in a practical system this heat could be re-gained through external heat exchangers of course, which is much cheaper than using parts of the reformer for that purpose.

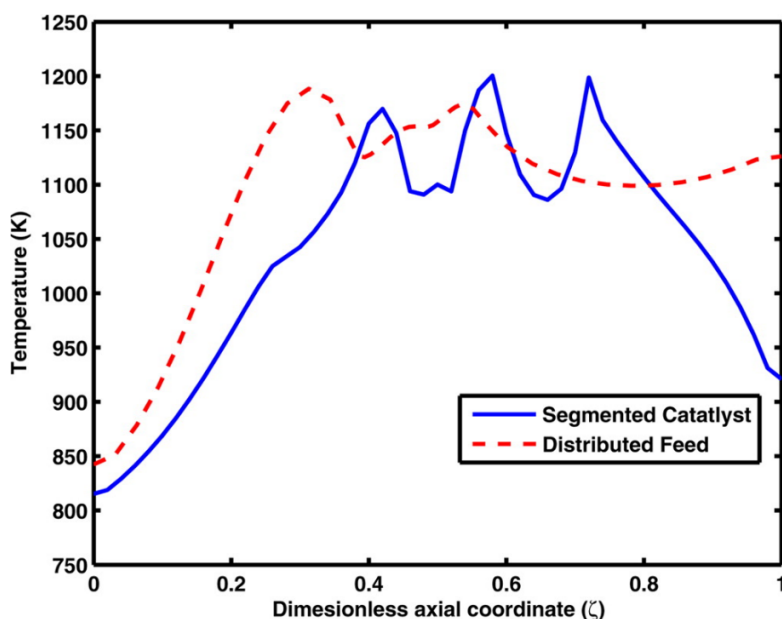


Figure 2.36: Optimal reactor centreline temperature for a coupled counter-current design with a segmented combustion and offset reforming catalyst (solid line, also presented in Figure 2.26b [72]), and distributed reactor feed (dashed line). Results are plotted against the axial dimensionless coordinate (ζ) from the reforming inlet. Reprinted with permission from [75]. Copyright (2004) American Chemical Society.

Methane conversions (Figure 2.37) at the outlets of the reforming (98.8%) and the combustion (99.7%) channels indicate that the feed distribution strategy is feasible, and moreover provided a board temperature plateau with minimal temperature extremes. A close relationship between both temperature and conversion profiles were obtained for the distributed feed and the segmented catalyst scenarios. However, a significant difference exists in how these strategies are implemented [75]. The integration of control instrumentation for multiple feed inlets is challenging in the case of compact microchannel assemblies. Also, distributing the feed evenly to all the respective microchannels would be complex. And so the strategy of segmenting catalysts seems more applicable to limit temperature extremes in microchannels. Though, the segmentation of catalysts has to transpire during the design stage of a coupled microchannel system, and is greatly influenced by spatial design and reaction-specific considerations.

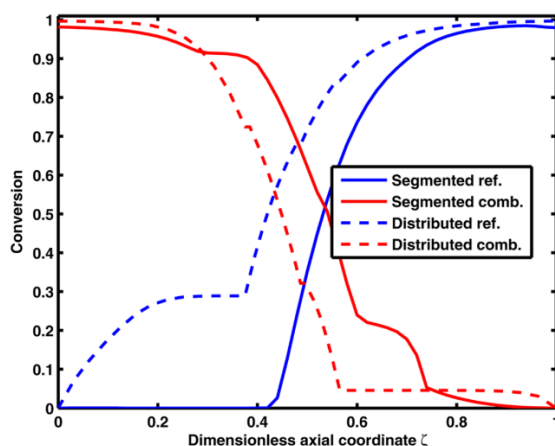


Figure 2.37: Comparison of reforming and combustion axial conversions of a coupled counter-current design with a segmented combustion and offset reforming catalyst (solid lines, representative of Figure 2.26b [72] and Figure 2.36), and distributed reactor feed (dashed lines). Results are plotted against the axial dimensionless coordinate (ζ) from the reforming inlet. Reprinted with permission from [75]. Copyright (2004) American Chemical Society.

2.3.5 Heat recirculative reactor geometry

Kim and Kwon [95] developed and tested a heat-recirculating annular microreactor, which entails the flame combustion of a propane/air mixture, which provided heat for the catalytic decomposition of ammonia towards hydrogen production in the outer shell of the reactor (Figure 2.38). In addition, the flue gas from the combustion reaction entered the innermost tube and pre-heated the incoming cold combustible mixture. Catalysts for the decomposition of ammonia included three separate formulations, namely 65% Ni/SiO₂/Al₂O₃, Ru and Ir, respectively. The catalysts were all in pellet form (200–400 μm). The authors investigated both ammonia and propane/air flow rates to provide isothermal operation and equilibrium ammonia decomposition. The Ru catalyst was preferred as the cheaper option above Ir, while it outperformed the Ni catalyst. Ultimately, a system efficiency of 13.7% and ammonia conversion of 98% were achieved at conditions corresponding to an ammonia flow of 10 mL/min, combustor inlet velocity of 3.1 m/s and equivalence ratio of 1.0. The efficiency might seem very low, but it has to be considered that such systems of smallest scale suffer from significant heat losses to the environment.

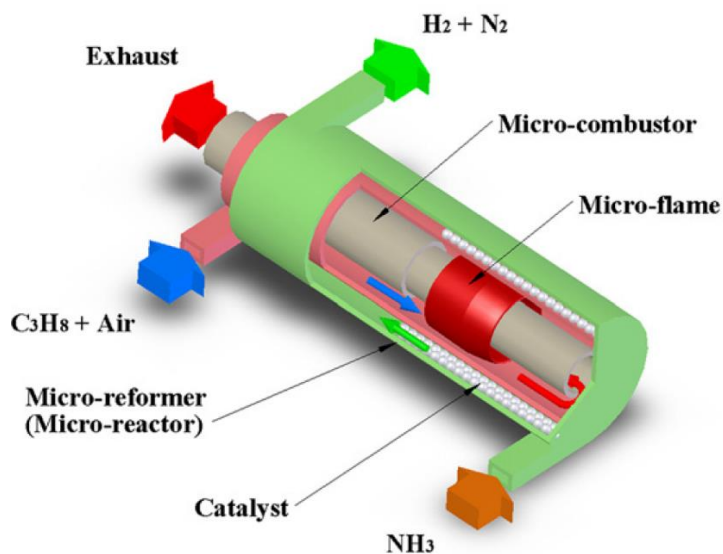


Figure 2.38: Annular-type microreactor for the catalytic reforming of ammonia, using heat-recirculating propane/air flame combustion. Reprinted from [95] with permission from Elsevier.

Butcher et al. [96] described the design of a methane steam reformer (Figure 2.39) consisting of 19 annular reaction tubes with annulus width of 300 μm , catalyst layer thickness of 30 μm and catalyst layer length of 254 mm. Heat recirculation was achieved by pre-heating the reforming feed stream within the inner tubes, while the process was heated by the flame combustion of methane in an outer reaction chamber. Within the combustion/reforming heat transfer region (L4 in Figure 2.39), a thermally conductive porous matrix was located to assist heat transfer towards the steam reforming reaction. The annular reactor was designed for a nominal methane reforming capacity of 19 SL/min, producing H_2 at a rate of 48.3 SL/min. The small annulus width reduced possible diffusional resistances in heat and mass transfer, supporting a high gas space velocity of 391 000 1/h at nominal operating conditions. Thermal efficiencies of 72.7–57.7% were expected operating the reactor in a methane reforming flow range of 12.7–48.1 SL/min.

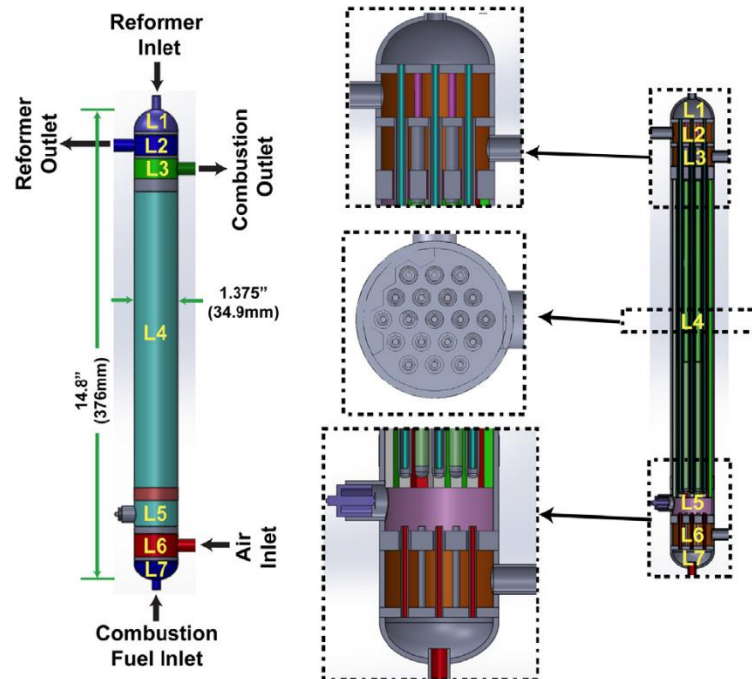


Figure 2.39: Nominal 10 kW annular-type methane steam reformer coupled with methane flame combustion. Reprinted from [96] with permission from Elsevier.

2.4 THERMAL EFFECTS IN EXPERIMENTAL MICROCHANNEL REACTORS DEMONSTRATED TO DATE

A counter-current methanol steam reformer (Figure 2.40) was designed and demonstrated by Kolios and co-workers [59,60]. Although reforming and combustion channels were not in the micro-scale range, the intimate thermal coupling of the “folded sheet” design ensured similar process intensifying characteristics. The folded stainless steel sheet separating the respective reaction chambers was 0.5 mm thick [97]. The reactor capacity was designed as a 10 kW_{th} system, capable of producing hydrogen at a rate of 3 Nm³/h [60,98]. The reactor was designed as a multifunctional device, which evaporates, superheats and reforms the methanol/water feed. In the downstream reforming section, a water-gas shift stage was incorporated to reduce the CO content to 4.3 vol.% [97]. This was necessary owing to the higher operating temperature of the reactor, which generated more CO than usually formed during methanol steam reforming. The reforming catalyst had a lower activity than what was expected, leading to the higher temperatures necessary to obtain satisfactory methanol conversion [97]. A reforming gas temperature in excess of 350°C was modelled in the region where the most combustion heat was released [97]. The fuel gas to the burner consisted of hydrogen which was combusted

catalytically, and had axially distributed inlets to ensure targeted heat release to the methanol evaporation and steam reforming sections [59]. A methanol conversion of $\sim 90\%$ was achieved at $10 \text{ kW}_{\text{th}}$ load, while the reactor demonstrated quick response time to dynamic changes in the methanol feed as a result of its short residence time characteristics [60,98].

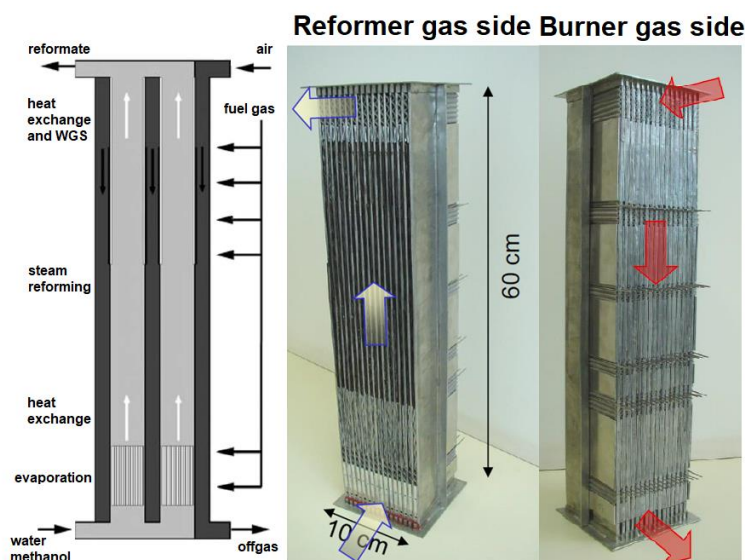


Figure 2.40: Counter-current design of the $10 \text{ kW}_{\text{th}}$ “folded sheet” reactor for the self-sustained reforming of methanol. Adapted from [59,98] with permission from Elsevier and G Eigenberger.

Brooks et al. [58] developed a microchannel reactor with integrated oil cooling capability for the CO_2 methanation (Sabatier) process (Figure 2.41). The reactor was designed and developed for space applications, with the production of methane propellant in mind. Carbon dioxide can be recovered from the atmosphere of Mars, or recycled within the shuttle environment. Hydrogen would be used as reactant and sourced from the oxygen generator (hydrogen by-product).

A 3 wt.% Ru/TiO_2 catalyst coated on metallic felts were used within the microchannels. In addition, a reactive heat-exchanger was included before the inlet to the microchannels to partially convert CO_2/H_2 and, to a certain extent, release reaction heat to the oil. With a one-dimensional numerical model it was calculated that the temperature at the inlet of the microchannels could rise to 650°C if the heat-exchanger was not implemented, and bring detrimental effects to the catalyst in that region. Finally, a mixing chamber was incorporated in the middle of the reactor to bring uniformity to the gas mixture. For a stoichiometric feed ratio of 4:1 ($\text{H}_2:\text{CO}_2$), a CO_2 conversion of 88.4% was achieved (residence time of 95.5 ms).

In this case a gas temperature gradient from 398°C at the inlet to 327°C at the outlet was resultant of the counter-flow strategy implemented, which is favourable for the conversion owing to the thermodynamic equilibrium of the reaction. The oil temperature recorded an increase from 323 to 388°C.

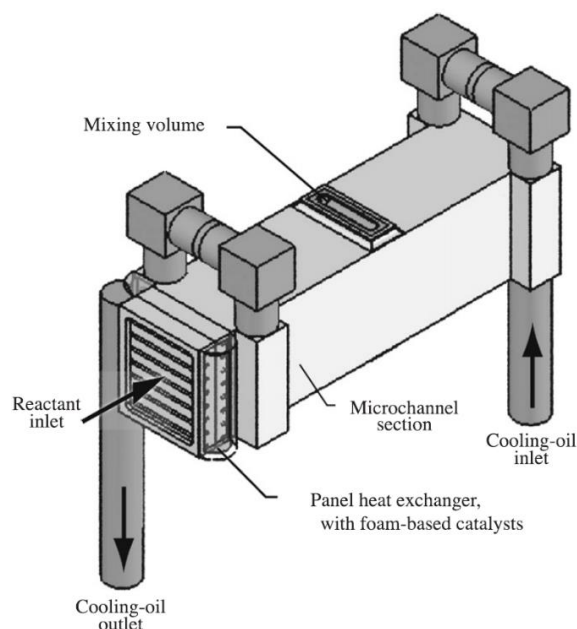


Figure 2.41: CAD drawing of the Sabatier reactor developed by PNNL with counter-current oil cooling. Reprinted from [58] with permission from Elsevier.

A co-currently operated methanol reformer with integrated afterburner was developed as hydrogen supply for a 5 kW high temperature PEM fuel cell by Kolb et al. [99]. The reactor plate stack was composed of 88 plates and had the following dimensions: length 130 mm, width 116 mm, height 100 mm. The reactor was operated at different load between 25% and 100% of the design capacity (feed flow rates: 17.8 L/min air, 3,172 g/h methanol, 2,750 g/h water) with a feed composition equivalent to $S/C = 1.5$ and $O/C = 0.2$ on the reformer side (oxidative steam reforming), while anode off-gas surrogate was applied on the afterburner side of the reactor which was composed of 35% CO_2 , 22.5% H_2 and 42.1% N_2 . Full conversion (>99.999%) of the methanol feed was achieved during all the experiments over the $\text{Pt}/\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ reforming catalyst [46] and also for hydrogen combustion. The temperatures were determined at different axial positions inside the reactor and at three levels 25 mm from the reactor top, in the center and 75 mm from the reactor top.

Figure 2.42 shows the temperature distributions at 25% and 100% load. All in all the temperature distribution in the reactor is quite narrow with maximum differences of 12 and 11

K at 100% and 25% load, respectively. While the temperature profile obtained at 100% load (Figure 2.42: bottom) has the declining shape as is expected from the combination of fast hydrogen combustion and slower reforming reactions, obviously a more dominant effect of heat losses to the environment changed the profile to a slight temperature maximum in the reactor core at lower load (Figure 2.42: top). However, the temperatures are very close in both cases to an isothermal operation, which partially might also originate from axial heat conduction through the walls of the stainless steel plates.

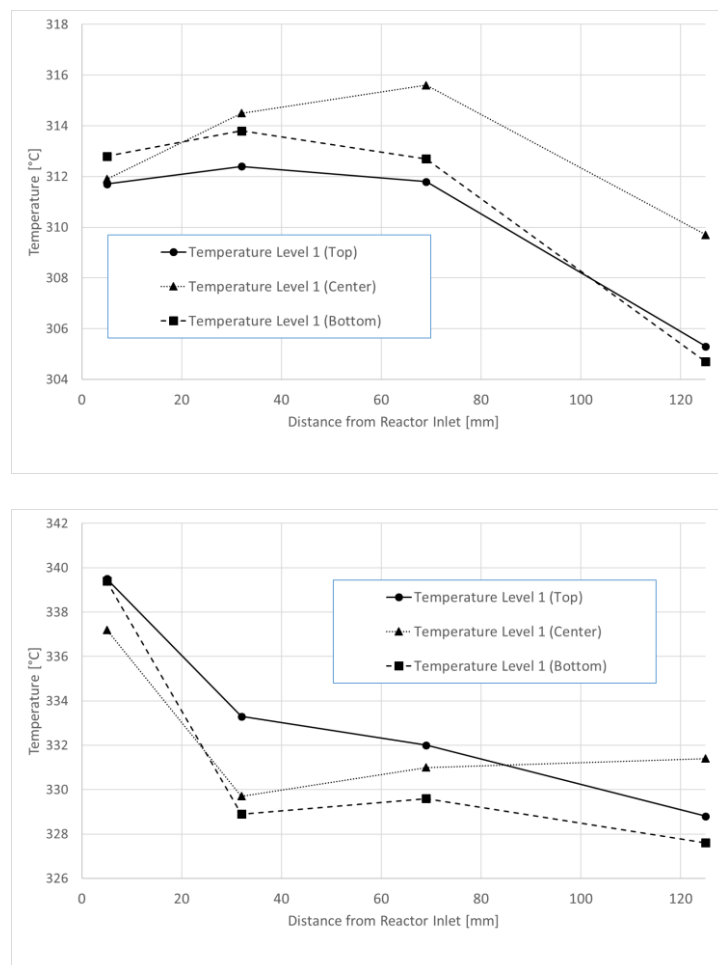


Figure 2.42: Temperature profile in a co-currently operated methanol reformer of 5 kW power equivalent with integrated catalytic afterburner; operating conditions: S/C = 1.54, O/C = 0.2; top: data obtained at 25% of the design feed flow rate; bottom: data obtained at 100% of the design feed flow rate [source: Fraunhofer IMM].

As shown by Kolb et al. [100] for a methanol reformer of smallest scale (100 W power equivalent) in Figure 2.43, isothermal operation is easier achievable when the reactor dimensions are smaller (here: 30 mm height, length and width) and heat conductivity through

the reactor walls more dominant. Similar to the much larger reactor discussed above, the declining temperature profile changes to a central maximum at partial load.

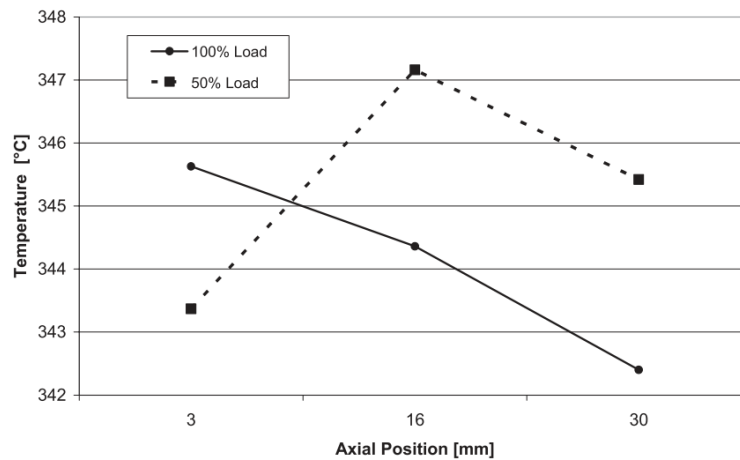


Figure 2.43: Temperature profile at different load in a co-currently operated methanol reformer with integrated catalytic afterburner and a power equivalent of 100 W. Reprinted from [100] with permission from John Wiley & Sons, Inc.

The effect of heat losses gets more and more important obviously when the reactor temperature increases. O'Connell et al. [101] designed and tested a co-currently operated reformer with a power equivalent of 5 kW for diesel fuel. Temperatures exceeding 800°C were required to achieve more or less complete conversion of the feed. The heat losses lead to a sharp temperature maximum exceeding 900°C at higher load in the reactor core as shown in Figure 2.44. The sharper peak at higher load originated also from maldistributions of the afterburner feed in the reactor.

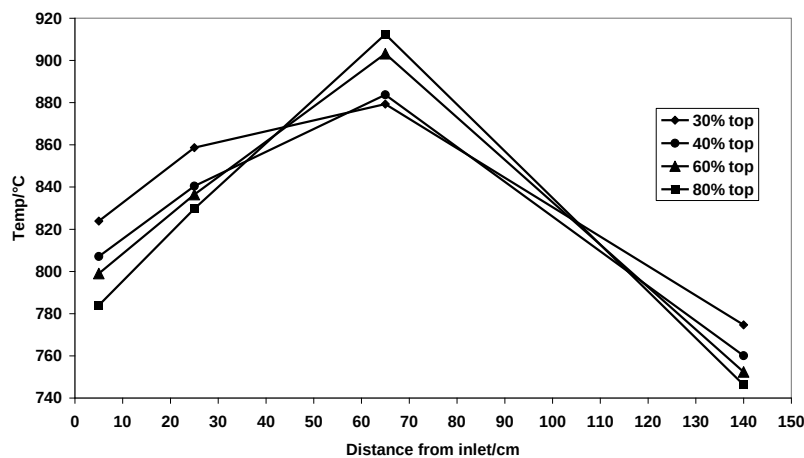


Figure 2.44: Temperature distribution for the top plates of a 5 kW diesel reformer as a function of load level. Reprinted from [101] with permission from Elsevier.

A single stage water-gas shift reactor was developed by Kolb et al. [55] with a net power equivalent in the range of 1 kW of the fuel cell it was designed to supply with hydrogen. It was composed of 36 plates and the plate stack of the reactor had overall dimensions of 145 mm length, 76 mm width and 35 mm height. Owing to the catalyst technology applied, the operating temperature was limited to 425°C. The reactor was cooled by air in a counter-current flow arrangement to utilize the increasing conversion according to the thermodynamic equilibrium near the reactor outlet. It could be shown (see Figure 2.45), that the heat of the water-gas shift reaction, which is generated to a large extent at the reactor inlet, leads to the peculiar situation, that the cooling air outlet temperature is higher than the reformat inlet temperature. Heat losses decreased the reactor temperatures towards the reactor shell.

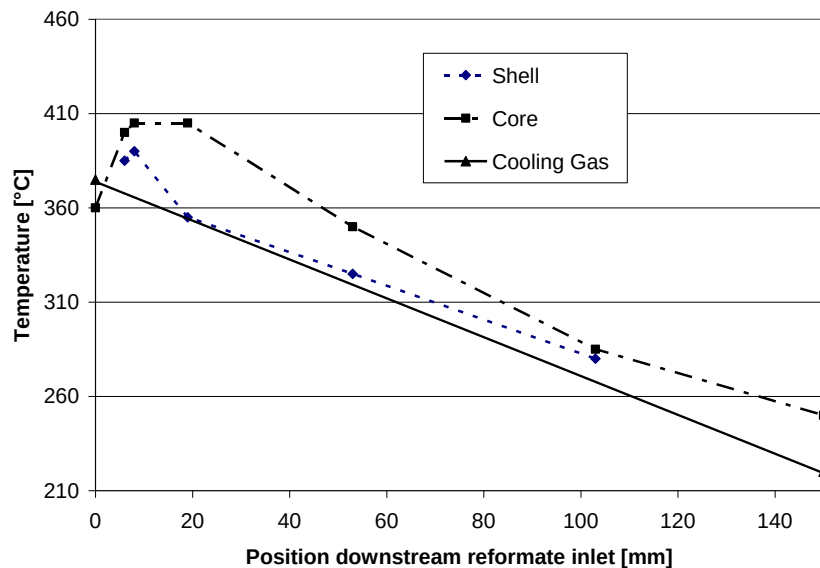


Figure 2.45: Axial temperature profile over the water-gas shift reactor; total reformat flow: 60.1 L/min; cooling gas flow: 87 L/min; cooling gas inlet temperature: 220°C. Reprinted from [55] with permission from Elsevier.

A single stage water-gas shift reactor with a net power equivalent of 5 kW of the fuel cell supplied (6.5 kW gross power, while 1.5 kW was reserved for balance-of-plant) was developed by O'Connell et al. [56]. The reactor was composed of 84 plates carrying reaction channels of 650 μm depth and 1,000 μm width, while the cooling channels were larger, 2 mm wide at the same depth. The whole plate stack of the reactor was 214 mm long, 139 mm wide and 70 mm high with an overall weight of 7.6 kg (see Figure 2.46). Between 94 and 98% conversion were achieved under the experimental conditions applied. The peak temperature of the declining temperature profiles increased with increasing load.

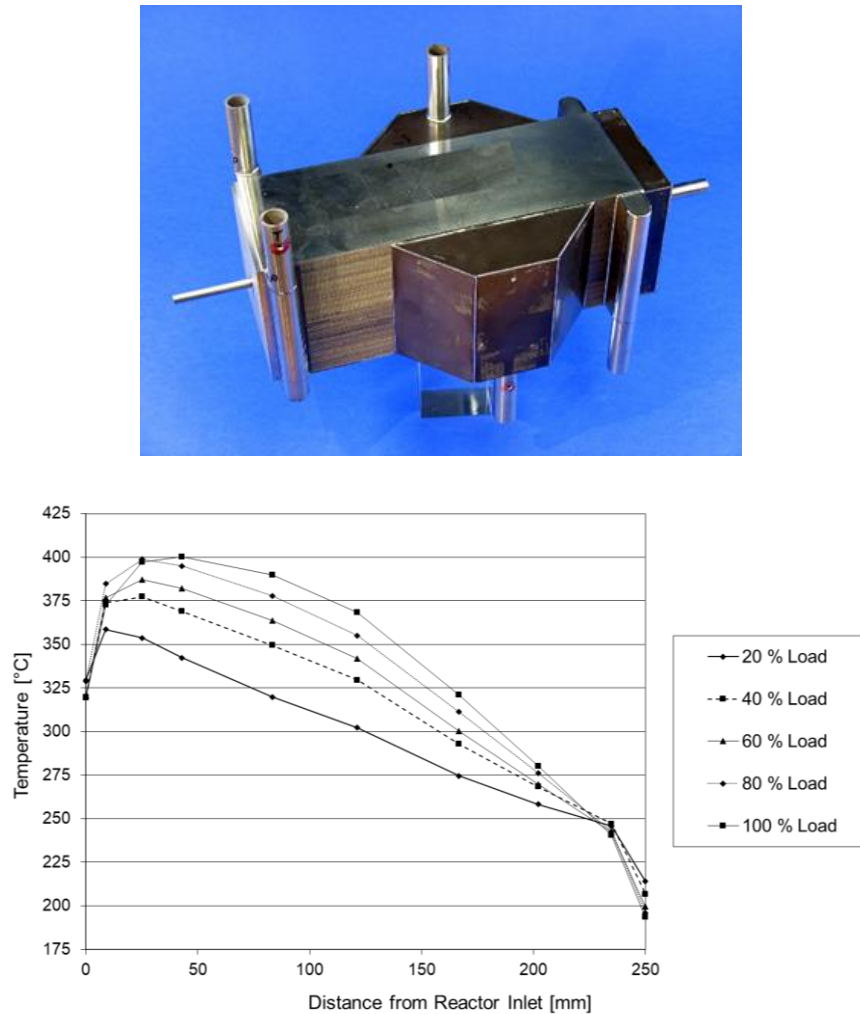


Figure 2.46: (top) Single stage water-gas shift reactor with a net power equivalent of 5 kW; (bottom) temperature profile over the reactor length axis as determined for different load levels in the reactor core [source: Fraunhofer IMM].

The preferential oxidation of carbon monoxide was successfully performed in single stage reactors with power equivalents of 1 kW and 5 kW by co-current evaporation cooling of water in the cooling section of the reactor/heat-exchangers [55,56]. The carbon monoxide contained in the feed of both reactors could be removed successfully to values below 20 ppm through the significantly improved heat management of the reaction. Figure 2.47 shows the temperature profile as obtained for the 5 kW reactor at different load. This is an impressive demonstration of the improvement of the heat management through the application of plate heat-exchanger reactor technology, because it is well known that this reaction/reactor system is very difficult to handle and requires several reactors positioned in series when monolithic reactors are applied.

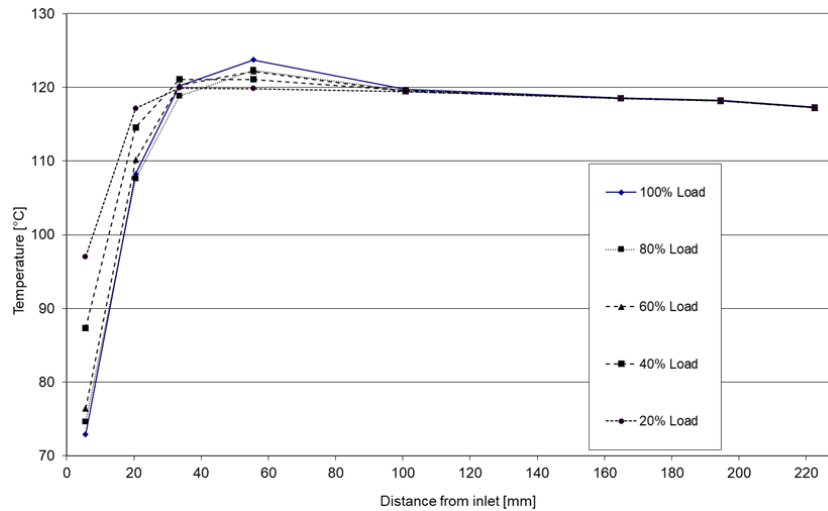


Figure 2.47: Temperature profile over the reactor length axis of a single stage preferential oxidation reactor with a net power equivalent of 5 kW as determined for different load levels in the reactor core [source: Fraunhofer IMM].

A catalytic plate reactor design was employed by Engelbrecht et al. [102] for the thermal coupling of ammonia decomposition and ammonia oxidation. The aim of the work was to establish an efficient process for the carbon-free generation of hydrogen for fuel cell applications. It is envisioned that ammonia will be one of the future, mass-produced energy dense chemicals that will be generated from renewable energy origin. The microchannel reactor contained 1800 microchannels ($W = 500 \mu\text{m}$, $H = 250 \mu\text{m}$ and $L = 10 \text{ cm}$) for both decomposition and oxidation. Ru and Pt catalysts supported on alumina were respectively used for decomposition and oxidation, with catalyst washcoat thicknesses of $45 \mu\text{m}$. The reactor was operated in a co-current configuration.

The reactor exhibited a hydrogen production rate of 8.92 NL/min and a thermal efficiency of 75.9% (calculated based on the lower heating values of ammonia and hydrogen) at the recommended operating point. However, equilibrium limited decomposition produced a hydrogen-rich stream containing 680 ppm ammonia, and so an ammonia purification step is required before fuel cell application. The co-current coupling of ammonia decomposition and oxidation produced a slight declining temperature gradient (118°C across 10 cm axial length) from the maximum obtained at the reactor inlet (Figure 2.48). In a follow-up CFD modelling study [103], the rate of heat transport to the endothermic reaction was highlighted during reactor start-up (and subsequently the fast ramp rate of hydrogen production). This characteristic is an indication of the extent of good thermal coupling between the two reactions.

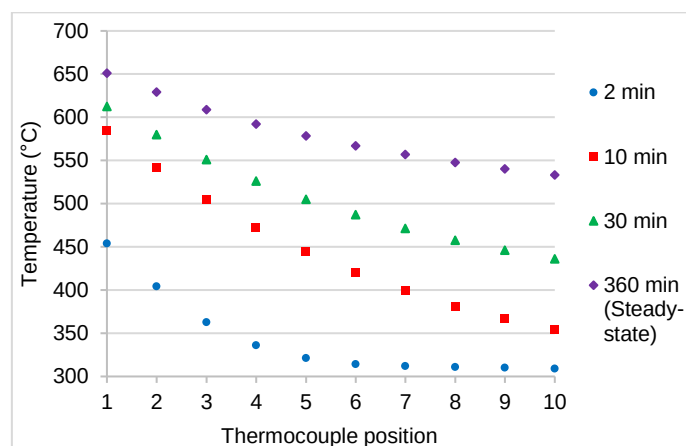


Figure 2.48: Dynamic temperature profile development in a co-current microchannel reactor for coupled ammonia decomposition and oxidation after 2, 10, 30 and 360 min from hot standby (300°C). Conditions correspond to 6 NL/min NH_3 decomposition flow rate, 4 NL/min NH_3 oxidation flow rate, and fuel-oxygen equivalence ratio of 1.4. Reprinted from [102] with permission from Elsevier.

2.5 LIMITATIONS OF CURRENT MICROCHANNEL DESIGN ASPECTS

The fabrication of microchannel plates and catalyst deposition to channel surfaces are cost-intensive processes [9], unless cheap fabrication techniques such as embossing of plates [13] and screen-printing of catalyst [104] are applied along with automated laser welding. Such autonomous manufacturing and the economy-of-scale of mass production will contribute to cost reductions.

Manufacturing tolerances should be considered, as some variations in microchannel and manifold structures can lead to flow maldistribution [84].

With respect to homogeneous/flame combustion, thermal systems are susceptible to thermal quenching when wall surfaces are cold, and radical quenching at high surface temperatures, which both lead to flame extinction [105]. Depending on the wall surface, techniques exist in order to inhibit radical quenching [105].

Moreover, short microchannel diameters may be below the typical quench distance, which prevents flame combustion to occur. This extends to the inherent safety of the small dimensions that can be used for microchannels. These are generally fuel specific (burning velocity) and depend on the thermal conductivity of the wall material [106–108]. Lastly, beyond the fuel specific limits of maximum gas velocity, flame instability and blowout will occur [29].

In the case of plate-type microchannel reactors, the direct contact between microchannel fins and catalyst coatings leads to believe that catalyst sintering at extreme temperatures could be problematic, especially if homogeneous combustion is the heat source [109]. Annular-type microchannel reactors provide some heat transfer resistance between the reforming catalyst and the hot combustion gas [109].

Practical design challenges should be noted, such as the auto-ignition of fuel/air mixtures when excessive temperatures are required for the progression of reforming reactions [59]. For instance during the coupling of methane steam reforming and methane/air combustion, the reforming reaction is known to occur at high temperatures ($>800^{\circ}\text{C}$ [59]), yet the auto-ignition temperature of methane in air is around 580°C . This issue can be solved if steam or carbon dioxide are contained in the feed of the burner, limiting the adiabatic temperature rise of the feed. Flame arresters can also limit the combustion reaction to the reactor body. By these means it is even possible to combust substantial amounts of hydrogen in a reactor as hot as 800°C , as has been demonstrated by O'Connell et al. [101]. The introduction of multiple axial inlet points is a possibility, however the uniform supply of fuel to all the microchannels complicates the design substantially.

2.6 OTHER DESIGN CONSIDERATIONS FOR THE DEVELOPMENT OF MICROCHANNEL SYSTEMS

Although CFD modelling is a valuable tool to evaluate heat and mass transport in microchannel systems, it is important to demonstrate the functionality of these reactors experimentally. Experimental work are typically extended to areas of investigation including: manufacturing and coating techniques, dynamic (start/stop) operation, balance-of-plant effectiveness, catalyst deactivation and troubleshooting, and costing of microchannel processors [13,110].

Generally, heat recovery from a reaction system is preferred [111]. This may extend to design changes which improve heat recirculation (feed pre-heaters etc.). For medium to large-scale kW systems, low-grade heat recovery is often also a prerequisite to achieve maximum system energy efficiency (e.g. waste heat boiler). However, a trade-off is always required between system complexity (and cost) against efficiency for systems of smaller than industrial scale.

Thermal insulation around reactors and other hot components improves heat utilisation significantly. An example is when reforming reactions, which are endothermic, are targeted and maximum heat needs to be utilised from the heat producing reaction. For lab/development

systems in the order of watts, heat losses may result in self-sustained operation not being achieved. Novel insulation concepts such as vacuum insulation and reflection of radiation losses for high reaction temperatures have to be taken into consideration.

Typically, microchannels have aspect ratios (L/D) much larger than conventional bed-type or tube reactors. Besides the increased catalyst surface area, heat transfer, as discussed in this review, is emphasised. Generally, microchannels are characterised by laminar flow ($1 < Re < 100$) [17]. Heat transfer (Nusselt number), which bears strong correlation to the Reynolds number, can be further increased with unconventional flow patterns or micro-structured fins [62]. However, this usually happens with an increased pressure drop [112].

The diffusion driven mass transport within microchannels (as a result of laminar flow) means that mass transfer (Sherwood number) is enhanced with smaller characteristic channel dimensions [1]. Flow patterns, such as zig-zags, improve reactant mixing and can lead to higher conversions [113]. On the other hand, hydrodynamic effects such as pressure drop will increase with these modifications, and a compensation is often required for an optimal microchannel design [1,62].

Due to microchannels having very small hydraulic diameters ($\sim 0.01\text{--}1\text{ mm}^2$), pressure drop effects may result in limitations of microchannel length [80]. In such cases, the ability to utilise microchannels in parallel becomes essential to achieve desired reactor throughput.

The addition of gas diffusers to the inlet and outlet sections of microchannel reactors will provide improved subdivision of the feed gas to the microchannels [57].

It is imperative that catalyst washcoats/deposits are applied to microchannels according to proven coating techniques [9,114,115]. Uneven coatings or the loss of catalyst with time might result in temperature and product composition anomalies. In extreme cases, catalyst replacement – if possible – is necessary. On the other hand, catalyst pellets may attrite during shaking (e.g. mobile reformers for hydrogen production), while powdered catalysts may agglomerate and block microchannels [116].

Additionally, care has to be taken when implementing microchannel reactors in real-world scenarios. Impurities such as sulphur- and nitrogen-containing compounds are detrimental to most base-metal catalysts used for reforming, methanation and hydrogenation processes [117]. Although undesired in all chemical processes, catalyst replacement in the event of deactivation is difficult – and in most cases impossible – using microchannels. In addition to the use of

purification technologies, large fixed-beds have the advantage of multiple catalytic beds, some of them providing protection (higher adsorption capacity) against poisoning in the case of feed gas impurity. This extends to high and low temperature regions which might affect undesired catalyst deactivation.

2.7 CONCLUSIONS

This paper reviewed the design configurations of thermally coupled microchannel reactors for gas processing. In many cases, modelling techniques were used to deliberate on the dynamic reaction space within the length of microchannels, while the performance of experimental reactors were also discussed throughout. Microchannel reactors have demonstrated applicability for hetero/homogeneous combustion, chemicals synthesis, fuel reforming, methanation, shift reactions and purification systems. For each process, certain thermal effects are favourable, and can be accomplished by configuring microchannel reactors in counter-current flow (typical for equilibrium favouring conditions), co-current flow (limiting maximum temperature operation) or cross-flow (to provide near-isothermal conditions). Although some limitations in terms of practicality and operability were discussed for each flow configuration, they should not negate the use of these configurations, provided the reactor is design and reaction specific, and exothermic and endothermic reactions are properly balanced to ensure thermal synchronisation.

Other strategies to improve temperature distributions, production rates and product selectivity have been mentioned via the proper selection of reactor materials, microchannel sizes, catalyst positioning and feed gas distribution. In particular, it was noticed that the thermal conductivity of the wall material, which essentially transfers heat to and from spatially segregated reaction chambers, is very important. Heat transfer should not be hampered by low conductivity materials, yet the efficiency of the heat exchanger device should not be lost by exceptionally high wall conductivities. Nevertheless, high heat conductivity might be an option where isothermal operation is required (reactors fabricated from Aluminium).

From the works presented, it is obvious that microchannel reactors have the ability to improve overall reaction kinetics and catalyst productivity, with fast heat and mass transfer rates. Even at high processing capacity, it is often not kinetics but thermodynamic equilibrium that governs reaction products. It is therefore possible, through carefully controlled temperature profiles

along microchannels, that improved product selectivity can be achieved when matching the axial temperature with thermodynamic isotherms.

The scalability of microchannel reactors allows for the design of multi-kilowatt and even megawatt systems to be realised, both from known mass transport rates and catalyst productivities of smaller microchannel reactors and fabrication techniques available now. The development of microreactors of that scale is on its way and will pave the ground for their application in a variety of fields such as power-to-gas, synthesis of liquid fuels and chemicals and energy generation. Heat loss at the very small design-scale could be problematic in scaling the thermal effects of large/heat-integrated reactors, although this effect becomes lesser for increased reactor sizes due to lower exposed surface-to-volume ratios. It is envisioned that within the next decade, the favourable and process intensifying characteristics of microchannel reactors will result in significant strides towards the demonstration of pilot- and commercial scale microchannel-based fuel processors, as a world-wide trend of “productivity” over “sheer size” is apparent.

2.8 REFERENCES

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CHAPTER 3

A HIGHLY EFFICIENT AUTOTHERMAL MICROCHANNEL REACTOR FOR AMMONIA DECOMPOSITION: ANALYSIS OF HYDROGEN PRODUCTION IN TRANSIENT AND STEADY-STATE REGIMES

CHAPTER OVERVIEW (ABSTRACT)

The experimental evaluation of an autothermal microchannel reactor for H₂ production from NH₃ decomposition is described. The reactor design incorporates an autothermal approach, with added NH₃ oxidation, for coupled heat supply to the endothermic decomposition reaction. An alternating catalytic plate arrangement is used to accomplish this thermal coupling in a cocurrent flow strategy. Detailed analysis of the transient operating regime associated with reactor start-up and steady-state results is presented. The effects of operating parameters on reactor performance are investigated, specifically, the NH₃ decomposition flow rate, NH₃ oxidation flow rate, and fuel-oxygen equivalence ratio. Overall, the reactor exhibits rapid response time during start-up; within 60 min, H₂ production is approximately 95% of steady-state values. The recommended operating point for steady-state H₂ production corresponds to an NH₃ decomposition flow rate of 6 NL min⁻¹, NH₃ oxidation flow rate of 4 NL min⁻¹, and fuel-oxygen equivalence ratio of 1.4. Under these flows, NH₃ conversion of 99.8% and H₂ equivalent fuel cell power output of 0.71 kW_e is achieved. The reactor shows good heat utilization with a thermal efficiency of 75.9%. An efficient autothermal reactor design is therefore demonstrated, which may be upscaled to a multi-kW H₂ production system for commercial implementation.

Engelbrecht, N., Chiuta, S., Bessarabov, D.G. 2018. A highly efficient autothermal microchannel reactor for ammonia decomposition: Analysis of hydrogen production in transient and steady-state regimes. *Journal of Power Sources*, 386:47–55.

3.1 INTRODUCTION

Recently hydrogen (H₂) received extensive consideration as a clean energy source through fuel cell applications [1–4]. However, global capacity relating to H₂ storage and distribution infrastructure is not yet established; it remains one of the greatest factors impeding the development of a H₂ energy economy [5,6]. Hydrogen also supports a low volumetric energy density. Hydrogen dense energy carriers such as ammonia (NH₃) and methanol (CH₃OH) are thus suitable for transport and on-site H₂ generation [1–4,6,7]. On the other hand, a recent universal trend has shaped to distance from fossil fuels and carbon-containing compounds for power generation [8,9]. As a carbon-free energy carrier, NH₃ is a particularly attractive option for H₂ generation as it supports a hydrogen density of 108.5 kg m⁻³ at 8.57 bar_a (saturated liquid at 20°C) [10]. Also, NH₃ has a large global production capacity of 100 million tons y⁻¹ [5]. The process of NH₃ decomposition (often called reforming) produces H₂ through a slightly endothermic reaction (reaction 3.1). This reaction takes place over a suitable catalyst (Ru or Ni) at temperatures of 500–700°C [11].



Although NH₃ decomposition is a convenient process for on-site H₂ generation, the endothermicity of reaction makes it dependent on a heat source [12]. As such, self-sustained (autothermal) reactor operation is necessary for independent and continuous H₂ supply in off-grid locations [11,13]. Thermal coupling of chemical processes is well-known and a powerful tool to increase process efficiency and reduce equipment size and cost [14]. To simplify logistical issues, NH₃ oxidation is considered to supply in the thermal requirements of the decomposition reaction. Consequently, a single transported fuel is required for H₂ generation. Ammonia oxidation (reaction 2) is a viable heat source, as atmospheric nitrogen (N₂) and water are the main product species. Other possible oxidation products include nitrous oxide (N₂O) and nitric oxide (NO) through reactions 3–4, however not desired in this application.

Heat supply from NH₃ oxidation/combustion is sustainable and may take place homogeneously (flame) or catalytically. The simplicity of homogeneous combustion is an attractive prospect

to satisfy thermal requirements. However, to achieve improved heat and mass transfer in small-to-medium-scale H_2 generation applications, homogeneous combustion may be susceptible to thermal and radical quenching [2,15,16]. In contrast, catalytic combustion supports broader operating limits and has the ability to improve fuel conversion at much lower reaction temperatures [14,16,17]. Material and catalyst stability is therefore sustainable at realistic flow velocities. In previous studies, lower reactor temperatures and using N_2 selective catalysts (e.g. Pt/Al_2O_3) proved to significantly reduce N_2O and NO_x formation [18,19]. Furthermore, fuel rich conditions influence thermodynamic equilibrium in favor of N_2 formation through so-called selective catalytic reduction (SCR) reactions [8,9,18].

To achieve distributed H_2 generation through NH_3 reforming, compact reactor setups are necessary. Also, an efficient thermal coupling between the endothermic NH_3 decomposition and exothermic NH_3 oxidation reaction is pre-requisite [2,17]. Microchannel reactor technology is easily scaled to desired generation capacity, and proves convenient when incorporated in modularized plants [12,16,17]. These reactors have characteristic small diffusion paths and essentially support fast reaction rates through process intensification [14,20]. A central heat-conducting plate is characteristic between spatially coupled microchannels [17]. A wide range of process conditions, reactions, catalysts and flow configuration (co-, counter- and cross-flow) contribute to the multi-functionality of these reactors [21]. The use of cocurrent flow configurations proved beneficial in the coupling with a highly exothermic reaction [15,22]. Enhanced heat transfer was achieved at the reactor inlet region where high reaction rates dominate. Similar thermal behavior is envisioned in the coupling with the highly exothermic NH_3 oxidation reaction.

Autothermal NH_3 decomposition in a microchannel reactor was the focus of previous modeling studies [15,16,23–25]. In all these studies, the oxidation of hydrocarbons is considered as the heat source. An experimental study was reported on NH_3 decomposition in a microchannel reactor, in which catalytic butane combustion provided in thermal requirements [26]. Although hydrocarbon combustion provides as a reliable heat source, CO_2 is formed and considered an unfavorable by-product [6,9]. Other studies have focused on the reforming of methanol [21,27–33], methane [12,13,17,22,34–45], ethane [14,46] and iso-octane [47] as fuel in reactor-heat exchangers, but not discussed further in this work. Recent work published by our research group [18] investigated coupled NH_3 decomposition and oxidation as an effective autothermal operating strategy. A significant improvement on the thermal efficiency of electrically heated

reactors (25.5% [48]) was obtained (57.3%). However, due to the small reactor size tested (45 W_e), the necessity exists to ascertain NH₃ as fuel for H₂ generation technology at increased volumetric throughput. Also, due to the high surface to volume ratio typical of the miniaturized reactor, the thermal efficiency can be increased further, when heat loss is reduced in an upscaled reactor.

This work is therefore a continuation of the work previously reported by Chiuta et al. [18]. Specifically, the objective of this study is to assess the performance of an upscaled (theoretical 1 kW_e) autothermal reactor for NH₃ decomposition. This reactor development and testing provides a basis for multi-kW H₂ power generation systems which can be commercialized. The effect of NH₃ decomposition flow rate, oxidation flow rate and fuel-oxygen equivalence ratio is investigated in order to identify operating parameters associated with improved steady-state conversion, H₂ production rate and reactor efficiency. In addition, transient reactor behavior is characterized to conclude on overall reactor performance.

3.2 METHODOLOGY

This section describes the apparatus used during the experimental investigation of the microchannel reactor. In particular, the reactor design, catalyst preparation and all apparatus used and procedures followed are conferred.

3.2.1 Reactor design

The microchannel reactor was designed and fabricated in collaboration with Fraunhofer-ICT-IMM (Mainz, Germany). To accommodate enhanced thermal-coupling between reactions the microchannel reactor was designed as stacked, alternating catalytic plates of oxidation and decomposition reaction zones (identical geometry) [49]. Each double-sided microstructured plate (stainless steel 310, German classification 1.4841) was chemically etched with 50 microchannels ($W = 500 \mu\text{m}$, $H = 250 \mu\text{m}$ and $L = 10 \text{ cm}$) on both sides of the plate (Figure 3.1) [50]. These plates were stacked in a face-to-face arrangement for oxidation and decomposition, respectively. Finally, two stacks of plates, each with 17 double-sided and two one-sided microstructured plates, one for decomposition and one for oxidation, were separated by a central plate incorporating ten evenly spaced 0.6 mm bores for thermocouples (Figure 3.2). These plates were laser-welded into a compact stack, to which was added gas diffusers and inlet and outlet tubing ($\text{OD} = \frac{1}{4} \text{ inch}$). In total, the reactor consisted of 1800 oxidation and 1800 decomposition microchannels. For the purpose of reactor start-up, a heating block

incorporating four heating cartridges (300 W, Watlow FIREROD®) with integrated K-type thermocouples was supplied with the reactor.

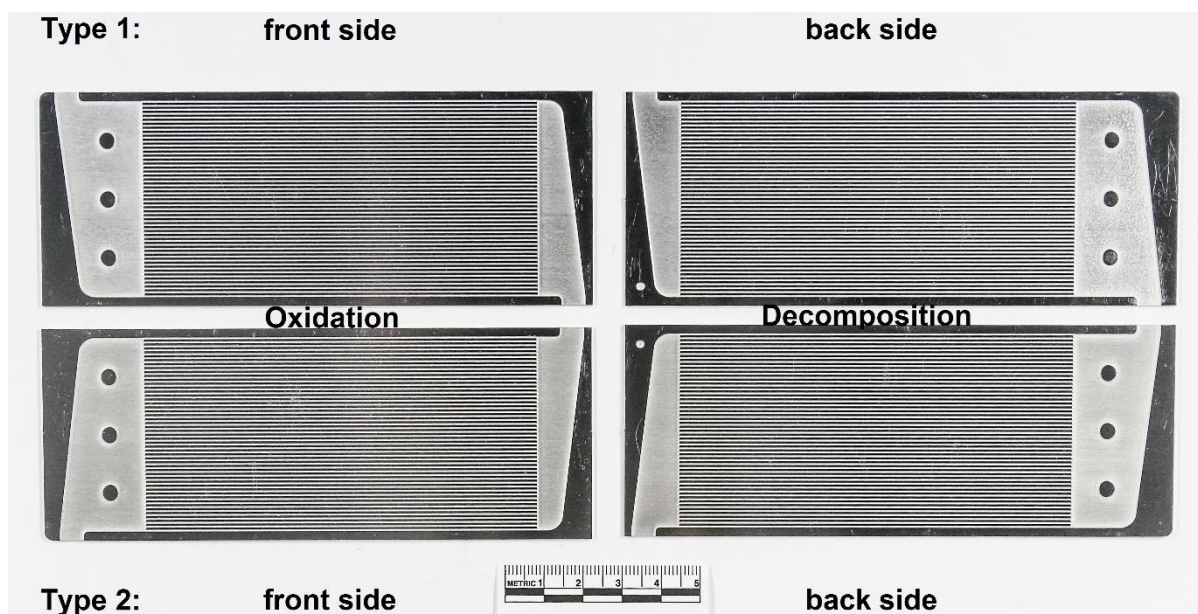


Figure 3.1: Alternating microchannel plate arrangement of NH_3 oxidation (left) and NH_3 decomposition (right) reaction zones.

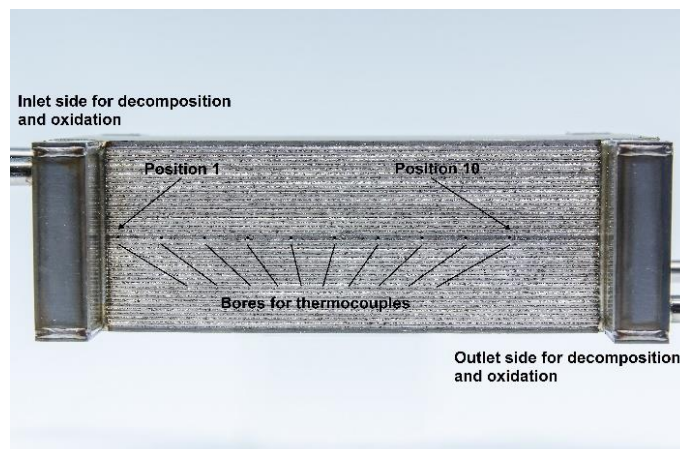


Figure 3.2: Schematic representation of laser-welded microchannel reactor with integrated bores for ten evenly spaced thermocouples.

3.2.2 Catalyst preparation

As in our recent work on autothermal NH_3 decomposition [18,51], we selected a commercial 8.5 wt.% $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst (Hypermec, 10010™) for NH_3 decomposition and a 5 wt.% $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst (Sigma-Aldrich, 205974) for the NH_3 oxidation reaction. These catalysts have BET surface areas of $113 \text{ m}^2 \text{ g}^{-1}$ and $134.7 \text{ m}^2 \text{ g}^{-1}$, respectively. Chiuta et al. [48] showed

that Ru catalyst performance is significantly better than a commercial Ni catalyst for NH_3 decomposition, thus its use in this work. The Pt catalyst was selected as it is a versatile and active catalyst for various oxidation reactions [30,45,52–54]. Identical preparation methods were followed for both these catalysts. The catalysts were milled to the desired particle size before commencing with the washcoating procedure. A chemical binder, polyvinyl alcohol, was dissolved in deionized water and the solution was stirred for 2 hours at 65°C. The solution was left to stand overnight, without stirring. The catalyst powder and acetic acid were then added, and the resulting mixture was stirred for 2 h at 65°C. Stirring was continued for approximately 72 hours to release all air bubbles and to obtain a homogeneous catalyst suspension. The microchannels were filled with the mixture before any excess suspension was removed. The catalyst was dried at ambient temperature before calcination in air was initiated at 450°C for 6 hours. A second calcination step was repeated at the same conditions. The final catalyst washcoat thickness was approximately 45 μm . This preparation method is a slight modification to the original procedure described in Ref. [55].

3.2.3 Experimental apparatus

The supply of anhydrous NH_3 (99.99%) was split via a T-piece to both reaction chambers. Pure NH_3 was supplied to the decomposition side, while a mixture of NH_3 and O_2 (99.99%) was fed to the oxidation side. These gases were regulated by respective Brooks SLA5850 thermal mass flow controllers. In addition, N_2 was connected via a 3-way valve to the NH_3 supply line for the reactor start-up and cooldown procedures. Two Watlow FIREROD[®] heating cartridges (300 W each) were used for the sole purpose of reactor start-up before autothermal operation was initiated. Ten K-type thermocouples (0.5 mm OD) were placed uniformly along the axial length of the reactor (Figure 3.2) to determine the reactor temperature profile. An AT9000 differential pressure transmitter was used for pressure drop measurements. The composition of the reformat gas was analyzed downstream of the reformer using a SRI8610C gas chromatograph (GC) equipped with two thermal conductivity detectors and one helium ionization detector. The total flow rate of the reformat gas was measured with a Bronkhorst[®] (EL-flow) mass flow meter. On the oxidation side, a water bath was used to cool the product gas. The condensate was separated from the fuel gas and collected in a round bottom flask. At the recommended operating point, the flue gas composition was analyzed using the GC.

3.2.4 Experimental procedure

Reactor start-up involved a heating procedure (approximately 45 min) using the heating cartridges to reach a light-off temperature (300°C) for the oxidation reaction. During both the start-up and cooldown procedures, a flow of N₂ (1 NL min⁻¹) was used in the decomposition and in the oxidation reaction zones to prevent thermal sintering of the catalysts. Once 300°C was reached, the operational flow rates were fixed for NH₃ decomposition and oxidation, and the heating cartridges were switched off. National InstrumentsTM LabVIEW software was used to control all flow controllers and log data in 1-min intervals. The mass flow measurements and thermocouple readings (ten) were recorded. Decomposition product gas samples were analyzed after 15 min and thereafter in 30-min intervals after initiation of autothermal operation.

Daily experiments, lasting a total of 6 h (continuous hours), were conducted to obtain one steady-state experimental data point. Approximately 280 h of experimental work was conducted at NH₃ decomposition flow rates corresponding to 2–8 NL min⁻¹. Depending on the decomposition flow rate, the total oxidation flow was varied in a range of 1–4 NL min⁻¹ to restrict the maximum reactor temperature exceeding 650°C (defined as the material stability limit). This limit is established as the maximum working temperature due to the nature of the corrosive (NH₃) and oxidising (O₂) environments that exist during reactor operation. More details regarding this limit are presented in the recent paper of Chiuta & Bessarabov [18]. The fuel-oxygen equivalence ratio (Eqn. 3.5) was varied between values of 1.2, 1.4, and 1.6, for all flow conditions. This parameter is defined as the ratio of ammonia fuel to oxygen relative to the average stoichiometric ratio of reactions (2–4). Finally, to investigate reactor performance stability, a continuous 24 h experiment was conducted at conditions corresponding to a decomposition flow rate of 8 NL min⁻¹, oxidation flow rate of 4 NL min⁻¹, and equivalence ratio of 1.4.

$$\phi = \frac{(a_{NH_3}/a_{O_2})}{(a_{NH_3}/a_{O_2})_{stoic}} \quad 3.5$$

3.3 RESULTS AND DISCUSSION

The experimental results pertaining to transient and steady-state reactor operation are now described. The reactor performance stability and recommended operating conditions are also discussed. The reactor performance is assessed on parameters including the NH_3 decomposition conversion (Eqn. 3.6), H_2 equivalent fuel cell power output (Eqn. 3.7), and reactor thermal efficiency (Eqn. 3.8). For these calculations a PEM fuel cell efficiency (η_{PEM}) of 60%, H_2 utilization rate (θ_{PEM}) of 80%, and lower heating values of 120.0 and 18.6 MJ kg^{-1} for H_2 and NH_3 , respectively, are assumed.

$$X_{\text{NH}_3} = \frac{\dot{n}_{\text{NH}_3 \text{ in}} - \dot{n}_{\text{NH}_3 \text{ out}}}{\dot{n}_{\text{NH}_3 \text{ in}}} \times 100\% \quad 3.6$$

$$P_{eq} = \eta_{\text{PEM}} \theta_{\text{PEM}} \dot{m}_{\text{H}_2} \text{LHV}_{\text{H}_2} \quad 3.7$$

$$\eta = \frac{(\text{LHV}_{\text{H}_2} \times \dot{m}_{\text{H}_2 \text{ out}})_{\text{decomp}}}{(\text{LHV}_{\text{NH}_3} \times \dot{m}_{\text{NH}_3 \text{ in}})_{\text{decomp}} + (\text{LHV}_{\text{NH}_3} \times \dot{m}_{\text{NH}_3 \text{ out}})_{\text{oxi}}} \times 100\% \quad 3.8$$

3.3.1 Transient operating regime

The dynamics of autothermal reactor operation is illustrated in Figure 3.3 for an NH_3 decomposition flow rate of 6 NL min^{-1} , NH_3 oxidation flow rate of 4 NL min^{-1} , and fuel-oxygen equivalence ratio of 1.4. This dynamic operating regime is a result of switching from the inert N_2 flow to the respective reactants for the decomposition and oxidation reactions. As soon as these flows are introduced to the reactor, the temperature increases sharply at the reactor inlet (thermocouple 1) due to the extent of the exothermic oxidation reaction (Figure 3.3a). A temperature of 454°C is recorded within 2 min at the first thermocouple position. Thereafter, the temperature profile across the reactor increases steadily as a result of continual surplus heat supply by the oxidation reaction. An interesting observation is that the downstream reactor temperature (thermocouple 10) shows a time lag; it is initially slow to respond to transient operation being initiated. The inlet and downstream reactor temperatures thus exhibit response times on different time-scales, characteristic of different orders of magnitude in reaction rates, at these positions.

As the reactor temperature increases, progressively more heat is consumed by the endothermic decomposition reaction, promoting H_2 formation (Figure 3.3b). About 95% of steady-state conversion values is achieved within 60 min after initiation. This transient behaviour is observed for all flow conditions investigated. Close to steady-state operation is obtained after

approximately 180 min time on stream. Theoretically, the energy balance, comprising reaction heat generation, heat consumption, and gas enthalpies at the reactor inlets and outlets, is balanced at steady-state.

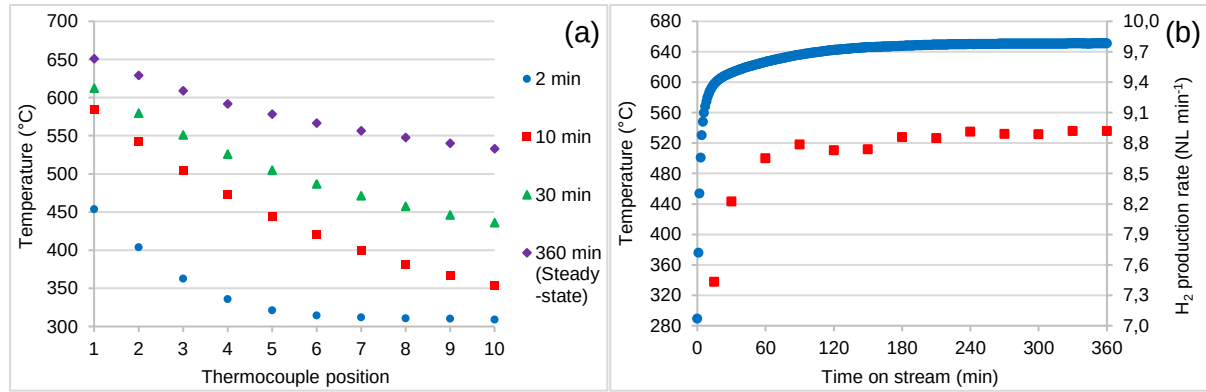


Figure 3.3: (a) Development of reactor temperature profile during the transient regime after 2, 10, 30 and 360 min. (b) Reactor inlet temperature (thermocouple 1) and H₂ production rate vs time on stream. Conditions correspond to 6 NL min⁻¹ NH₃ decomposition flow rate, 4 NL min⁻¹ NH₃ oxidation flow rate, and fuel-oxygen equivalence ratio of 1.4.

3.3.2 Steady-state reactor performance

3.3.2.1 Effect of decomposition and oxidation flow rates

The effects of NH₃ decomposition flow rate (2–8 NL min⁻¹) and NH₃ oxidation flow rate (1–4 NL min⁻¹) on steady-state measurements for the maximum reactor temperature (measured at the reactor inlet) and NH₃ decomposition conversion are shown in Figure 3.4 for an equivalence ratio of 1.4. With increasing decomposition flow, the maximum reactor temperature decreases as a result of increased heat consumption in the decomposition chamber. For the purposes of comparison, consider a decomposition flow rate of 6 NL min⁻¹ and oxidation flow rate of 3 NL min⁻¹. Here, a maximum reactor temperature of 604°C is noted. However, when a decomposition flow rate of 8 NL min⁻¹ (33.3% increase in flow) is used at the same oxidation flow, the temperature decreases by 58°C, to 546 °C. Although the decomposition reaction is only mildly endothermic, the increased enthalpy requirement also consumes heat and reduces the steady-state temperature. The corresponding NH₃ conversion under these flow conditions decreases from 89.4% to 58.9%. Generally, the NH₃ decomposition conversion (Figure 3.4b) shows strong correlation to the maximum reactor temperature for the corresponding oxidation flow rates.

Overall, an increase in oxidation flow results in significant increases in maximum reactor temperature at constant decomposition flow rates. For comparison, if a 33.3% increase in oxidation flow (from 3 to 4 NL min⁻¹) is considered at a decomposition flow rate of 6 NL min⁻¹, the maximum reactor temperature increases by 47°C, to 651°C. With respect to operability limits, the oxidation reaction is thus restricted to narrow flow ranges for reasonable decomposition flows (6–8 NL min⁻¹) due to the large exotherm of the oxidation reaction. As a result, flow ranges (for both reactions) that provide satisfactory reactor performance are identified for sustainable reactor operation. Conditions corresponding to a decomposition flow rate of 6 NL min⁻¹ and oxidation flow rate of 4 NL min⁻¹ come close to satisfying the constraints of material stability. Under these flow conditions, an NH₃ conversion of 99.8% is achieved (Figure 3.4b).

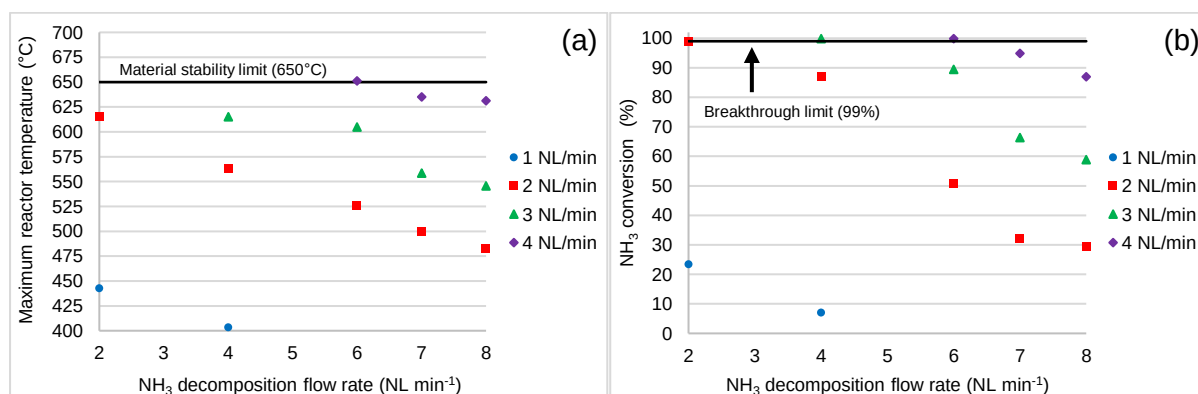


Figure 3.4: Effect of NH₃ oxidation flow rate (1–4 NL min⁻¹) and NH₃ decomposition flow rate (2–8 NL min⁻¹) on steady-state measurements for (a) maximum reactor temperature and (b) NH₃ decomposition conversion. Conditions correspond to a fuel-oxygen equivalence ratio of 1.4.

In an effort to increase reactor throughput, decomposition flow rates of 7–8 NL min⁻¹ and an oxidation flow of 5 NL min⁻¹ were investigated to increase NH₃ conversion greater than the breakthrough limit (99%) towards H₂ production. For these conditions, an increase in temperature at the reactor inlet (to 680°C, beyond the limit of material stability) within 60 min is observed. This sharp increase in temperature is a result of excess heat produced in the reactor that is not utilized by the endothermic decomposition reaction. Operational considerations associated with flame/homogeneous oxidation should be in place as this reaction might propagate beyond the catalyst washcoat and ultimately outside the reactor's inlet distribution manifold. This observation is crucial as the fuel-oxygen feed ratio is within the flammability

limits of NH_3 . The material stability limit (650°C) associated with a slight red glow of the stainless steel substrate at the reactor inlet is therefore maintained.

Although the maximum power output recorded (832 W_e) is obtained for a decomposition flow rate of 8 NL min^{-1} and oxidation flow rate of 4 NL min^{-1} , an undesirable NH_3 conversion (86.9%) is achieved for this flow condition. The power output is noticeably lower than the theoretical maximum calculated for 100% conversion (Figure 3.5a). Again, the maximum decomposition flow rate that provides satisfactory reactor performance is 6 NL min^{-1} at an oxidation flow of 4 NL min^{-1} . A H_2 equivalent fuel cell power output of 716 W_e is obtained, which is close to that of the theoretical maximum (708.5 W_e). This flow condition also produces the highest thermal efficiency of 75.9% (Figure 3.5b). Although the flow condition corresponding to a decomposition flow of 8 NL min^{-1} and oxidation flow of 4 NL min^{-1} provides a higher H_2 throughput, the thermal efficiency is lower (71.1%) as a result of excess NH_3 (7 vol.%) observed in the product gas, which is not decomposed to form H_2 .

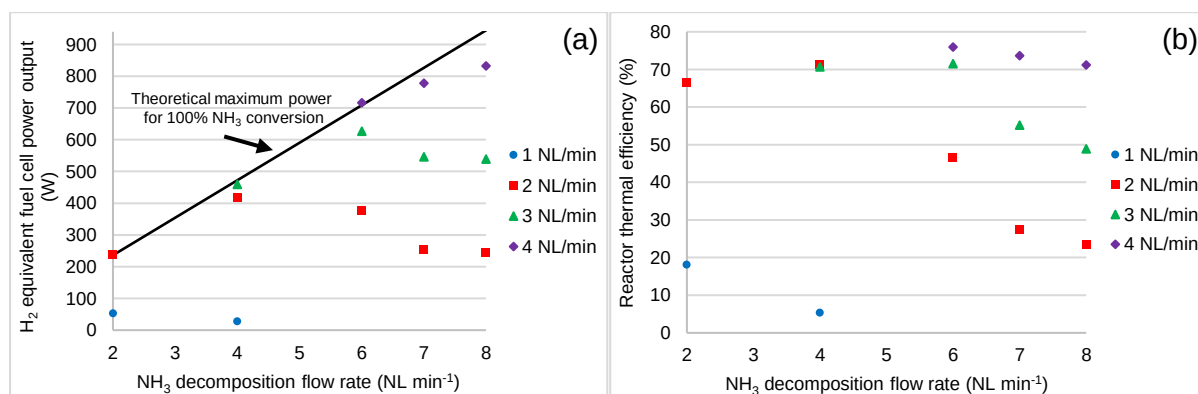


Figure 3.5: Effect of NH_3 oxidation flow rate (1–4 NL min^{-1}) and NH_3 decomposition flow rate (2–8 NL min^{-1}) on steady-state measurements for (a) H_2 equivalent fuel cell power output and (b) reactor thermal efficiency. Conditions correspond to a fuel-oxygen equivalence ratio of 1.4.

The residual NH_3 content in the feedstock to PEM fuel cells is imperative as fuel cell performance will deteriorate considerably in the presence of NH_3 . Some sources even report a decrease in fuel cell catalyst activity at NH_3 levels as low as 1 ppm over a one-week period [56]. The decrease in activity is attributed to the alkaline nature of NH_3 at the fuel cell anode. Formed NH_4^+ ions react with sulphonic (SO_3^-) groups, characteristic of Nafion[®] fuel cell membranes. Consequently, the membrane water content and conductivity decreases, leading to diminishing fuel cell performance [57,58]. Although the NH_4^+ ions are expected to affect the

anode side the most, diffusion of NH_4^+ ions to the cathode side is also noteworthy as membranes are typically only 10–100 μm thick [56]. Although substantial poisoning effects is observed with NH_3 in anode feed gas, studies have shown that fuel cell performance is recoverable with time (in the order of days) when a neat feed of H_2 is introduced to the anode [57,59].

3.3.2.2 Effect of fuel-oxygen feed ratio

The effect of a variation in the fuel-oxygen equivalence ratio (Eqn. 3.5) on the maximum reactor temperature and NH_3 decomposition conversion is illustrated in Figure 3.6. Constant feed ratios of 1.2, 1.4, and 1.6 are considered, for decomposition flow rates of 6–8 NL min^{-1} and an oxidation flow rate of 4 NL min^{-1} . First, an increase in the maximum reactor temperature is observed when the equivalence ratio is decreased from 1.4 to 1.2. As a result, similar increases in NH_3 conversion are obtained for all flow conditions presented. For the decomposition flow condition of 8 NL min^{-1} and 4 NL min^{-1} oxidation flow, the temperature increases from 631°C to 637°C. The corresponding NH_3 conversion also shows an increase, from 86.9% to 91.6%, when the equivalence ratio is reduced.

This increase in reactor performance is due to the equivalence ratio being closer to the stoichiometric feed conditions for the oxidation reactions. Specifically, more O_2 is available for reaction and therefore more heat is released into the reactor system. Although better reactor performance is achieved, the formation of NO_2 is visually observed in the condensing flask. The formation of NO_2 takes place via reaction 4, after which NO oxidises to NO_2 in the presence of O_2 . From the stoichiometry of this reaction, it is evident that an increased O_2 feed fraction will promote this reaction. Similar observations were made in our previous work for fuel-lean feed mixtures [18]. Besides identifying good reactor performance, considerations regarding flue gas are also essential. Nitric oxide and NO_2 are highly toxic gases. Reactor operation at the 1.2 fuel-oxygen equivalence ratio is therefore not recommended.

In contrast, when the equivalence ratio is increased from 1.4 to 1.6, the maximum reactor temperature and NH_3 conversion decreases for all flow conditions considered here. This observation is a result of less heat provided to the reactor, as the imbalance of NH_3 to O_2 is enlarged. For comparison the 8 NL min^{-1} decomposition flow and 4 NL min^{-1} oxidation flow condition yields a maximum reactor temperature of 593°C, which is 38°C lower than in the case of the 1.4 equivalence ratio data point. The corresponding NH_3 conversion also shows a

reduction of 8.1%, to 78.8%. A decreasing effect on the reactor thermal efficiency is evident as more NH_3 is fed to the reactor on the oxidation side, while less H_2 is produced through decomposition. From an operational perspective, the 1.6 equivalence ratio manipulated thermodynamic equilibrium in favor of N_2 formation through SCR reactions [8,9,18]. As a result, little to no NO_2 formation is visually observed for all flow conditions, yet the reactor performance is not as enhanced as in the cases of the 1.2 or 1.4 equivalence ratios.

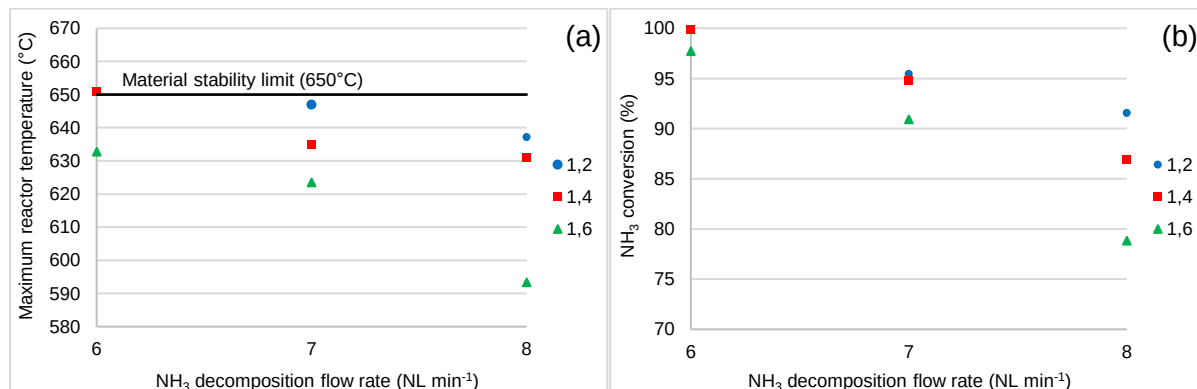


Figure 3.6: Effect of fuel-oxygen equivalence ratio (1.2–1.6) and NH_3 decomposition flow rate (6–8 NL min^{-1}) on steady-state measurements for (a) maximum reactor temperature and (b) NH_3 decomposition conversion. Conditions correspond to an NH_3 oxidation flow rate of 4 NL min^{-1} .

3.3.3 Performance stability test

A 24 h stability test was performed at conditions corresponding to a decomposition flow rate of 8 NL min^{-1} , oxidation flow rate of 4 NL min^{-1} and equivalence ratio of 1.4. These flow rates are the highest flows investigated here for NH_3 decomposition and oxidation, respectively. They were selected to introduce demanding reactor conditions. This test was carried out in an effort to determine any inconsistencies in catalyst and material stability, over an extended test period, which may cause decreased steady-state reactor temperature and NH_3 conversion. Results of the maximum reactor temperature and NH_3 conversion (Figure 3.7) show that no detectible catalyst deactivation occurs during testing. On the contrary, the temperature varies in a range of 625–632 $^{\circ}\text{C}$ and NH_3 conversion increases steadily up to 90.9% over the 24 h period. Some temperature variations is attributed to natural fluctuations, especially as the temperature at the reactor inlet is observed to be very sensitive, due to high reaction rates occurring in this region. The slight increase in NH_3 conversion is credited to the outlet reactor temperature, which exhibits a much slower response time from the start of the stability test.

This phenomenon is discussed in section 3.3.1 (for Figure 3.3a). On conclusion of the test, the reactor was visually inspected, and no structural defects were observed.

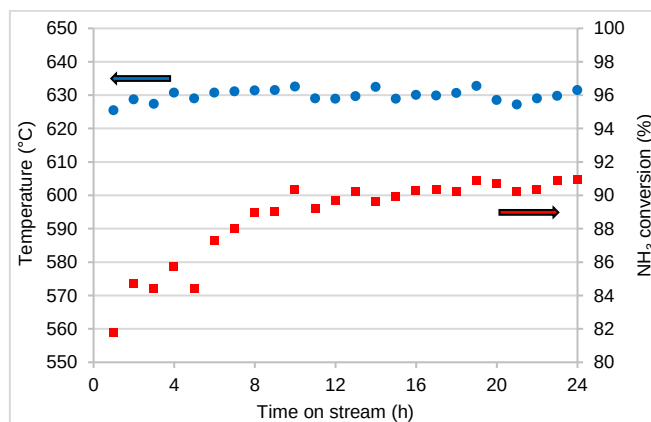


Figure 3.7: Maximum reactor temperature and NH₃ decomposition conversion during reactor stability test lasting 24 h. Conditions correspond to an NH₃ decomposition flow rate of 8 NL min⁻¹, NH₃ oxidation flow rate of 4 NL min⁻¹, and fuel-oxygen equivalence ratio of 1.4.

3.3.4 Recommended operating conditions

A summary of reactor specifications and recommended operating conditions are tabulated in Table 3.1. The recommended operating point identified which closely satisfies the limit of material stability and supports good NH₃ conversion is a decomposition flow rate of 6 NL min⁻¹, oxidation flow rate of 4 NL min⁻¹, and equivalence ratio of 1.4. For these conditions the NH₃ conversion obtained is 99.8%. The reactor also shows high throughput with a H₂ equivalent fuel cell power output of 0.71 kW_e (8.92 NL min⁻¹ H₂). Furthermore, the thermal efficiency obtained (75.9%) is substantially higher than that (57.3%) attained by Chiuta & Bessarabov [18] during the first generation autothermal reactor testing. In their work the recommended operating point gives only 45 W_e power output. The improvement in reactor efficiency is largely due to the increased reactor volume vs outer surface area exposed to the insulation material. Heat losses are subsequently minimized and more heat is now utilized in the thermal coupling of the oxidation and decomposition reactions.

The NH₃ conversion obtained here allows for an NH₃ outlet concentration of 680 ppm. However, this concentration of NH₃ is still beyond the limit of PEM fuel cell tolerance. As mentioned by Refs. [18,60], alkaline fuel cells are resistant towards reasonable traces of NH₃ in H₂ supply streams, and in this case a viable power generation technology. Should the aim be to utilize PEM fuel cells, it is recommended that a H₂ selective membrane is used to purify feed

streams to NH_3 concentrations below an acceptable limit for fuel cell operation (<1 ppm) [56]. For large-scale implementation of PEM fuel cells, a H_2 purification method such as pressure swing adsorption is useful as an existing technology that can be utilized, with low operating costs associated. These purification methods will ensure long-term fuel cell catalyst activity for sustainable power supply.

Table 3.1: Summary of recommended operating conditions and performance parameters of autothermal microchannel reactor for ammonia decomposition.

Decomposition catalyst	8.5 wt.% Ru/ Al_2O_3	
Oxidation catalyst	5 wt.% Pt/ Al_2O_3	
NH_3 decomposition flow rate	6.0	NL min^{-1}
NH_3 oxidation flow rate	4.0	NL min^{-1}
Fuel-oxygen equivalence ratio	1.4	unitless
Maximum reactor temperature	651	$^{\circ}\text{C}$
NH_3 decomposition conversion	99.8	%
Residual NH_3 concentration	680	ppm
H_2 production rate	8.92	NL min^{-1}
H_2 equivalent fuel cell power output	0.71	kW_e
Thermal efficiency	75.9	%

Although the aim of this work was to characterize the performance of the reactor based on the NH_3 reforming reaction, considerations regarding the flue gas composition from the oxidation chamber is also noteworthy. Firstly, equilibrium data is calculated in AspenPlusTM using the Gibbs free energy minimization technique with the Peng-Robinson fluid property package. The downstream reactor temperature (530°C) is used in equilibrium calculations, as it will most likely determine final product composition. At the recommended operating point, it is evident that the majority of excess NH_3 is decomposed to form H_2 on the Pt catalyst (3.2). Note however that the data is presented on a dry basis (db), enlarging the percentile composition of dry gases. The other major component of the flue gas is N_2 , produced mainly through reaction 2, and also the decomposition reaction (reaction 1). The Pt catalyst shows to be selective towards N_2 production with other products, i.e. N_2O and NO_x , in minority (summation $< 3\%$).

However, to quantify NO and NO₂ proved elusive with the GC, as these gases are problematic to separate.

Table 3.2: Flue gas composition (db) from the NH₃ oxidation chamber at the recommended operating point.

Species	Equilibrium	Experimental
NH ₃	41 ppm	1.48%
O ₂	trace	none detected
N ₂	85.9%	51.7%
H ₂	14.1%	43.9%
N ₂ O	trace	2.64%
NO _x	trace	balance

3.4 CONCLUSIONS

A microchannel reactor was developed and tested for H₂ production through the NH₃ decomposition reaction. The reactor was designed as alternating catalytic plates which allowed for an autothermal (self-sufficient) heating approach through a secondary NH₃ oxidation reaction. The reactor showed rapid temperature response during start-up and was able to produce significant H₂ flow after 60 min of operation, compared to steady-state values. A recommended operating point was identified which closely satisfied the limit of material stability, yet provided satisfactory performance in terms of NH₃ conversion and H₂ throughput. A conversion of 99.8% was achieved with a H₂ equivalent fuel cell power output of 0.71 kW_e at conditions corresponding to a decomposition flow rate of 6 NL min⁻¹, oxidation flow rate of 4 NL min⁻¹, and fuel-oxygen equivalence ratio of 1.4. Although good reactor performance was achieved, residual NH₃ concentrations are such that a H₂ purification step should be established to prevent fuel cell catalyst degradation in a practical scenario. The work described in this paper nonetheless demonstrated that increased H₂ generation from NH₃ decomposition is viable through a highly efficient process. As a result, this work introduces groundwork for self-sufficient multi-kW power generation systems suitable for commercial implementation.

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CHAPTER 4

THERMAL MANAGEMENT AND METHANATION PERFORMANCE OF A MICROCHANNEL-BASED SABATIER REACTOR/HEAT EXCHANGER UTILISING RENEWABLE HYDROGEN

CHAPTER OVERVIEW (ABSTRACT)

Power-to-methane is a concept that offers the storage and utilisation of renewable energy, while recycling industrial CO₂ emissions, for carbon-based fuel production. An experimental microchannel reactor, that supports self-sustained operation, was evaluated for the Sabatier (methanation) reaction, using renewable H₂ from a solar-to-hydrogen storage facility. Hydrogen, a common heat transfer medium, also provided the reactor's cooling requirements. Particular focus was placed on evaluation of the flow configuration within the reactor (co- and counter-current flow), because improved thermal management may offer enhanced CO₂ methanation reaction equilibrium. The effects of the following, within specified ranges, were determined, in terms of the reactor's thermal behaviour and the resulting methanation performance: the total methanation flow (4–7 NL min⁻¹), coolant flow (0.8–5.6 NL min⁻¹) and reaction pressure (5 and 10 bar_g). The counter-current flow configuration provided a decreasing temperature profile, with improved methanation performance and heat recovery. The recommended operating point was found to be under the following experimental conditions: a methanation flow of 7 NL min⁻¹, coolant flow of 5.2 NL min⁻¹ and reaction pressure of 10 bar_g. A CO₂ conversion of 90.5% and CH₄ power output of 667.1 W were achieved, while an overall methanation process efficiency of 76.6% was attained.

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4.1 INTRODUCTION

Solar and wind energy are probably the most abundant sources of renewable energies, worldwide; in some economies they already constitute large portions of the power generated. The use of renewables limits CO₂ emissions, and allows countries to conform to the 2016 Paris Climate Change Agreement. However, the fluctuations in solar and wind energy, due to their natural intermittency, is a cause for concern, making these sources of renewable energies difficult to integrate into national power grids as baseload power [1–3]. The power-to-gas (PtG) concept was proposed in efforts to utilise excess renewable power during peak supply and to generate hydrogen (H₂) via water electrolysis [4]. However, H₂ has a low volumetric energy density, which presents difficulties in terms of H₂ transportation and storage [5]. The processing of H₂ to produce other energy carriers, e.g., methane (CH₄) or energy-dense liquids (methanol and dimethyl ether), has strengthened the concept. When there is an increase in the demand for power, the energy stored in these chemicals (energy carriers) can be converted back to generate electricity—hence providing power grid balancing.

High purity synthetic natural gas (SNG (containing mainly CH₄)) is an attractive option for PtG; it has an enormous storage capacity in natural gas pipelines [6]. Other compounds such as C_{2–4} hydrocarbons can be blended to synthetic CH₄, should natural gas pipeline standards necessitate it. Furthermore, CH₄ also supports various other applications in the transport and chemical industries [6–8]. For example, in South Africa, in 2018, the country's Department of Energy announced that the country's energy matrix will diversify and increase the share of natural gas for power generation [9]. In turn, this will bring substantial development to the country's gas industry. There is also a global trend towards natural gas for power and fuel production because it results in lower process emissions, compared with the use of coal and oil.

The production of synthetic CH₄ (by methanation) follows a reaction pathway referred to as the Sabatier reaction (reaction 4.1)—it involves the direct catalytic conversion of H₂ and CO₂. A secondary (and undesirable) catalytic reaction, which yields CO, is the well known reverse water–gas shift (RWGS) reaction (reaction 4.2).



The sequestration of CO₂ emissions is viable when high purity waste streams (6–15% CO₂ in industrial flue gas streams [10–12]) are available for the application of the subsequent methanation [6]. Potential point sources of CO₂ therefore include, but not limited to, fossil fuel combustion plants, cement kilns and breweries. Integrating the methanation process into an existing infrastructure, such as anaerobic digesters or biogas plants (roughly 50–70% CH₄, with the majority balance CO₂, depending on the feedstock [13–15]), could also produce pipeline-grade SNG. Typically, landfill gas and biogas have several impurities (e.g., H₂S, NH₃ and O₂) and therefore require purification before they can be fed to a catalytic methanation process [16,17]. Currently, the energy required for and operating costs associated with CO₂ separation from the atmosphere (2019 global averaged marine surface concentration: 409.83 ppm [18]) hinders its current application as a potential source of CO₂ [6].

In this study, we address catalytic CO₂ methanation. The Sabatier reaction (reaction 4.1) is an exothermic process, therefore able to sustain its own heat requirements [5]. However, the process does require some degree of heat management to prevent thermal runaway [19]. In large-scale methanation processes, waste heat utilisation, using existing industrial processes, is feasible [4]. In small-scale applications, however, novel reactor/heat exchanger technologies must be incorporated in order to achieve acceptable levels of process efficiency. Microchannel reactors are a sophisticated technology that supports catalytic conversion—it originated from the concept of the process intensification of heat exchangers. Microchannel technology provides good heat dissipation from the reaction zone and it eliminates adverse diffusional effects, thereby offering improved mass transfer [19–23]. Thermally self-sustaining reactors act as multifunctional reactor/heat exchangers, therefore, the degrees of freedom required for suitable operation decrease, and the design and control strategy is thus simplified. Essentially, more compact designs are possible through process intensification—allowing the achievement of comparable performances to those of much larger conventional reactors [24].

Pérez et al. [25] evaluated a multichannel reactor for CO₂ methanation at pressures up to 15 bar_g, using a 25.2 wt.% Ni/Al₂O₃ catalyst. At a fixed temperature of 350°C and space velocity of 30 000 h⁻¹, a CO₂ conversion of up to 96.1% was attained, with a CH₄ output of 6.15 NL g_{cat}⁻¹ h⁻¹. The scale-up of the multichannel reactor to a processing capacity of 15 kW was described for the RENOVAGAS project. In that case, the multichannel reactor was submerged in a heat transfer fluid to provide the required thermal management. Thompson [26] evaluated three isothermal microchannel-based Sabatier reactors, in series, each operating at a different

temperature, to offer improved CO₂ conversion. A single-pass conversion of up to 96% was attained at reactor temperatures corresponding to 365°C, 294°C and 234°C, and methanation flow rates in the order of 0.1–5.0 mL min⁻¹. Other studies on the topic include isothermal microchannel reactors for syngas methanation [27] and selective CO/CO₂ methanation in H₂-rich streams for fuel cell application [28–31].

As the CO₂ methanation reaction is exothermic, it offers us the possibility to improve the equilibrium of CO₂ methanation through the establishment of reactor temperature profiles that support lower outlet temperatures [5,32]. Brooks et al. [33] investigated CO₂ methanation in a microchannel reactor, as an application of fuel production, using metabolically generated CO₂ during potential manned missions to Mars. The reactor was designed with a counter-current flow of coolant oil, while a 3 wt.% Ru/TiO₂ methanation catalyst was used. The authors investigated multiple flow conditions (~30–244 NmL min⁻¹) at atmospheric pressure and found that, at some data points, thermodynamic equilibrium was reached. A CO₂ conversion of 88.4% was attained at a gas inlet temperature of 398°C, outlet temperature of 327°C and residence time of 95.5 ms. It is known, however, that at pressures above atmospheric pressure the operation favours methanation equilibrium, giving improved CO₂ conversions [34]. Chwoła et al. [35] reported experimental results on a pilot-scale microchannel reactor system coupled to a CO₂ capturing unit at a Polish-based power plant. Two methanation reactors in series produced synthetic CH₄ at a purity of 82 vol.% and total CO₂/H₂ flow rates of up to 23.0 Nm³ h⁻¹. In both reactors, thermal oil was used for temperature regulation; the reactors operated in a temperature range of 280–350°C. Neuberg et al. [36] recently proposed the coupling of a high temperature monolithic reactor, supporting a durable catalyst, to a lower temperature second-stage microchannel reactor with a counter-current flow of coolant oil in an effort to improve methanation equilibrium. These reactors are to be integrated into a biogas plant and supplied with the H₂ equivalent of 50 kW electrolyser power load.

Vidal Vázquez et al. [37] used computational fluid dynamics (CFD) to investigate the flow distribution and methanation performance of a corrugated plate reactor/heat exchanger with nickel-based hydrotalcite catalyst. A near-uniform flow distribution and high corrugated plate surface area resulted in satisfactory CO₂ conversion (92%) at conditions corresponding to 573 K, 5 bar and a space velocity of 4 400 h⁻¹. Raghu and Kaisare [38] performed a 2D CFD modelling investigation into the thermal characteristics of a U-bend microchannel reactor. They found that heat exchange from the methanation reaction to the cold methanation feed

provided lower temperatures near the outlet of the reaction chamber, hence improving the yield of CH₄ formation. Important factors of methanation assemblies that affect overall process efficiency, such as the magnitude of heat recuperation and heat loss, are not clearly apparent through modelling.

There nonetheless remains much important work to be done with regards to determining the thermal characteristics and methanation performance of experimental microchannel reactor/heat exchangers for CO₂ methanation, with particular focus on process intensification, i.e., increased pressure and space velocity demonstration, improved equilibrium operation, coupled with heat recuperating strategies.

The work reported here is an extension to earlier experimental and CFD modelling investigations carried out by our research group on a microchannel reactor for CO₂ methanation [39]. There, methanation flow rates (50–150 NmL min⁻¹) were such that the reactor was evaluated under isothermal conditions (electric heating). Here, in the present study, the microchannel reactor is scaled-up significantly in order to accommodate higher methanation flow rates, to support thermally self-sustained operation.

In the present study, renewable H₂ from a solar-to-hydrogen storage facility is used for the methanation reaction, and the high thermal capacity of H₂ is exploited as a cooling medium in both co-current and counter-current flow configurations in the reactor/heat exchanger. The effects of the total methanation flow rate (4–7 NL min⁻¹), coolant flow rate (0.8–5.6 NL min⁻¹) and reaction pressure (5–10 bar_g) were investigated by performing a critical evaluation of the subsequent steady-state temperature profiles developed for the respective flow configurations. This work is the first to experimentally evaluate, and compare, the effects of different flow configurations in a microchannel-based Sabatier reactor, the results of which support equilibrium favouring steady-state temperature profiles. Finally, the microchannel reactor's methanation performance and selectivity towards CH₄ production was determined. We conclude with a recommendation regarding the best associated strategy for improved thermal management, heat recuperation and methanation performance – in a microchannel-based Sabatier reactor/heat exchanger, utilising renewable hydrogen.

4.2 EXPERIMENTAL METHODOLOGY

4.2.1 HySA Infrastructure's solar-to-hydrogen facility

An array of solar panels (with 21 kW_p capacity) is used to generate renewable power, which is intermediately stored in lead–acid batteries with 120 kWh capacity. Two commercial proton exchange membrane electrolyzers (Proton S40 and S10) are used to generate H₂ at a combined rate of 3 kg/day. HySA laboratories are fed directly, at a supply pressure of 13.8 bar_g. In addition, a hydrogen booster is used to compress and store up to 45 kg of H₂ at 200 bar_g, from which the laboratories can also be supplied with H₂. The H₂ storage facility is illustrated in Figure 4.1.



Figure 4.1: Ultra-pure hydrogen storage at 200 bar—supplying HySA laboratories with renewable hydrogen.

4.2.2 Microchannel reactor/heat exchanger design

The microchannel-based Sabatier reactor/heat exchanger (Figure 4.2) was designed and fabricated in collaboration with Fraunhofer-IMM (Mainz, Germany). [40]. A stainless steel (SS 316Ti, German classification 1.4571) was selected for use as metal substrate, due to its durability under high temperature and at above atmospheric pressure working conditions. The reactor was designed as alternating catalytic plates, allowing for intimate heat exchange between the methanation reaction and a cooling medium. Two stacks of plates were separated by a middle plate, which included ten ports ($\varnothing = 0.6$ mm) for thermocouples (Figure 4.2b). These thermocouple ports were located at positions between 2.5 mm and 92.5 mm (10 mm spacings) from the start of the methanation microchannels. The stacks comprised 17 double-

sided plates, with 50 microchannels ($W = 500 \mu\text{m}$, $H = 250 \mu\text{m}$ and $L = 100 \text{ mm}$) chemically etched onto the faces of each side of the plates, respectively, for methanation and coolant flow [41]. These plates were stacked in a face-to-face arrangement, together with the relevant end-plates. Two heating blocks (Figure 4.2b) at respective sides of the reactor were incorporated to support four heating cartridges for start-up procedures. Finally, the reactor was laser welded with strengthened gas diffuser manifolds, and $\frac{1}{4}$ inch inlet and outlet piping (Figure 4.2b).

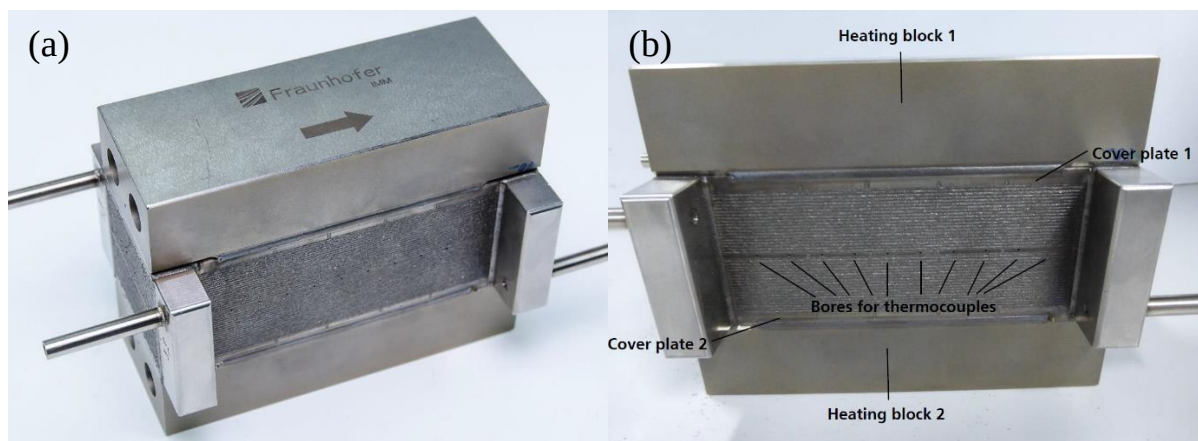


Figure 4.2: Illustrations: (a) the microchannel-based Sabatier reactor/heat exchanger, and (b) the reactor/heat exchanger including the $\frac{1}{4}$ inch inlet and outlet tubing, heating blocks, gas diffuser manifolds and bores for thermocouples.

4.2.3 Catalyst preparation

A commercial 5.0 wt.% Ru/Al₂O₃ catalyst (Sigma-Aldrich, 84032) was used to catalyse the CO₂ methanation reaction. In our previous work [39], an 8.5 wt.% Ru/Al₂O₃ catalyst was used. However, in an effort to now reduce the dependency on expensive precious metals, the catalytic loading of Ru was reduced to 5.0 wt.%. The catalyst milling, processing, washcoating and calcination procedures are described elsewhere [42]; the original procedure described by Zapf et al. [43] was slightly modified. The reactor contained a total of 3687 mg of Ru/Al₂O₃ catalyst and the average microchannel washcoat thickness was 45 μm .

4.2.4 Experimental apparatus

The methanation reactor assembly is illustrated in Figure 4.3. High purity renewable H₂ ($\geq 99.999\%$) from the storage facility was used in all the methanation experiments. The supply of H₂ was connected via a 3-way valve to N₂ ($\geq 99.999\%$), used for start-up and cooling down procedures. Bottled CO₂ ($\geq 99.9\%$) was used as the second reactant gas; it was mixed with the

H₂ before the inlet of the reactor. To recuperate reaction heat from the methanation process, a pure flow of H₂ was fed to the reactor's cooling chamber. Respective thermal mass flow controllers (Brooks, SLA5800) were used to control all gas flow rates. To investigate both co-current and counter-current cooling configurations, the ¼ inch piping of the H₂ coolant stream was modified upon conclusion of the set of co-current experiments, to allow for the reversal of the flow direction within the reactor.

During reactor start-up, four heating cartridges (Watlow FIREROD[®], 300 W each) were merely used to reach the light-off temperature of the methanation reaction, after which they were switched off, to initiate self-sustained (autothermal) operation. The hot methanation product gas pre-heated the cold methanation feed in an external tube-in-tube heat exchanger, connected to the inlet of the methanation chamber. Ten K-type thermocouples ($\varnothing = 0.5$ mm) were used for temperature measurements of the reactor core, and positioned axially along the length of the reactor (Figure 4.2b). A differential pressure meter (Azbil, AT9000) was used to indicate the combined pressure drop of the methanation chamber and the external heat exchanger. Needle valves, downstream of the reactor, were used to control the respective pressures of the methanation and coolant gas streams. Condensate formation during the Sabatier process was separated using a condenser assembly with coolant fluid, set at a temperature of 0°C. Further gas drying was done using silica beads, prior to the measurement of the dry product gas flow rate using a thermal mass flow meter (Bronkhorst[®], EL-flow). The composition of the product gas was analysed using an online gas chromatograph (SRI, 8610C GC), fitted with a 6 ft Hayesep D and 6 ft Molecular Sieve 13X column. The product gas was quantified using a thermal conductivity detector within the GC. National Instruments[™] LabVIEW software was used to control all flow controllers, and log the product flow rate and temperature measurements in 1-min intervals.



Figure 4.3: Sabatier reactor: surrounded by thermal insulation and with an external heat exchanger to pre-heat the cold methanation feed.

4.2.5 Experimental procedure

Pure N₂ flow (1.5 NL min⁻¹) was used during reactor start-up and cooling down procedures, for both the methanation and the cooling chambers of the reactor. Upon reactor commissioning, the Ru catalyst was reduced to its active state using a pure H₂ flow (1 NL min⁻¹) at 300°C for a 1-h period. Experiments were started by ramping the temperature of the reactor block to the desired light-off temperature (410°C), using the heating cartridges, for all daily experimental runs. Once this temperature was reached, the experimental flow rates were adjusted accordingly. The reaction pressure was increased. Use was still made of the heaters for approximately 10 min. This step ensured that the methanation process fully established, and that the external heat exchanger was heated-up with hot product gas. Thereafter, the heaters were switched off, and self-sustained operation commenced.

For the methanation reaction, combined flow rates of 4–7 NL min⁻¹ were used (CO₂ + H₂) to allow self-sustained thermal operation, but limited to a maximum H₂ processing rate of close to 1 kW (design specification ~6 NL min⁻¹ H₂). The H₂ coolant flow rates ranged from 0.8 to 5.6 NL min⁻¹, to restrict the reactor temperature from dropping below 400°C (where lower CO₂ conversions were obtained), or exceed a maximum of 450°C. All the experiments were conducted at a stoichiometric methanation feed ratio of 4:1 (H₂:CO₂). Elevated reactor pressures (5 and 10 bar_g) were investigated, as results of our previous work had indicated that above atmospheric pressure conditions favoured the Sabatier reaction's thermodynamic equilibrium [39]. Each experiment lasted for a continuous 2-h period, after which steady-state

measurements were recorded. To improve the reliability of thermal observations, daily experiments were carried out for one methanation flow rate and at one pressure condition, whilst adjusting the coolant flow rate between the respective steady-states. Experiments were carried out over a period of about 170 h; experiments included the initial trial runs, official experiments and repeated data points.

4.3 RESULTS AND DISCUSSION

The experimental results of steady-state reactor operation are now described. The reactor performance was assessed based on the following parameters: the CO₂ conversion (Eqn. 4.3), CH₄ selectivity (Eqn. 4.4), CH₄ power output (Eqn. 4.5) and thermal efficiency (Eqn. 4.6). For the calculations of the CH₄ power output and thermal efficiency, lower heating values of 120 MJ kg⁻¹ and 50 MJ kg⁻¹ were assumed for H₂ and CH₄, respectively [44]. Finally, the heat recovered in the H₂ coolant stream (Eqn. 4.7) was added to the CH₄ power output to calculate the overall process efficiency of the reactor (Eqn. 4.8). In the discussions that follow, the reference conditions for normal flow were taken as 20°C and 1 bar_a.

$$X_{CO_2} = \frac{\dot{n}_{CO_2 in} - \dot{n}_{CO_2 out}}{\dot{n}_{CO_2 in}} \times 100\% \quad 4.3$$

$$S_{CH_4} = \frac{\dot{n}_{CH_4 out}}{\dot{n}_{CH_4 out} + \dot{n}_{CO out}} \times 100\% \quad 4.4$$

$$P = LHV_i \times \dot{m}_i \quad 4.5$$

$$Thermal \ \eta = \frac{(LHV_{CH_4} \times \dot{m}_{CH_4 out})_{meth}}{(LHV_{H_2} \times \dot{m}_{H_2 in})_{meth}} \times 100\% \quad 4.6$$

$$\dot{Q}_{rec} = \left(\dot{m}_{H_2 in} \times \int_{293.15}^{T_{out}} C_{p_{H_2}} dT \right)_{cool} \quad 4.7$$

$$Overall \ \eta = \frac{(LHV_{CH_4} \times \dot{m}_{CH_4 out})_{meth} + \dot{Q}_{rec}}{(LHV_{H_2} \times \dot{m}_{H_2 in})_{meth}} \times 100\% \quad 4.8$$

4.3.1 Reactor thermal behaviour

4.3.1.1 Co-current flow configuration

Figure 4.4 illustrates the steady-state axial temperature profiles of selected methanation experiments conducted in the co-current flow configuration. In these experiments, both the methanation flow and the H₂ coolant flow entered the microchannel reactor at the same side (Figure 4.4, axial location 1), and flowed in parallel to the respective exits of the reactor (Figure

4.4, axial location 10). The temperature measurements reported here are those of the reactor block (Figure 4.2b).

For the lowest total methanation flow rate examined (4.0 NL min⁻¹), the highest temperature recorded was located near the middle of the reactor (Figure 4.4, axial location 5–6), for both pressures investigated. For the 4.0 NL min⁻¹ methanation flow and 5 bar_g experimental data point, the maximum temperature was recorded as 415.7°C, while the inlet temperature was 403.1°C and the outlet 408.2°C. In this case, a H₂ coolant flow of only 0.8 NL min⁻¹ was required to ensure that self-sustained operation took place. The heat balance over the reactor comprises: (i) the enthalpy change of both methanation and coolant flows, (ii) reaction heat released and (iii) heat lost to the environment through the insulation material. It is envisioned that axial heat conduction plays some role in the reactor's thermal behaviour, as SS 316Ti has a thermal conductivity of ~15 W m⁻¹ K⁻¹ at 410°C. For the methanation flow rate of 4 NL min⁻¹, the two temperature profiles showed some decrease in the reactor temperature towards the exit of the reactor (Figure 4.4, axial location 6–10) after the temperature maximums were obtained. A total methanation flow of 3.0 NL min⁻¹ did not provide sufficient reaction heat for steady-state operation to take place. Any coolant flows above 1 NL min⁻¹ caused thermal extinction within the reactor at the methanation flow conditions of 4 NL min⁻¹ and 5 bar_g.

For operation at an increased pressure (10 bar_g), a slightly higher coolant flow was required, 1.2 NL min⁻¹, as a result of the enhanced methanation activity at this pressure. The higher inlet coolant flow meant that the inlet temperature was only 401.7°C. The temperature maximum was recorded as 414.0°C. At 10 bar_g, the apparent residence time between the gas and the catalyst is longer, which generally improves CO₂ conversion. Consequently, here, lower steady-state temperatures were required to sustain the methanation reaction, compared to at 5 bar_g operation. The roughly 4°C increase in the near-outlet temperature region (axial location 8–10) for 5 bar_g operation was sufficient to provide near-equilibrium CO₂ conversion, and compensate for the shorter apparent residence time and slower kinetics at 5 bar_g.

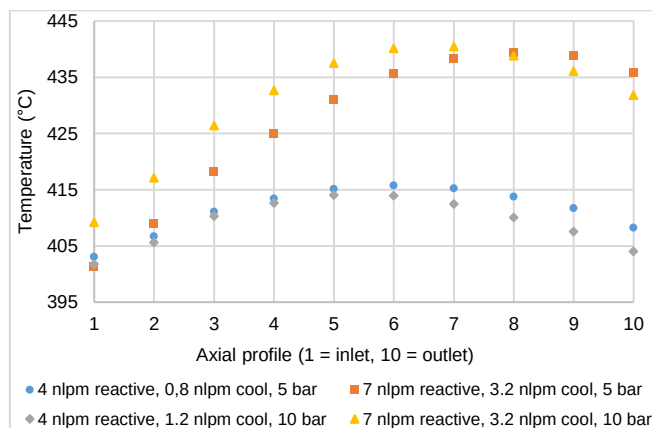


Figure 4.4: Comparison of steady-state axial temperature profiles for the co-current reactor flow configuration, for the following conditions: total methanation flow of 4.0–7.0 NL min⁻¹, H₂ coolant flow of 0.8–3.2 NL min⁻¹, and reaction pressure of 5 and 10 bar_g.

For a methanation flow of 7.0 NL min⁻¹, residence time effects caused the main reaction zone to expand towards a broader length range of the microchannel reactor. First, at the reaction pressure of 5 bar_g, a generally increasing temperature gradient was observed: the inlet temperature was 401.2°C, a temperature maximum of 439.4°C was located at axial position 8 and the outlet temperature was 435.7°C. This leads us to believe that the main reaction zone extends to close to the exit of the reactor, as a result of both (i) short apparent residence times and (ii) slower kinetics at 7.0 NL min⁻¹ and 5 bar_g. Due to the increasing amount of reaction heat released at a methanation flow of 7.0 NL min⁻¹, a coolant flow rate of 3.2 NL min⁻¹ was required to restrict the maximum steady-state temperature from increasing further. The higher coolant flow rate contributed to convective heat transfer towards the exit of the reactor, thus contributing to the characteristic temperature profile observed.

For a methanation flow of 7.0 NL min⁻¹ at 10 bar_g pressure, a coolant flow rate of 3.6 NL min⁻¹ was feasible, providing near-equilibrium CO₂ conversion and a temperature maximum of 441.3°C. For comparative purposes, an axial temperature profile corresponding to a coolant flow rate of 3.2 NL min⁻¹ is now illustrated (Figure 4.4) and discussed for this pressure. The inlet temperature was higher, at 409.2°C, and the temperature maximum recorded was 440.5°C at axial location 7. The less severe temperature gradient at 10 bar_g pressure (31.3°C) compared to at 5 bar_g (38.2°C) is attributed to the longer apparent residence time between the gas and the catalyst, and the reaction zone shifting towards the middle of the reactor, as a result of the faster kinetics at 10 bar_g.

4.3.1.2 Counter-current flow configuration

In contrast, in counter-current flow operation, the methanation flow still entered the microchannel reactor at axial location 1, while the H₂ coolant flow entered the microchannel reactor at axial location 10, and exited the reactor at the methanation inlet side. Figure 4.5 is plotted assuming the methanation inlet is at axial location 1 (In subsequent discussions, the same configuration applies.).

First, the steady-state temperature profile for a methanation flow of 4 NL min⁻¹ and reaction pressure of 5 bar_g has an almost identical shape to the case of the co-current configuration, although a slightly higher coolant flow of 1 NL min⁻¹ was used here. In this case, the maximum temperature was recorded as 422.4°C, while the inlet temperature was 412.4°C and the outlet 411.2°C. On average, these values are 6.3°C higher than in the co-current case. This is attributed to improved heat recirculation by the pure H₂ flow towards the main reaction zone in the counter-current configuration.

When the reaction pressure was increased to 10 bar_g, it is clear that the main reaction zone is located closer to the inlet of the reactor, as the maximum temperature was recorded as 414.8°C and the outlet temperature decreased to 400.6°C. In this case, the outlet temperature at axial location 10 was 5.7°C lower than the inlet temperature (406.3°C), as a result of the higher coolant flow rate used (1.4 NL min⁻¹). Again, it was observed that increased pressure operation at 10 bar_g could sustain the methanation reaction at lower temperatures, and it allowed for the coolant flow to be increased to 1.4 NL min⁻¹ (compared to only 1 NL min⁻¹ in the 5 bar_g case).

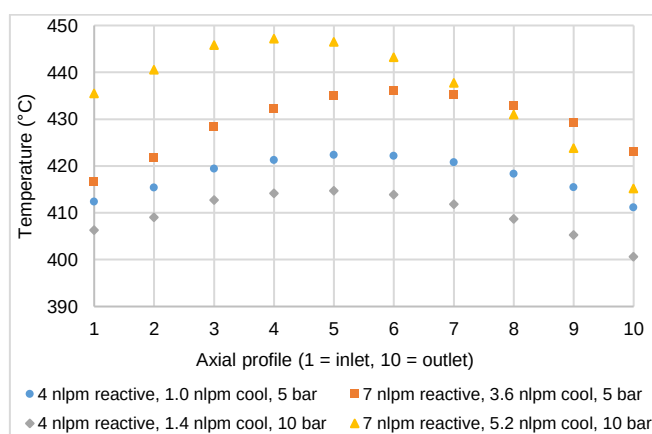


Figure 4.5: Comparison of steady-state axial temperature profiles for the counter-current reactor flow configuration, for the following conditions: total methanation flow of 4.0–7.0 NL min⁻¹, H₂ coolant flow of 1.0–5.2 NL min⁻¹, and reaction pressure of 5 and 10 bar_g.

For the high methanation flow rate of 7 NL min⁻¹, significant changes in the microchannel reactor's thermal behaviour were observed, compared to in the co-current case. First, for the 5 bar_g reaction pressure, the inlet flow of the cold methanation feed of 3.6 NL min⁻¹ H₂ caused some shift in the temperature profile; the maximum temperature of 436.1°C was now located at axial position 6. The temperature at the methanation outlet (423.1°C) was still higher than at the inlet (416.6°C), yet a degree of heat circulation was noticed, suggesting that reactor operation at 10 bar_g would be even more promising—to improve methanation equilibrium.

Typically, it would be favourable if the main reaction zone was located near the methanation inlet, converting most of the CO₂ to CH₄. At roughly half way down the length of the microchannels, the CO₂ conversion would be equilibrium limited. Lower temperatures towards the exit of the microchannels would improve equilibrium. Subsequently, smaller amounts of CO₂ would be converted, while the process remains equilibrium limited towards the exit of the reactor; albeit with an improved equilibrium. This phenomenon has been described for other equilibrium-limited processes, such as the water–gas shift reaction to improve H₂ yield.

Indeed, the experimental data point that indicated the best reactor thermal behaviour was at a methanation flow of 7 NL min⁻¹, coolant flow of 5.2 NL min⁻¹ and reaction pressure of 10 bar_g. The methanation inlet temperature was substantially higher than in all the other cases. An inlet temperature of 435.5°C was recorded, while the temperature maximum was 447.2°C at axial location 4. This region is expected to be the main reaction zone. Towards the exit of the microchannel reactor, the reactor temperature decreased significantly, to a methanation exit temperature of 415.2°C. This thermal behaviour is expected to provide improved CO₂ conversion and increase the ultimate yield of CH₄.

Overall, it was observed that the counter-current configuration resulted in higher temperature maximums at equivalent methanation flows and pressures, compared to in the co-current flow configuration. This is as a result of improved heat recirculation to the main reaction zone here. Subsequently, higher coolant flow rates are required to restrict thermal runaway in the counter-current case, while the co-current configuration tended towards scenarios of thermal blowout when moderately high coolant flows were used.

As mentioned earlier (section 4.3.1.1), axial heat conduction plays some role in reducing the theoretical heat exchanger efficiency; it contributes to the shape of the axial temperature profile. Had the reactor been fabricated from a material with a different thermal conductivity,

e.g., a low-conductivity ceramic ($1\text{--}3\text{ W m}^{-1}\text{ K}^{-1}$), the decreasing temperature profile that is observed could have been even greater at these experimental conditions. However, depending on the type of ceramic material, other challenges with regard to reactor design and fabrication aspects need to be dealt with—this is not expanded upon here.

4.3.2 Catalytic activity and selectivity

For the sake of brevity, 20 experimental data points, from a total of 38 experiments conducted, are given in Table 4.1. This table illustrates the effects of varying the methanation flow rates, coolant flow rates and reaction pressure on the methanation performance parameters defined earlier: CO₂ conversion, CH₄ selectivity and CH₄ output. To assist in the analysis, equilibrium CO₂ conversions were calculated using Aspen Plus V8.6 software. A Gibbs reactor was simulated, including all product components obtained during the experimental investigation. This was done for both the 5 and 10 bar_g reaction pressures, while using the experimentally measured methanation outlet temperatures to calculate the equilibrium values. The experimental results tabulated in Table 4.1 are used for a performance comparison of co- and counter-current flow configurations, reported in sections 4.3.2.1 and 4.3.2.2, respectively. During the performance evaluation of the microchannel reactor, no detectible catalyst deactivation – whether chemical poisoning, mechanical fouling or thermal degradation (sintering) – was observed.

4.3.2.1 Co-current flow configuration

First, in the case of the co-current configuration and 5 bar_g reaction pressure, we recorded CO₂ conversions up to 89.5% for a methanation flow of 4.0 NL min⁻¹ and coolant flow of 0.8 NL min⁻¹. Through quantification of the dry product gas, a CH₄ fraction of 0.626 and CO fraction of 0.002 were measured, resulting in a CH₄ selectivity of 99.7%. CO formation takes place via the RWGS reaction (reaction 4.2), and is favoured at higher temperatures due to its endothermic nature. At higher methanation flow rates, the deviation from the equilibrium CO₂ conversion became more apparent: for a methanation flow of 7.0 NL min⁻¹, the CO₂ conversion was 85.8%, while the equilibrium value was 89.5%. Is it therefore clear that the apparent gas–catalyst contact time is insufficient at 5 bar_g to allow equilibrium values of CO₂ to be converted at high methanation flow rates. With increased pressure operation (10 bar_g), the contact time is roughly double that at 5 bar_g, and will allow for better CO₂ conversions to be achieved.

At 10 bar_g reaction pressure, a methanation flow of 6 NL min⁻¹ provided near-equilibrium CO₂ conversions. At a coolant flow rate of 2.8 NL min⁻¹, the conversion was calculated as 90.8%, while the equilibrium conversion was 92.7%. Interestingly, when the coolant flow rate was increased to 3.2 NL min⁻¹, the conversion increased to 91.1%. On the other hand, in the latter case, the CH₄ fraction obtained was 0.667, while at the lower coolant flow rate the CH₄ fraction was slightly poorer (0.659). This was attributed to the effects of the maximum temperature within the reactor. For the higher coolant flow rate of 3.2 NL min⁻¹, the maximum temperature was 433.3°C, compared to 437.2°C at a coolant flow of 2.8 NL min⁻¹. The slightly lower temperature contributed to an increase in CH₄ formation, due to the reaction being very close to equilibrium at a flow of 6 NL min⁻¹. Essentially this is a characteristic associated with thermodynamic equilibrium of the exothermic Sabatier reaction. At a methanation flow rate of 7 NL min⁻¹, the maximum CH₄ output was calculated as 19.2 NL g_{cat}⁻¹ h⁻¹, while a CO₂ conversion of 89.1% was obtained.

Table 4.1: Performance evaluation of selected CO₂ methanation experiments in co- and counter-current flow configurations of the microchannel reactor.

Methanation flow (NL min ⁻¹)	Coolant flow (NL min ⁻¹)	Mole fraction				Equilibrium CO ₂ conversion (%)	X CO ₂ (%)	S CH ₄ (%)	CH ₄ output (NL g _{cat} ⁻¹ h ⁻¹)	Inlet temp (°C)	Max temp (°C)	Outlet temp (°C)
		H ₂	CH ₄	CO	CO ₂							
Co-current, 5 bar_g												
4.0	0.8	0.292	0.626	0.002	0.080	91.8	89.5	99.7	11.8	403.1	415.7	408.2
5.0	1.0	0.330	0.572	0.003	0.095	91.2	87.5	99.5	14.6	405.3	423.1	416.8
6.0	2.0	0.323	0.563	0.003	0.111	90.7	87.4	99.5	16.9	402.7	427.9	422.7
7.0	2.8	0.360	0.540	0.003	0.097	89.5	85.8	99.4	18.8	407.5	441.6	436.7
Co-current, 10 bar_g												
5.0	2.0	0.252	0.668	0.002	0.078	93.1	91.2	99.7	14.9	406.0	425.6	417.1
6.0	2.8	0.265	0.659	0.001	0.075	92.7	90.8	99.8	16.6	415.8	437.2	423.2
6.0	3.2	0.258	0.667	0.001	0.074	92.6	91.1	99.8	16.5	406.0	433.3	424.9
7.0	3.2	0.297	0.611	0.002	0.090	92.1	89.1	99.7	19.2	409.2	440.5	431.8
Counter-current, 5 bar_g												
4.0	1.0	0.277	0.611	0.001	0.112	91.6	89.6	99.9	11.5	412.4	422.4	411.2
5.0	1.4	0.309	0.560	0.002	0.129	91.1	87.7	99.6	13.9	414.8	428.5	417.7
6.0	2.0	0.304	0.570	0.002	0.124	90.3	88.1	99.6	16.1	426.9	442.4	427.3
6.0	2.8	0.349	0.521	0.003	0.128	90.6	85.7	99.5	15.7	423.5	438.5	423.7
7.0	3.2	0.418	0.447	0.003	0.132	90.4	81.2	99.2	16.7	419.8	439.9	426.6
7.0	3.6	0.446	0.407	0.004	0.144	90.7	78.7	99.1	16.2	416.6	436.1	423.1
Counter-current, 10 bar_g												
4.0	1.4	0.248	0.655	0.000	0.097	94.1	91.1	100	12.0	406.3	414.8	400.6
5.0	2.8	0.252	0.647	0.001	0.100	93.7	90.9	99.9	15.3	414.8	425.0	406.5
6.0	3.6	0.267	0.632	0.000	0.101	93.1	90.2	100	16.7	427.2	438.8	415.8
6.0	4.0	0.253	0.658	0.001	0.088	93.5	91.0	99.9	17.1	425.5	435.7	409.9
7.0	5.2	0.260	0.639	0.001	0.100	93.2	90.5	99.9	19.8	435.5	447.2	415.2
7.0	5.6	0.284	0.613	0.001	0.102	93.3	89.5	99.8	19.2	429.8	441.8	412.6

4.3.2.2 Counter-current flow configuration

As discussed in section 4.3.1.2, the counter-current flow configuration recirculated reaction heat back to the main reaction zone via the H₂ coolant stream, as it flowed in the opposite direction to the methanation reaction. Now, consider the counter-current 5 bar_g operating point at a methanation flow rate of 6 NL min⁻¹ and coolant flow rate of 2.0 NL min⁻¹. Compared to in the co-current case at the same flows, the steady-state temperature profile for the counter-current operation now stabilized at much higher temperatures, especially at the inlet and in the

middle of the reactor. An inlet temperature of 426.9°C and maximum temperature of 442.4°C led to the conversion of slightly more CO₂ (88.1%) than in co-current operation (87.4%). In the co-current case, the inlet temperature and temperature maximum were 402.7°C and 427.9°C, respectively, while the outlet temperature was only 4.6°C lower than the equivalent counter-current temperature.

The one instance where the counter-current flow configuration showed sub-standard methanation activity was at a reaction pressure of 5 bar_g and a high methanation flow rate of 7 NL min⁻¹. A CO₂ conversion of only 81.2% and CH₄ product fraction of 0.447 was obtained at a coolant flow rate of 3.2 NL min⁻¹. This was attributed to the combination of a high methanation flow rate, low reaction pressure and a counter-current temperature profile that provided, albeit only briefly, a high enough temperature (439.9°C at axial location 6) to convert substantial amounts of CO₂. In contrast, at a coolant flow rate of 2.8 NL min⁻¹, the co-current flow configuration gave temperatures above 436.7°C at axial locations 6–10, providing, to a certain extent, a higher CO₂ conversion (85.8%) and CH₄ product fraction (0.540). For counter-current methanation flow rates of 6 NL min⁻¹ and 7 NL min⁻¹, we observed that the CO₂ conversion decreased further with increased coolant flow rates of 2.8 NL min⁻¹ and 3.6 NL min⁻¹, respectively, which is indicative of slower reaction rates at 5 bar_g. As in the co-current case (section 4.3.2.1), increased pressure operation at 10 bar_g is necessary to ultimately obtain satisfactory reactor performance.

In counter-current flow, at 10 bar_g, the application of low methanation and coolant flow rates resulted in very mild axial temperatures. The temperature profile for a methanation flow of 4 NL min⁻¹ and coolant flow of 1.4 NL min⁻¹ only reached a maximum temperature of 414.8°C at axial location 5 (Figure 4.5). The combined effects of 10 bar_g pressure and longer residence times resulted in this experiment being one of the best performing in terms of CO₂ conversion (91.1%) and CH₄ selectivity (100%). Of course, due to the low methanation flow rate, a CH₄ output of only 12.0 NL g_{cat}⁻¹ h⁻¹ was attained. Throughout the analysis of these experimental data, the H₂ product fraction is seen to be significant in all cases. For the data point discussed above, the H₂ product fraction was the lowest for all the experiments reported here, 0.248. Here, it is important to consider the stoichiometry of the Sabatier reaction (reaction 4.1). Four moles of H₂ react with one mole of CO₂ to produce only one mole of CH₄ (assuming the water is condensed and not considered in the equation). Hence, any unreacted H₂ seems magnified during the quantification of the dry product gas due to this stoichiometric ratio.

At a methanation flow rate of 6 NL min⁻¹ and coolant flow rate of 3.6 NL min⁻¹, the CO₂ conversion was calculated as 90.2%. Interestingly, no CO formation took place, thus ensuring that a CH₄ selectivity of 100% was attained. The absence of CO is generally ascribed to the low outlet temperatures that counter-current operation supports. In this scenario, the inlet temperature was 427.2°C, the temperature maximum 438.8°C at axial location 5 and the methanation outlet temperature 415.8°C. When the coolant flow rate was increased further (to 4.0 NL min⁻¹), the methanation outlet temperature decreased to 409.9°C, resulting in a CO₂ conversion increase to 91.0%. A similar observation was made in the co-current case at 10 barg pressure. The CH₄ product fraction, measured as 0.658, was the highest reported value of all the counter-current experiments.

To maximise the CH₄ output, a methanation flow rate of 7 NL min⁻¹ is recommended. At a coolant flow rate of 5.2 NL min⁻¹, the CO₂ conversion was still high at 90.5%, while the output was calculated as 19.8 NL g_{cat}⁻¹ h⁻¹. Of importance here is that CO formation was very limited, affording a CH₄ selectivity of 99.9%.

These attributes of the methanation performance and selectivity are ascribed to the axial temperature profile discussed in section 4.3.1.2. In short, a temperature maximum of 447.2°C at axial location 4 and a low methanation outlet temperature of 415.2°C were essential to provide these favourable methanation characteristics. Unfortunately, when attempts were made to improve the heat recovery, by increasing the coolant flow rate even further (5.6 NL min⁻¹), some limitation in the methanation activity was observed (89.5% CO₂ conversion and 19.2 NL g_{cat}⁻¹ h⁻¹ CH₄ output) due to the demanding methanation flow rate (7 NL min⁻¹) imposed on the reactor; even with the benefit of enhanced thermal behaviour. It was at this point that we determined that the functional operating regime of our microchannel reactor had been fully established.

In summary, probably the greatest benefit of counter-current operation – at least at 10 barg pressure, where high methanation activity prevails – is achieving useful higher inlet temperatures, coupled with maximum temperatures in the middle of the reactor (slightly higher than the equivalent co-current temperature maximums). With the added benefit of lower outlet temperatures, the CO₂ conversions, which are associated with an improved equilibrium, can be obtained, even at high methanation flow rates.

4.3.3 Recommended operating conditions

For a methanation flow rate of 7 NL min⁻¹ and reaction pressure of 10 bar_g, the counter-current flow configuration offered a steady-state axial temperature profile within the microchannel reactor, which provided improved equilibrium CO₂ conversion. In addition, the counter-current flow configuration allowed higher coolant flow rates to be used within the stable operating regime of the reactor, ensuring better heat recovery compared to in the co-current case.

Table 4.2 summarises the recommended operating conditions and the associated microchannel reactor performance. To maximise the reactor throughput, the following is recommended as the best operating point: reaction pressure of 10 bar_g, methanation flow rate of 7 NL min⁻¹ and coolant flow rate of 5.2 NL min⁻¹. At these conditions, the following was achieved: a near-equilibrium CO₂ conversion of 90.5%, CH₄ selectivity of 99.89% and CH₄ output of 19.8 NL g_{cat}⁻¹ h⁻¹. The dry product gas contained 63.9 vol.% CH₄.

Table 4.2: Summary of recommended operating conditions and performance parameters of the microchannel reactor/heat exchanger.

Recommended operating conditions		
Methanation catalyst	5.0 wt.% Ru/Al ₂ O ₃	
Total methanation flow rate	7.0	NL min ⁻¹
H ₂ power input (P)	928.3	W
Residence time (7.0 NL min ⁻¹)	129.7	ms
H ₂ :CO ₂ ratio	4:1	
H ₂ coolant flow rate	5.2	NL min ⁻¹
Microchannel reactor performance		
Maximum reactor temperature	447.2	°C
Temperature gradient	20.3	°C
Pressure drop	13.4	kPa
CO ₂ conversion (X _{CO2})	90.5	%
CH ₄ selectivity (S _{CH4})	99.89	%
CH ₄ output	19.8	NL g _{cat} ⁻¹ h ⁻¹
CH ₄ content (dry)	63.9	vol.%
CH ₄ power output (P)	667.1	W
Thermal efficiency	71.9	%
Recovered heat in H ₂ ($\dot{Q}_{\text{rec}}$)	43.7	W (@ 435.5°C)
Overall efficiency	76.6	%

A comparison of the reactor performance reported here is made to other reports of microchannel-based technology for pure CO₂ methanation in Table 4.3. In our earlier work, conducted on a much smaller isothermal microchannel reactor, a CH₄ output of only 16.9 NL g_{cat}⁻¹ h⁻¹ was achieved at a methanation flow rate of 150 NmL min⁻¹, albeit at 5 bar_g pressure [39]. In the case of the isothermal reactor, the 5 bar_g and 10 bar_g operating points showed minimal difference in terms of reactor performance. Our present work reveals that self-sustained operation is highly dependent on the axial temperature profile within the reactor, which, in turn, is improved by increasing the reaction pressure (10 bar_g). At the scale of this methanation reactor (5.6 NL min⁻¹ H₂), the reaction heat released is much more moderated than expected. In turn, heat recuperating strategies included operational means (optimised temperature profiles via counter-current flow) and physical means (an external feed pre-heater/heat exchanger and additional reactor insulation) to ensure self-sustained operation and satisfactory methanation performance.

Table 4.3: A performance comparison of microchannel-based Sabatier reactors reported in the literature.

Reference	Exp. / model based microchannels	Thermal conditions, (coolant)	Catalyst	Temperature (°C)	Pressure	Methanation flow (NL min ⁻¹)	Conversion of CO ₂ (%)	Selectivity towards CH ₄ (%)
[25]	Exp.	Isothermal	25.2 wt.% Ni/Al ₂ O ₃	350	15 bar _g	1.33	96.0	>99.0
[26]	Exp.	Series of three isothermal reactors	Ru-supported	365, 294, 234	–	0.0001	96.0	–
[33]	Exp.	Counter-current flow, (thermal oil)	3 wt.% Ru/TiO ₂	Inlet: 398 Outlet: 327	1 atm	~0.122	88.4	–
[35]	Exp.	Series of two isothermal reactors, (thermal oil)	Ni-supported	300, 350	3 bar _a	371.6	98.0	–
[37]	Model	Isothermal, *	15 wt.% Ni/Mg/Al hydrotalcite	300	5 bar	2.0	92.0	–
[39]	Exp.	Isothermal	8.5 wt.% Ru/Al ₂ O ₃	400	5 bar _g	0.15	83.4	97.7
This work	Exp.	Co- and counter-current flow, (pure H ₂)	5 wt.% Ru/Al ₂ O ₃	Inlet: 435.5 Max: 447.2 Outlet: 415.2	10 bar _g	7.0	90.5	99.89

* Corrugated plate reactor/heat exchanger

Although near-equilibrium CO₂ conversion was achieved, the stoichiometric ratio of the methanation reaction is such that even small amounts of unreacted H₂ leads to significant H₂ fractions in the product gas. At the recommended operating point, the H₂ fraction was 26.0 vol.%. This leads us to believe that a single methanation reactor is insufficient for the production of high purity CH₄, specifically, with a content >90 vol.%, for storage application in natural gas pipelines, or the use thereof as a green transportation fuel. Additional reaction steps or purification techniques are therefore necessary, in an effort to produce high purity CH₄. It has however been demonstrated, in an earlier paper of ours, that a similar H₂/CO₂/CH₄-containing fuel can be directly combusted in a micro gas turbine for combined heat and power generation [45].

Figure 4.6 shows a Sankey diagram of the microchannel reactor/heat exchanger energy balance during CO₂ methanation at the recommended operating point. Of the 928.3 W of hydrogen energy that was fed to the reactor, 667.1 W was converted to methane. This power input/output was calculated based on Eqn. 4.5. A thermal efficiency of 71.9% was obtained (Eqn. 4.6). The H₂ coolant stream of 5.2 NL min⁻¹ was able to recover 43.7 W of heat (Eqn. 4.7) at a coolant stream outlet temperature of 435.5°C, ensuring that an overall efficiency of 76.6% was obtained (Eqn. 4.8). The 26.0 vol.% unreacted H₂ in the product stream accounted for 82.1 W in the product, which was not included in the efficiency calculations. The purpose of methanation here is, after all, to convert as much H₂ and CO₂ into CH₄ as possible. Carbon monoxide accounted for a mere 0.4 W, due to the high selectivity obtained in the methanation process.

The external heat exchanger was able to contribute 23.2 W of heat to the reactor system, heating the incoming cold methanation feed to 180.0°C. It was determined that, within the heat exchanger, the hot flue gas from the methanation reaction reached its saturation temperature and partially condensed within the heat exchanger. It was therefore calculated that an additional amount of 93.0 W of sensible and latent heat in the methanation product was not utilised; it was lost to the atmosphere. Notwithstanding that, the 23.2 W of recuperated heat proved to be a valuable heat inflow to the reactor; it certainly contributed to the temperature profiles reported earlier (section 4.3.1). Finally, based on the balance of energy, it is estimated (indicated with * in Figure 4.6) that 42.0 W of heat was lost from the system to the atmosphere. It should be noted that the energy balance was calculated using the experimentally measured flow rates,

gaseous fractions and temperatures, hence the values could include an experimental error of up to 5%.

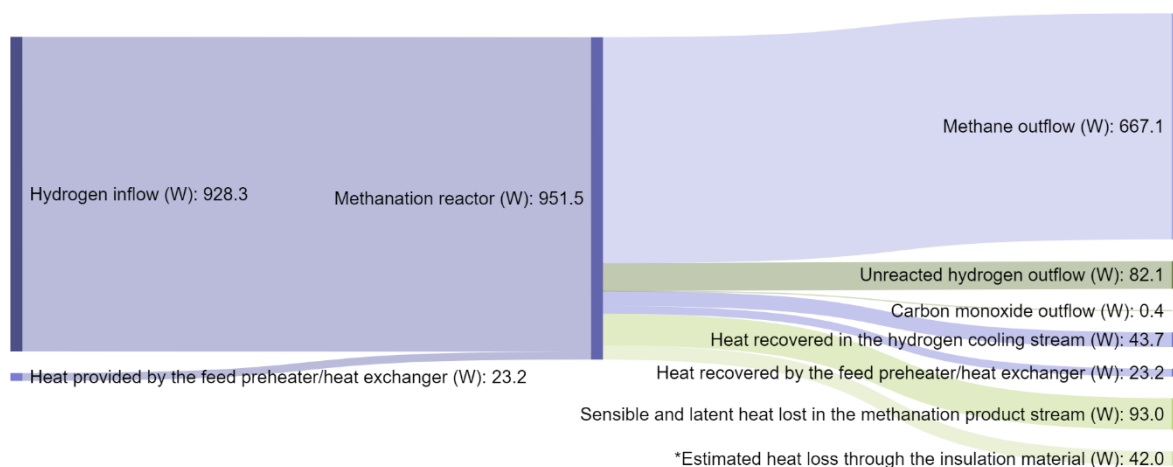


Figure 4.6: Sankey diagram of the microchannel reactor/heat exchanger energy balance during CO₂ methanation at the recommended operating point: methanation flow of 7 NL min⁻¹, coolant flow of 5.2 NL min⁻¹, and reaction pressure of 10 barg. Reference temperature for calculations: 20°C.

4.4 CONCLUSIONS

The PtG concept (CO₂ methanation) is an innovative approach to store renewably generated energy; it provides large-scale grid balancing, while it simultaneously sequesters CO₂ emissions from industrial point sources. Furthermore, PtG will be supported by the use of process intensifying reactor technologies that offer load-following capabilities, ease of operation and compact process assemblies. In this work, a catalytic microchannel reactor was experimentally evaluated for CO₂ methanation—it supported an integrated cooling capability with pure H₂ as the heat transfer medium. Renewable H₂ from a solar-to-hydrogen storage facility was used, for the purposes of both the methanation reaction and the cooling medium. The effects of the total methanation flow rate (4–7 NL min⁻¹), coolant flow rate (0.8–5.6 NL min⁻¹) and reaction pressure (5 and 10 barg) were considered. A significant part of this work was focussed on the thermal management of the reactor, by directly comparing co- and counter-current flow configurations and their associated effects on the reactor's steady-state axial temperature profiles. A decreasing temperature profile, supporting improved methanation equilibrium, was obtained with the counter-current flow configuration. It was further

demonstrated that the microchannel reactor provided enhanced methanation performance and heat recuperation.

At the recommended operating point (exp. conditions: methanation flow of 7 NL min⁻¹, coolant flow of 5.2 NL min⁻¹, and reaction pressure of 10 barg), a maximum reactor temperature of 447.2°C was measured—it was located between the methanation inlet and the middle of the reactor. At the outlet of the microchannels, the reactor temperature was as low as 415.2°C, which contributed to the improved methanation equilibrium. We achieved the following methanation performance: CO₂ conversion of 90.5% and CH₄ output of 19.8 NL g_{cat}⁻¹ h⁻¹. We determined the hydrogen-to-methane thermal efficiency to be 71.9%. With the heat recuperated, using the H₂ as cooling medium, the overall methanation process efficiency could be expressed as 76.6%. This efficiency can be compared to that achieved with much larger conventional reactor-based methanation technologies.

This work demonstrates that a microchannel reactor can offer process intensifying characteristics towards the exothermic CO₂ methanation reaction, with the proviso that suitable operating strategies be followed to maximise the reactor performance. PtG technology is bound to be a future alternative to store and utilise renewable energy. Microchannel reactors are well suited for PtG applications, especially as they are compact and can operate at notable turn-down ratios—typical requirements for the storage of intermittent renewable energy.

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CHAPTER 5

DEVELOPMENT OF A CO₂ METHANATION DEMONSTRATOR: EXPERIMENTS AND VALIDATION OF HEAT AND MASS TRANSPORT USING COMPUTATIONAL FLUID DYNAMICS

CHAPTER OVERVIEW

This chapter presents a combination of experimental and modelling work, devoted to the design, development and assessment of a compact and portable CO₂ methanation demonstrator—incorporating the same microchannel reactor as presented in Chapter 4—for the self-sustained production of methane from renewable H₂. This chapter describes the validation of the CO₂ methanation demonstrator's steady-state performance to that attained as described earlier, in the bench-top evaluation (Chapter 4), as well as confers reactor dynamics during an extended dynamic response test. Finally, the development and experimental validation of a comprehensive 2D CFD model of the thermally coupled CO₂ methanation process within the microchannel reactor is addressed.

5.1 INTRODUCTION

In 2008, South Africa's Department of Science and Innovation (DSI) established the National Hydrogen and Fuel Cells Technologies Research, Development and Innovation Strategy to develop, demonstrate and commercialise H₂ technologies as sustainable energy solutions. The National Strategy was branded Hydrogen South Africa (HySA), which would host key programmes to demonstrate and commercialise these H₂ technologies, while promoting the use of South Africa's platinum group metal (PGM) resources and abundant renewable energies, primarily solar photovoltaic energy.

As part of HySA's activities on power-to-gas (PtG) technology, hosted by HySA Infrastructure at the North-West University (Potchefstroom Campus), there exists a need to demonstrate the conversion of renewable H₂ into useful chemical carriers such as CH₄, with large-scale storage and industrial fuel application. The purpose of this chapter is to present the design, assembly and performance demonstration of a compact and portable CO₂ methanation demonstrator, which could be presented at DSI HySA workshops and other exhibitions, as an effective renewable H₂ processing unit. The same microchannel-based methanation reactor presented in Chapter 4 will be used in this demonstrator, with a few key design modifications and simplifications to improve its balance-of-plant's compactness, presentability, operability and automation of the methanation system.

The scientific content of this chapter is further expanded by presenting the development and experimental validation of a non-isothermal, two-dimensional (2D) computational fluid dynamic (CFD) model based on the methanation reactor, which employs microchannels as heterogeneous catalyst substrate to facilitate the methanation reaction. The steady-state temperature profiles that are characteristically determined by the main methanation reaction zone and downstream, the equilibrium favouring zone, are validated computationally with this model. In addition, the associated heat and mass transport properties in the axial dimension of the microchannels, which could not be quantified experimentally, are described with the model.

5.2 EXPERIMENTAL METHODOLOGY

5.2.1 Thermal considerations for the methanation demonstrator design

The CO₂ methanation reaction (Eqn. 5.1) is an exothermic process, releasing roughly 20% of the heating potential of the reacted H₂ as heat, when the reaction is carried out at temperatures

>400°C and at elevated pressure. Although lower reaction temperatures are favourable to the exothermic reaction's thermodynamic equilibrium, it had been observed that temperatures >400°C support the required kinetic turn-over rates of the catalyst (5 wt.% Ru/Al₂O₃) (section 4.3.2), which allows the release of reaction heat, and ultimately supports the autothermal operability of the methanation reactor.



During the bench-top investigation of the autothermal microchannel reactor for CO₂ methanation, the maximum total methanation flow rate was found to be 7 NL min⁻¹, corresponding to a H₂ flow rate of 5.6 NL min⁻¹ and heating potential (LHV_{H_2}) of 928.3 W (close to the 1 kW design specification). The reaction heat that was released, which was either partially used in the feed pre-heater, recovered in the H₂ coolant stream or lost through sensible, latent and atmospheric losses, accounted to 201.9 W. With the feed pre-heater, the incoming cold methanation feed (H₂/CO₂) was heated to 180.0°C, before entering the microchannel reactor. The sensible heat gained by the feed stream (23.2 W) was found to be an essential part of the energy balance around the reactor, and ultimately contributed to the reactor's thermal behaviour (discussed in section 4.3.1.2). In the counter-current flow direction to the methanation reaction, the H₂ coolant flow was set at a flow rate of 5.2 NL min⁻¹, which gained 43.7 W of heat to exit the reactor at 435.5°C. It is proposed that this heat is usable by other (external) processes to the methanation reactor.

For the design of the compact methanation demonstrator, and having established that the H₂ coolant flow rate (5.2 NL min⁻¹) was comparable to the H₂ flow rate (5.6 NL min⁻¹) for methanation, a fraction of the 43.7 W can be internally utilised in the methanation reactor. It will act as a feed pre-heating stage, replacing the need for the external feed pre-heater in the bench-top investigation. The discrepancy in the energy balance (43.7 W vs 23.2 W) will, in part, be reduced by the fact that only the H₂ reactant can be pre-heated in the secondary loop, and not the cold CO₂ feed. Of importance is that this design change is only possible for the scale of this methanation reactor (~0.6–1 kW) because larger reactors will have lower external surface-to-volume ratios (lower specific heat loss to the atmosphere), and significant cooling would be required. In essence, in the case of this reactor, the heat lost through the insulation material is of such magnitude that some form of heat recycling is necessary to ensure autothermal operation.

5.2.2 Methanation demonstrator design

Subsequently, for simplifying the design and compactness of the methanation demonstrator, no dedicated H₂ coolant stream was fed to the reactor here (as was done in the case of the bench-top evaluation, Chapter 4). In the demonstrator's case, the H₂ reactant to the methanation chamber first passes counter-currently to be pre-heated (still ensuring an equilibrium favouring temperature profile via counter-current flow), before being mixed with the CO₂ feed and then entering the methanation chamber. A piping and instrumentation (P&I) diagram of the methanation demonstrator is illustrated in Figure 5.1—the notations used in the presentation and discussion of the P&I diagram are defined in Table 5.1.

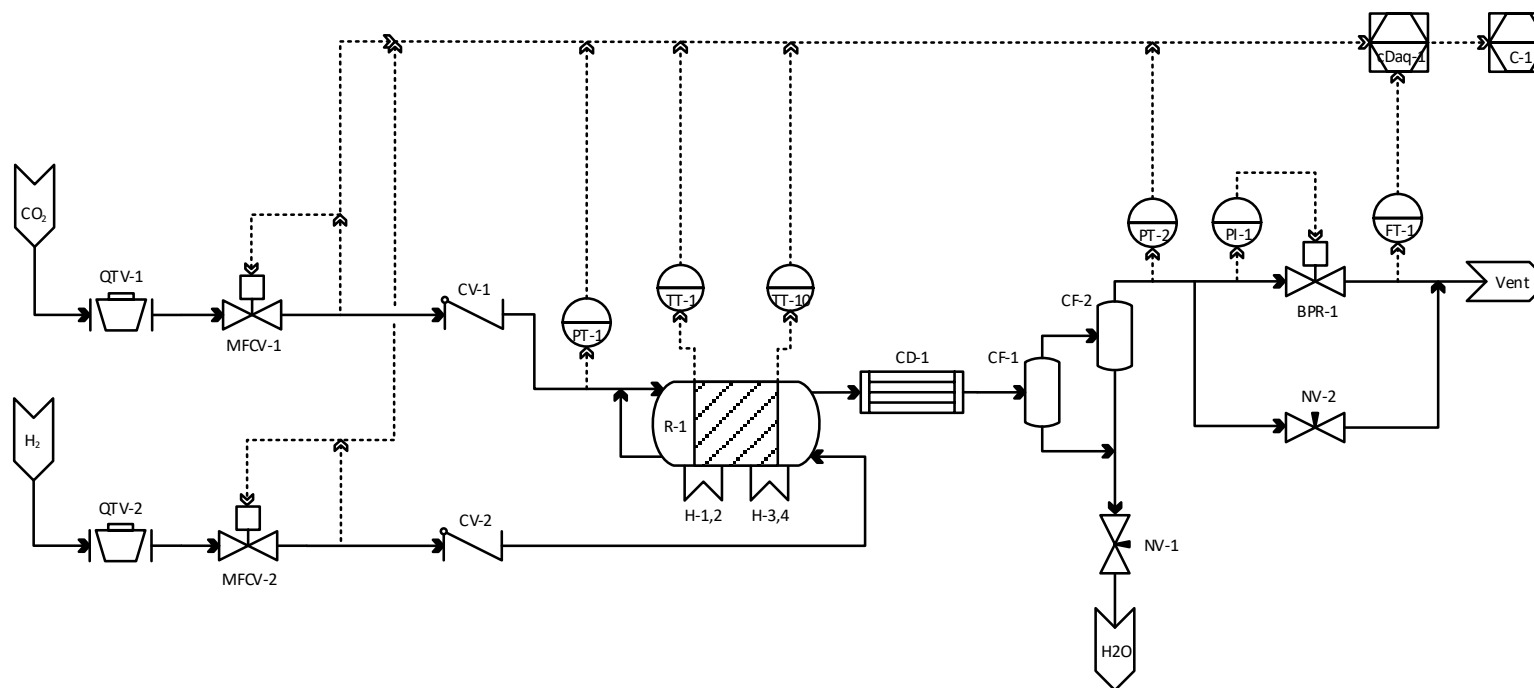


Figure 5.1: P&I diagram of the CO₂ methanation demonstrator (notations defined in Table 5.1).

Table 5.1: Notations used in the P&I diagram presented in Figure 5.1.

Process stream	Description	Equipment notation	Description	Instrument notation	Description
H ₂	Hydrogen, 5.6 NL min ⁻¹	BPR	Back pressure regulator, (manual)	C	Computer
CO ₂	Carbon dioxide, 1.4 NL min ⁻¹	CD	6 m coil condenser, (¼ pipe)	cDaq	Compact Daq
H ₂ O	Water condensate, 150 mL h ⁻¹	CF	Auto-drain coalescing filter	FT	Flow transmitter
Vent	Product gas to the gas chromatograph or vent, 1.9 NL min ⁻¹	CV	Check valve	PI	Pressure indicator
		H	Temperature-controlled heater	PT	Pressure transmitter
		MFCV	Mass flow control valve	TT	Temperature transmitter
		NV	Needle valve		
		QTV	Quarter-turn valve		
		R	Reactor		

5.2.2.1 Feed gas preparation

The methanation demonstrator was designed and assembled using Swagelok ¼ inch OD piping, with 0.89 mm pipe wall thickness. The design is such that only the external piping of the demonstrator is stainless steel braided, convoluted hoses to connect H₂ and CO₂ gas supplies, and the handling of the product gas (vent) and water condensate. Two manual shut-off valves (QTV-1,2), located on the front panel of the demonstrator (Figure 5.2), are opened before the demonstrator is used, to supply H₂ and CO₂ to the internal mass flow controllers (MFCV-1,2). These flow controllers (Brooks SLA5800 series thermal mass flow controllers), calibrated for H₂ and CO₂, respectively, are used to supply the methanation reactor with H₂ and CO₂ at 10 bar_g pressure, and at the desired operational flow rates, and in a stoichiometric molar feed ratio of 4:1 (H₂:CO₂). Non-return valves (CV-1,2) of spring and poppet type, are used as safety mechanisms to prevent the reverse flow of H₂ into the CO₂ supply line, and vice versa, in possible cases of unequal gas pressure supply.



Figure 5.2: Photograph of the compact methanation demonstrator.

5.2.2.2 Controlling and monitoring reactor temperature and pressure

As in the case of the benchtop evaluation of the microchannel-based methanation reactor, four heating cartridges (Watlow FIREROD®, 300 W each), indicated on the P&I diagram as H-1 to H-4, are used to reach the light-off temperature of the methanation reaction (415°C), after which they are switched off, to initiate self-sustained (autothermal) operation. The power to these heating cartridges is controlled by a Shinko JCS series temperature controller, through a

10 A–220 V relay. The face of the temperature controller is located on the front panel of the demonstrator, and visible in Figure 5.2. Ten K-type thermocouples with 0.5 mm OD (TT-1,...,10) are used for temperature measurements of the reactor core. They are positioned axially along the length of the microchannel reactor (Figure 4.2b).

Around the time that the light-off temperature of the methanation reaction is reached, the gas pressure of the flow-controlled H₂ and CO₂ is gradually increased to 10 bar_g with a manual back pressure regulator (BPR-1) of Swagelok's KPB series. This back pressure regulator, with pressure indicating gauge (PI-1) and bypass needle valve (NV-2), is also located on the front panel of the demonstrator (Figure 5.2). A WIKA A10 series electronic pressure transmitter (PT-1), located on the CO₂ supply line and immediately upstream of the confluence with the pre-heated H₂ reactant, is used to measure the gas pressure at the inlet of the methanation chamber. This location for the pressure transmitter is the nearest, safest location to accurately measure the reactor's gas inlet pressure. A second electronic pressure transmitter (PT-2) measures the methanation product gas outlet pressure. This pressure transmitter is located downstream of two coalescing filters (discussed further in section 5.2.2.3), and immediately upstream of the back pressure regulator.

5.2.2.3 Water removal and product gas flow measurement

The product gas stream from the methanation chamber needs to lose approximately 116 W of sensible and latent heat for a flow condition of 7 NL min⁻¹, before the product water is removed at 25°C by two coalescing filters. This heat dissipation takes place in a ¼ inch coiled pipe of 6 m length (CD-1). To assist in the natural convective air flow across the coiled pipe condenser, the demonstrator was developed with an open bottom, while a 60 W (220 V) axial cooling fan was installed at the top–rear section of the demonstrator cabinet. During experiments, it was determined that approximately 4.5 m of the coil condenser is used for heat exchange. When the product gas is cooled to 25°C, the liquid water condensate is firstly removed in a coalescing filter (CF-1), with its filter elements removed—essentially a water catch pot, with an aluminium head and a polyamide material bowl (Classic Filters, AN212-271-CP). A second coalescing filter (CF-2) is used downstream of CF-1, to remove water droplets as small as 0.01 µm at a removal efficiency of 99.99%. Its filter elements are constructed of epoxy ester bonded microfibers (Classic Filters, AN212-271-5CE). Of importance is that CF-1 and CF-2 have liquid capacities of approximately 200 mL and 140 mL, respectively, and are drained

simultaneously with the use of a manual needle valve (NV-1). Finally, the flow rate of the liquid-free product gas is measured with a thermal mass flow meter (Bronkhorst[®], EL-flow), indicated as FT-1. The product gas exits the demonstrator and is vented through the piping infrastructure of the laboratory, or diverted to an SRI8610C gas chromatograph (described in section 4.2.4) for periodic gas species quantification.

5.2.2.4 Process automation and data logging

National Instruments[™] LabVIEW software is used to control the H₂ and CO₂ flow inputs to the controllers, and, simultaneously, log the reactor inlet and outlet pressure, axial temperature measurements and product gas flow rate in 1-min intervals. A snapshot of the LabVIEW control interface is presented in Figure 5.3.

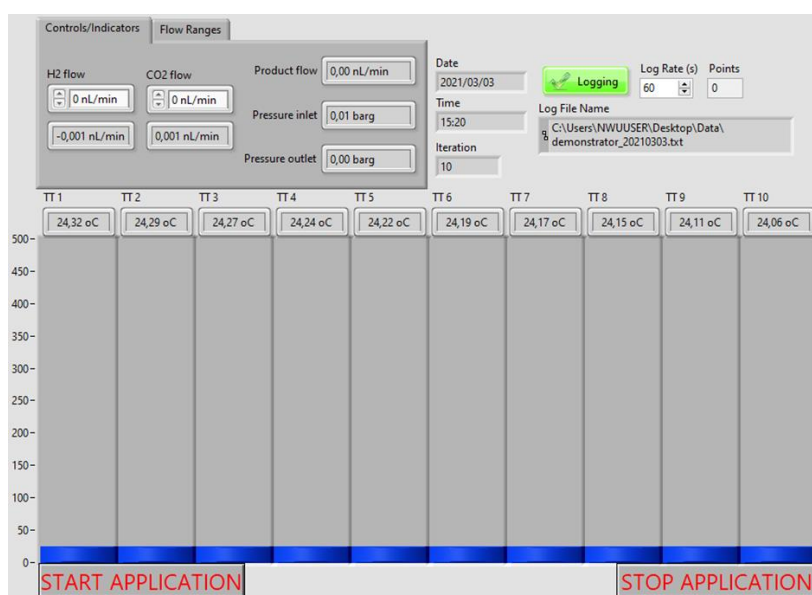


Figure 5.3: Control, monitoring and data logging of the methanation demonstrator's reaction conditions using a LabVIEW software application.

Typically, all the flow rate inputs and the product gas flow measurements have units of NL min⁻¹. The thermal mass flow meter is calibrated for pure H₂ flow, hence a flow correction is necessary when measuring the product gas with H₂, CO₂, CH₄ and CO gaseous components, due to the product gas having a thermal conductivity representative of the gas mixture. The GC measurements and product flow rate are therefore further processed using Microsoft Excel to complete molar balances, and calculate CO₂ conversion and CH₄ selectivity. Inlet and outlet reactor pressure measurements have the unit of barg, and temperature measurements have the unit of °C. No post-processing of the data for these parameters is necessary.

5.3 EXPERIMENTATION: RESULTS AND DISCUSSION

5.3.1 Methanation demonstrator: Thermal behaviour, and comparison to the bench-top investigation

The flow configuration of the methanation demonstrator described here follows the same counter-current flow configuration as for the bench-top investigation (section 4.3.1.2). The demonstrator's design is described in detail in section 5.2.2. Steady-state axial temperature profiles obtained within the demonstrator, for methanation flows of 5–7 NL min⁻¹ and a reactor pressure of 10 bar_g, are presented in Figure 5.4. The methanation flow enters the microchannel reactor at axial location 1, while the cold H₂ flow that is to be pre-heated for methanation enters the microchannel reactor at axial location 10, and exits the reactor at axial location 1 (where it is to be mixed with the CO₂ and fed to the methanation chamber). In the subsequent discussions, this configuration applies.

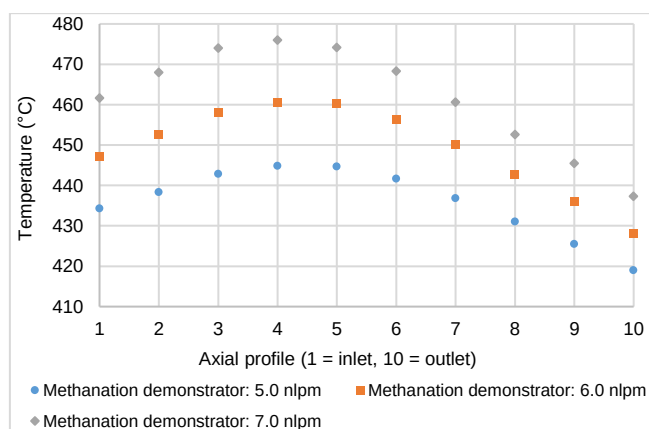


Figure 5.4: Comparison of steady-state axial temperature profiles for the methanation demonstrator, for the following conditions: total methanation flow of 5.0–7.0 NL min⁻¹ and reaction pressure of 10 bar_g.

For all three flow rates presented in Figure 5.4, typical equilibrium favouring steady-state temperature profiles were observed, with methanation inlet temperatures higher than those at the reactor outlet. Upon first observation, the counter-current pre-heating of the H₂ reactant to the methanation chamber achieved the same effects as in the bench-top case, where a dedicated counter-current flow of H₂ coolant was used (the methanation flow was pre-heated by external means). For a flow of 5 NL min⁻¹, an inlet temperature of 434.3°C was measured, while the outlet was 15.3°C lower (419.0°C). Due to the increased reaction heat that was released when

the 7 NL min⁻¹ flow condition was applied, the inlet temperature was as high as 461.7°C, while the methanation outlet temperature was 437.3°C.

The highest axial temperature for each methanation flow was attained at axial location 4, with the highest flow condition (7 NL min⁻¹) providing a maximum temperature of 476.0°C. It may be argued that such a high temperature is excessive for methanation, and that the methanation demonstrator's design does not favour substantial heat loss through a dedicated H₂ cooling stream (as in the bench-top case). Therefore, sustained operation of the methanation demonstrator at 7 NL min⁻¹ is not quite suited to the increased heat recycling via H₂ feed pre-heating and the measure of thermal insulation used around the reactor. Factors that discourage reactor operation at these high temperatures, including increased equilibrium limitation (lower CO₂ conversion) and questionable long-term catalyst stability, therefore come to mind. Nevertheless, a comparison of steady-state axial temperature profiles of the bench-top reactor and the demonstrator scenarios is necessary to fully understand their respective operating regimes and characteristic differences.

In Figure 5.5, two steady-state axial temperature profiles of the methanation demonstrator are compared to the profiles of the bench-top reactor (section 4.3.1.2), for flow rates of 5 and 7 NL min⁻¹ and at 10 bar_g pressure. For the presentation of the bench-top reactor's temperature profiles, H₂ coolant flows of 2.8 and 5.2 NL min⁻¹ were used, respectively, for the methanation flows of 5 and 7 NL min⁻¹. Generally, large offsets in the axial temperature profiles were observed, with the methanation demonstrator supporting hotter temperature profiles for equivalent flows of the bench-top reactor. For the 5 NL min⁻¹ flow condition, the demonstrator showed, on average, axial temperatures 17.4°C higher than that for the bench-top reactor, while for the 7 NL min⁻¹ flow condition, the axial temperatures were on average 25.2°C higher.

In addition, the methanation demonstrator supported slightly stronger temperature declines towards the reactor outlet. This can be ascribed to better heat recirculation by the pre-heated H₂ to the methanation chamber, which possibly shifted the main reaction zone even closer to the methanation inlet, compared to in the bench-top investigation. During the evaluation of the bench-top reactor, and for the 7 NL min⁻¹ flow condition, the H₂/CO₂ feed was pre-heated to 180.0°C in an external heat exchanger, while for the demonstrator, even better heat recirculation is achieved in the pre-heated H₂ feed. Of course, some heat is transferred to the cold CO₂ reactant during the mixing stage immediately upstream of the methanation chamber

inlet. Interestingly, with the increased heat recirculation in the methanation demonstrator, the steady-state axial temperature profile for the 5 NL min⁻¹ flow condition is very similar to that obtained in the bench-top investigation for 7 NL min⁻¹. It is therefore quite possible that the operation of the methanation demonstrator is best suited at a methanation flow rate of 5 NL min⁻¹. However, an assessment of the CO₂ conversion and CH₄ selectivity is required to ultimately make conclusions regarding the recommended operating conditions for the methanation demonstrator (as discussed further in section 5.3.2).

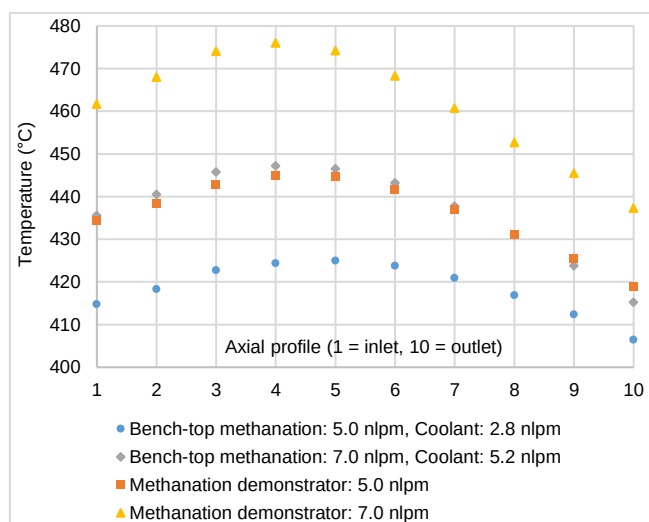


Figure 5.5: Comparison of steady-state axial temperature profiles between the bench-top methanation reactor (section 4.3.1.2) and the methanation demonstrator, for the following conditions: total methanation flow of 5.0–7.0 NL min⁻¹ and reaction pressure of 10 bar_g.

5.3.2 Catalytic activity and selectivity

This section describes an assessment of the methanation performance of the demonstrator. A varying methanation flow rate (5–7 NL min⁻¹) was used to differentiate and analyse the methanation demonstrator's performance in terms of product gas composition, CO₂ conversion, CH₄ selectivity and CH₄ output (Table 5.2). To assist in the analysis, equilibrium CO₂ conversions were calculated using Aspen Plus V8.6 software. A Gibbs reactor was simulated, including all product components obtained during the experimental investigation, while using the experimentally measured methanation outlet temperatures to calculate the equilibrium values. In the earlier bench-top investigation, 10 bar_g reaction pressure provided the best temperature profiles and methanation performance (section 4.3.2); hence, the demonstrator was evaluated only at this reaction pressure. During the performance evaluation

of the methanation demonstrator, no detectible catalyst deactivation (chemical poisoning, mechanical fouling or thermal degradation/sintering) was observed.

Table 5.2: Performance evaluation of CO₂ methanation in the demonstrator in the counter-current flow configuration and at 10 bar_g.

Methanation flow (NL min ⁻¹)	Mole fraction				Equilibrium CO ₂ conversion (%)	X CO ₂ (%)	S CH ₄ (%)	CH ₄ output (NL g _{cat} ⁻¹ h ⁻¹)	Inlet temp (°C)	Max temp (°C)	Outlet temp (°C)
	H ₂	CH ₄	CO	CO ₂							
5.0	0.260	0.671	0.0004	0.069	92.9	91.1	99.94	14.6	434.3	444.8	419.0
6.0	0.273	0.654	0.0007	0.073	92.3	90.5	99.89	17.8	447.1	460.4	428.1
7.0	0.309	0.613	0.0000	0.078	91.7	88.9	100.0	19.3	461.7	476.0	437.3

The 5 NL min⁻¹ methanation flow rate, mentioned in section 5.3.1 as having a similar steady-state temperature profile to the 7 NL min⁻¹ methanation flow condition in the bench-top investigation, provided satisfactory (near-equilibrium) methanation performance, boasting a CH₄ product fraction of 0.671 and CO₂ conversion of 91.1%. Roughly 400 ppm of CO was measured in the product gas stream, offering a CH₄ selectivity of >99.9%. When a higher methanation flow rate of 7 NL min⁻¹ was used to evaluate the methanation demonstrator, the axial temperatures increased substantially due to the increased heat release of the exothermic methanation reaction (476.0°C temperature maximum). Although the microchannel reactor may sustain a CO₂ conversion of >90% for this flow condition (recommended operating point mentioned in section 4.3.3), equilibrium limitation at higher reactor temperatures may well be responsible for the lower CO₂ conversion (88.9%) in the demonstrator's case. The respective CH₄ outputs for the 5 and 7 NL min⁻¹ methanation flow conditions were calculated as 14.6 and 19.3 NL g_{cat}⁻¹ h⁻¹, respectively. These CH₄ productivities correlated well with results obtained for the reactor in the bench-top case, taking into consideration the small variances in CO₂ conversion towards CH₄ production.

A Sankey diagram of the methanation demonstrator's energy balance is illustrated in Figure 5.6 for a methanation flow rate of 5 NL min⁻¹. This flow rate is the recommended operating point for demonstrating the thermal and methanation characteristics of this compact system. At

the flow rate of 5 NL min⁻¹, similar thermal characteristics to those at the recommended operating point of the bench-top assembly were evident, although in the latter case the methanation flow was 7 NL min⁻¹. The improved heat recirculation and insulative properties of the methanation demonstrator are discussed shortly, which allows satisfactory steady-state performance at the 5 NL min⁻¹ flow condition. The H₂ component of the feed stream (4 NL min⁻¹) had a lower heating potential of 663.0 W. The CH₄ output of 14.6 NL g_{cat}⁻¹ h⁻¹ (Table 5.2) corresponded to 492.3 W of power output, resulting in the methanation demonstrator having a thermal efficiency of 74.2%. The 26.0 vol.% unreacted H₂ in the product stream accounted for 57.6 W, while the produced 400 ppm of CO corresponded to 0.1 W. The H₂ and CO heating potentials were not included in the efficiency calculation. The pre-heated H₂ (at the flow rate of 4 NL min⁻¹) gained 24.4 W in the counter-current flow configuration, which resulted in the H₂ stream heating to 326.0°C, before being mixed with the 1 NL min⁻¹ CO₂ and fed to the methanation chamber. In the case of the bench-top assembly, the external heat exchanger provided a lower 23.2 W of heat to a combined 7 NL min⁻¹ of H₂ and CO₂ at the methanation chamber inlet.

The product gas stream contained 84.9 W of sensible and latent heat, which was lost to the atmosphere. Based on the balance of energy, it is estimated (indicated with * in Figure 5.6) that an additional 28.1 W of heat was lost from the system to the atmosphere. This heat loss included (i) the undesired cooling of the pre-heated H₂ gas stream from 434.3°C (pre-heating chamber outlet) to 326.0°C (measured at the mixing point with the CO₂ feed, in close proximity to the inlet of the methanation chamber) and (ii) heat conduction through the insulation material and subsequent convective heat transfer to the atmosphere. With greater insulation material thickness, the heat loss from the methanation reactor was reduced from 43.0 W in the bench-top case (section 4.3.3). On the other hand, the better insulation resulted in the higher steady-state temperature profile observed for the 7 NL min⁻¹ flow condition (section 5.3.1). It should be noted that the energy balance was calculated using the experimentally measured flow rates, gaseous fractions and temperatures, hence the values could include an experimental error of up to 5%. The magnitude of this experimental error was verified with repeated experimental data points on different days of assessing the performance of the methanation demonstrator.

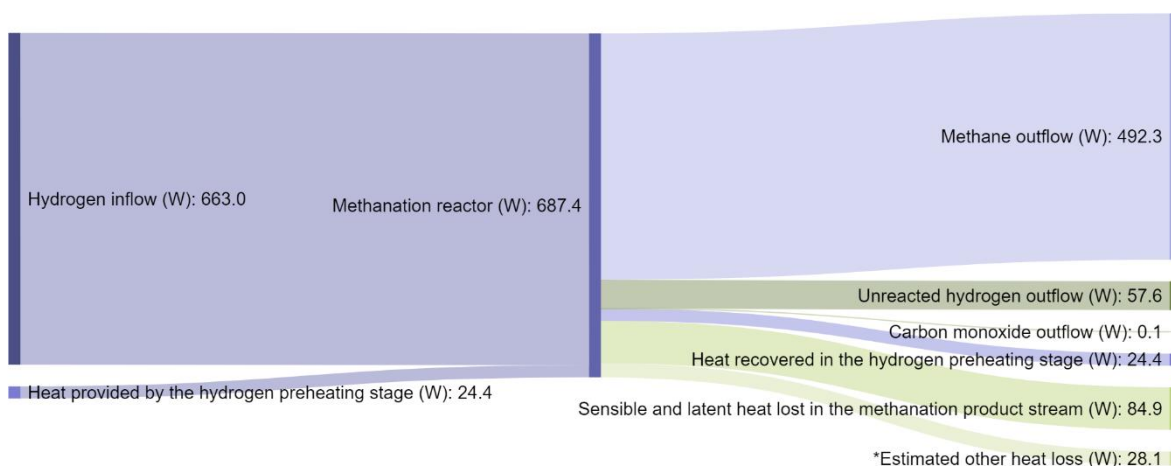


Figure 5.6: Sankey diagram of the methanation demonstrator's energy balance during CO₂ methanation at the recommended operating point: methanation flow of 5 NL min⁻¹ and reaction pressure of 10 bar_g. Reference temperature for calculations: 20°C.

5.3.3 Reactor dynamics during an extended 24 h durability test

Although the thermal aspects of the autothermal microchannel reactor for methanation were evaluated at steady-state conditions, both in the bench-top assembly and the demonstrator, evaluating reactor dynamics is important from a practical perspective. When converting renewable H₂ and CO₂ towards energy carriers such as CH₄, the supply rate of H₂ could determine the methanation reactor's throughput, because the H₂ is generated from fluctuating renewable energy sources. Typically, H₂ storage buffers are used to provide a more stable feed rate of H₂ to the methanation reactor; however, to a certain extent, the reactor should be able to handle variable throughput.

An uninterrupted 24 h dynamic response test was carried out (Figure 5.7); a methanation flow rate of 7.0 NL min⁻¹ was applied during periods of 0–4 h, 8–12 h and 16–20 h, and changed to a methanation flow of 5.0 NL min⁻¹ during periods of 4–8 h, 12–16 h and 20–24 h. These flow rates were selected to introduce demanding dynamic reactor conditions—these were the respective low and high flows evaluated for the methanation demonstrator. The reaction pressure was kept constant at 10 bar_g. The dry product gas flow rate and a sample for analysis by gas chromatography was taken every hour, to determine the CO₂ conversion and CH₄ selectivity, for the duration of the experiment.

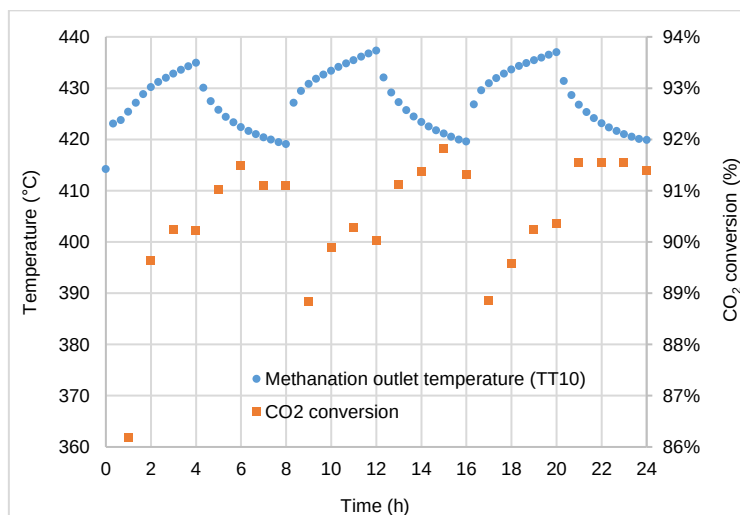


Figure 5.7: Dynamic responses of the methanation demonstrator's outlet temperature and CO₂ conversion during an extended 24 h durability test, for the following conditions: methanation flow of 7.0 NL min⁻¹ during periods of 0–4 h, 8–12 h and 16–20 h, alternate methanation flow of 5.0 NL min⁻¹ during periods of 4–8 h, 12–16 h and 20–24 h, and constant reaction pressure of 10 barg.

The findings of the durability test are presented in Figure 5.7, by illustrating time-dependent measurements of the methanation reactor's outlet temperature and the calculated CO₂ conversion. First, it is clear that for the duration of the test the reactor outlet temperature increased (7.0 NL min⁻¹) and declined (5.0 NL min⁻¹), depending on the flow rate that was applied. The reactor outlet temperature varied in the range 437–419°C. The extremes of this temperature range are close to the steady-state outlet temperatures for the high and low flows, respectively. As was observed during the evaluation of the autothermal microchannel reactor for NH₃ decomposition (Figure 3.3a), the reactor temperature has dynamics in the order of hours as the outlet temperature asymptotically nears the respective steady states.

There is a characteristic separation visible in the CO₂ conversion, upon comparing the flow rates of 7.0 NL min⁻¹ and 5.0 NL min⁻¹. As the outlet temperature increased with time for the periods when the 7.0 NL min⁻¹ flow condition was applied, the CO₂ conversion noticeably increased up to a range of 90.0–90.5%, where equilibrium limitation most likely sets in. As for the periods when the 5.0 NL min⁻¹ flow condition was applied, the CO₂ conversion remained in a range of 91.0–91.8%. The reactor dynamics were more noticeable in the unsteady outlet temperature due to the limited reaction heat being produced using this lower flow rate (natural

cooling of the reactor block). During the entire durability test, the selectivity towards CH₄ production was only once measured to be <99.8% (at hour 10, for the 7.0 NL min⁻¹ flow condition: 99.7%). Overall, the methanation demonstrator operated satisfactorily for a thermally self-sustaining and continuous 24 h period. Similar thermal and methanation dynamics were observed during the three periods when the high flow rate (7.0 NL min⁻¹) was applied, as well as characteristic dynamics during the three instances of using the low flow rate (5.0 NL min⁻¹).

5.3.4 Conclusions

Microchannel reactor technology is attractive for use in the catalytic CO₂ methanation process. The effects of flow configuration and a number of operating parameters (i.e. methanation flow rate, cooling flow rate and reaction pressure) were investigated earlier (Chapter 4), in efforts to identify suitable operating conditions for high-throughput, equilibrium favouring reaction conditions. In this chapter, the design and experimental performance assessment of a compact and portable CO₂ methanation demonstrator is described for the production of CH₄ from renewable H₂. The methanation reactor exhibited satisfactory, and near-equilibrium, methanation performance at the recommended operating point; in the case of the demonstrator this was found to be a total methanation flow rate of 5 NL min⁻¹ and 10 barg reaction pressure. A steady-state axial temperature, which favoured improved methanation equilibrium (similar to what was found in the bench-top investigation, described in section 4.3.3), was achieved. A CO₂ conversion of 91.1% and thermal efficiency of 74.2% were attained at the recommended operating point and at steady state.

Reporting on a dynamic performance assessment to simulate variable input of renewable H₂ to the reactor is included. Whereas significant improvements were achieved in terms of the methanation reactor's compactness, user friendliness, automation and presentability, there were some limitations associated with a lower recommended methanation flow rate, largely due to the improved thermal insulation used around the reactor. Notwithstanding, the methanation demonstrator was successfully designed, with the aim of supporting a compact and presentable chemical processing unit that exemplifies technology development towards PtG for renewable energy storage applications.

5.4 CFD MODEL DEVELOPMENT

To assist in the evaluation of heat and mass transport associated with the catalytic CO₂ methanation reaction, a comprehensive 2D CFD model of the microchannel-based demonstrator was developed to describe the reaction coupled transport characteristics. First, the CFD model assists in validating the thermally coupled process within the autothermal microchannel reactor, by quantifying heat transfer from the exothermic methanation reaction towards the pre-heated H₂ feed stream, and then comparing steady-state axial temperature profiles between the computations and the experimental reactor. Second, the CFD model reveals kinetic rates of species consumption and generation within the axial dimension of the microchannels, not quantifiable during the experimental evaluation of the reactor. Without speculation, it is therefore now possible to determine at which axial location the main reaction zone is located within the microchannel reactor, as well as to observe equilibrium favouring reaction rates towards the outlet of the reactor. The model development (using the Comsol Multiphysics V4.4 software package), and associated results and discussion, are now described.

5.4.1 Model geometry

The discretised model geometry of the autothermal microchannel reactor for CO₂ methanation is presented in Figure 5.8. Two microchannels, thermally coupled through a conductive wall, yet spatially segregated with each having its own fluid inlet and outlet (in counter-current flow configuration), were modelled. The top microchannel, with a wall-coated porous catalyst layer, is dedicated to the CO₂ methanation reaction, while the bottom microchannel is used for the pre-heating of the H₂ feed stream. Here, the following heights apply: the methanation microchannel 250 µm (including 45 µm for the porous catalyst washcoat layer), the conductive layer 500 µm and the microchannel for H₂ pre-heating 250 µm. The microchannel system was modelled as 10 cm long, similar to in the experimental reactor. To accurately compute heat and mass transport characteristics at localised points in the model, discretisation (meshing) was done according to a mapped distribution, with finer element distributions dedicated to regions where accurate computations are vital (e.g. locations of fast reaction rates, fluid inlets and outlets, and interfacial boundaries). In total, the model was discretised into 45 600 elements for computation.

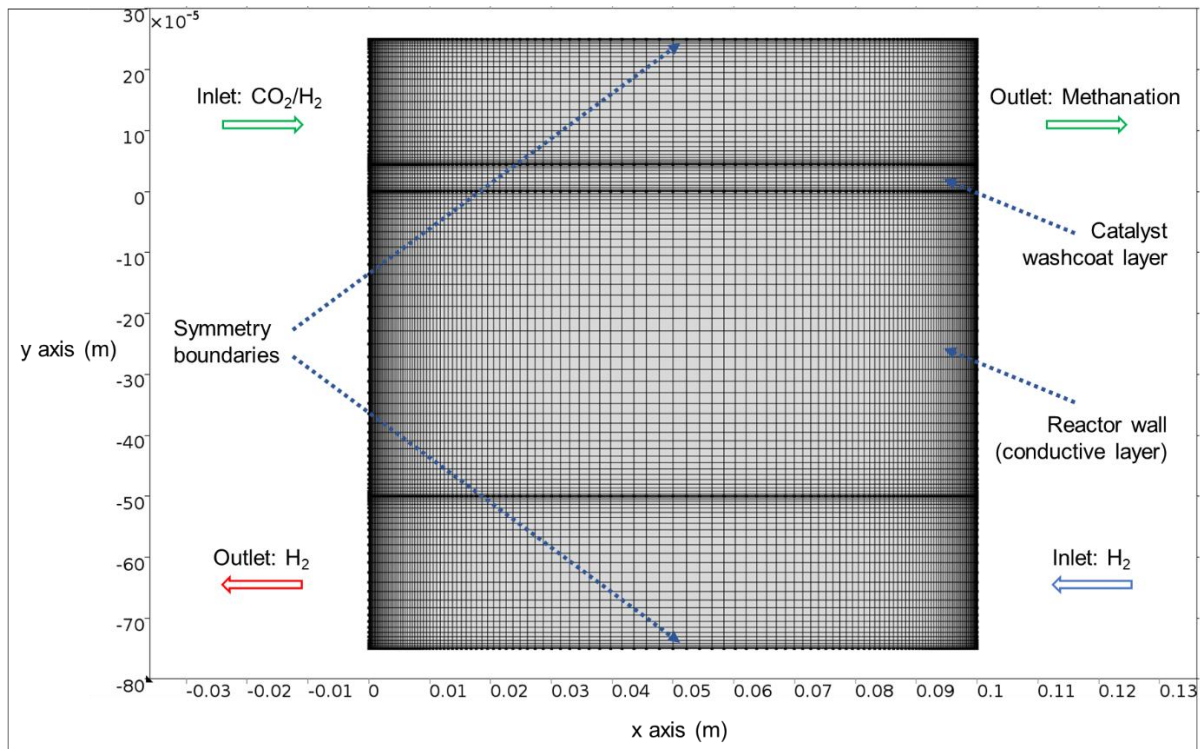


Figure 5.8: Discretised model geometry of the autothermal microchannel reactor for CO₂ methanation. The meshed geometry contains 45 600 computational elements. Regions of interest include microchannel inlets and outlets, the conductive reactor wall, and porous catalyst layer, and symmetric boundary assumptions. Note that the geometric aspect ratio of the microchannel system has been altered for ease of presentation, but the unit of width and length remains m (y and x coordinates).

5.4.2 Model assumptions

The following model assumptions were made during its development to satisfy the governing equations (see section 5.4.3) and in some cases to achieve model simplification:

- Equal flow distribution is assumed between the microchannels, and allows the modelling of two single (thermally coupled) microchannels, for CO₂ methanation and H₂ pre-heating, respectively, to describe the transport properties of the entire microchannel reactor.
- Both the CO₂ methanation reaction as well as the H₂ pre-heating stream are modelled as ideal gas mixtures.
- A calculation of the Reynolds number ($Re < 15$) reveals a laminar flow regime (taking into account the temperature dependency of gas densities and viscosities), and can be assumed as laminar for the range of operating conditions imposed on the microchannel.

- The CO₂ methanation reaction takes place exclusively in the porous catalyst layer (neglecting any homogenous reaction).
- Although ppm levels of CO (up to 700 ppm) were detected as a result of the reverse water–gas shift (RWGS) reaction during the experimental assessment of the methanation demonstrator (section 5.3.2), a dedicated kinetic rate expression to describe CO formation was not included. Here, it is assumed that the secondary RWGS reaction’s impact on the thermal aspects of the microchannel reactor is negligible at the extent at which the reaction was observed to take place.
- Lastly, local thermal equilibrium are assumed within the catalyst layer (between the gas and the solid), as well as at the interfacial boundaries of the solid catalyst and the solid metal wall.

5.4.3 Governing equations

A summary of the main governing equations used to develop the CFD model are given in Table 5.3. First, the ideal gas law was assumed to be valid in all the gaseous phases. Navier–Stokes equations were used to describe momentum conservation in the free-fluid regions of both the CO₂ methanation and the H₂ pre-heating microchannels. On the other hand, the Brinkman–Forchheimer-extended Darcy equation was used to describe momentum conservation in the porous catalyst layer. The Stefan–Maxwell multicomponent diffusion model was used to describe species continuity in the free-fluid phases, as well as in the porous catalyst washcoat. The term describing species consumption and formation due to the CO₂ methanation reaction was only applicable in the species continuity equation for the porous catalyst phase. Convective and diffusive mass transport was assumed in all the gaseous phases.

Since the microchannel reactor is modelled as a non-isothermal system, continuity in heat transfer via convection and conduction, as well as heat accumulation, was assumed at local points. The respective energy equations for the free-fluid regions, the porous catalyst phase for CO₂ methanation and the thermally conductive wall included terms for out-of-plane heat transfer (heat loss). A heat loss coefficient of 15 W m⁻² K⁻¹ was used to describe thermal losses above the 400.0°C setpoint (boundary temperature associated with the respective methanation and H₂ pre-heating inlet temperatures). Similar to the species consumption and generation term associated with the CO₂ methanation reaction, the heat generation term was also only applicable in the energy equation for the porous catalyst phase.

Table 5.3: Governing equations used to describe the autothermal microchannel reactor for CO₂ methanation.

Free-fluid phase (CO₂ methanation)	
Ideal gas law	$\rho = \frac{P}{RT} \sum_{i=1}^4 y_i M_i$
Continuity equation	$\nabla \cdot (\rho \mathbf{V}) = 0$
Navier–Stokes momentum equation	$\mathbf{V} \cdot \nabla (\rho \mathbf{V}) = -\nabla P + \nabla \cdot (\mu \nabla \mathbf{V})$
Species continuity equation	$\mathbf{V} \cdot \nabla (\rho \omega_i) = \nabla \cdot (\rho D_{ij} \nabla \omega_i)$
Energy equation	$\mathbf{V} \cdot \nabla T (d_z \rho C_p) = \nabla \cdot (d_z k \nabla T) + Q_{oop}$
Porous catalyst phase (CO₂ methanation)	
Ideal gas law	$\rho = \frac{P}{RT} \sum_{i=1}^4 y_i M_i$
Continuity equation	$\nabla \cdot (\varepsilon \rho \mathbf{V}) = 0$
Brinkman–Forchheimer-extended Darcy equation	$\mathbf{V} \cdot \nabla (\varepsilon \rho \mathbf{V}) = -\nabla P + \nabla \cdot (\mu_{eff} \nabla \mathbf{V}) - \frac{\mu}{\kappa} \mathbf{V} - \frac{\varepsilon \rho C_F}{\sqrt{\kappa}} \mathbf{V} \mathbf{V}$
Species continuity equation	$\mathbf{V} \cdot \nabla (\varepsilon \rho \omega_i) = \nabla \cdot (\varepsilon \rho D_{ij eff} \nabla \omega_i) + (1 - \varepsilon) \sum_{i=1}^4 a_i M_i \rho_s R_r$
Energy equation	$\mathbf{V} \cdot \nabla T (d_z \varepsilon \rho C_p) = \nabla \cdot (d_z \varepsilon k_{eff} \nabla T) + (1 - \varepsilon) d_z \Delta H_r \rho_s R_r + Q_{oop}$
Free-fluid phase (H₂ pre-heating)	
Ideal gas law	$\rho = \frac{P}{RT} M_{H_2}$
Continuity equation	$\nabla \cdot (\rho \mathbf{V}) = 0$
Navier–Stokes momentum equation	$\mathbf{V} \cdot \nabla (\rho \mathbf{V}) = -\nabla P + \nabla \cdot (\mu \nabla \mathbf{V})$
Species continuity equation	$\mathbf{V} \cdot \nabla (\rho \omega_i) = \nabla \cdot (\rho D_{ij} \nabla \omega_i)$
Energy equation	$\mathbf{V} \cdot \nabla T (d_z \rho C_p) = \nabla \cdot (d_z k \nabla T) + Q_{oop}$
Solid (conductive wall)	
Energy equation	$\nabla T (d_z \rho C_p) = \nabla \cdot (d_z k \nabla T) + Q_{oop}$
	$Q_{oop} = q_{up} + q_{down}$
	$q_{up} = q_{down} = h \cdot (T_{ext} - T)$

5.4.4 Boundary conditions

A summary of the boundary conditions associated with the microchannel reactor model is given in Table 5.4. A laminar inflow of reactants (CO₂/H₂) to the methanation microchannel and pure H₂ to the pre-heating microchannel is imposed at the respective microchannel inlets. The magnitude of the velocities was calculated using the corresponding volumetric flow rates when even flow distribution between the microchannels was assumed, and using the cross-sectional open area of a single microchannel. The molar ratio of the feed gas to the methanation

microchannel was set as 1:4 (CO₂/H₂). The respective inlet temperatures of the methanation and H₂ pre-heating microchannels were assumed to be 400.0°C. The experimental reactor contained fluid distribution manifolds at the respective inlets and outlets. It was therefore deemed reasonable to assume that the inlet gas flows were heated by axial conduction within the fluid distribution manifolds. Of course, the certainty in this assumption is more reliable in the case of the gas inlet temperature to the methanation microchannel, since pre-heating of the H₂ component of the feed gas was carried out up to 326.0°C. Nevertheless, an assumption that the gas entered the microchannels at room temperature would have been unrealistic.

Table 5.4: Boundary conditions that outline the autothermal microchannel reactor for CO₂ methanation.

Boundary condition	
Channel inlet	$v_x = v_x^{in}, v_y^{in} = v_z^{in} = 0, T^{in} = 400^\circ\text{C}, \omega^{in} = \omega_0$
Channel outlet	$P = 10 \text{ bar}_g, \frac{\delta T}{\delta x} = \frac{\delta v}{\delta x} = \frac{\delta \omega_i}{\delta x} = 0$
Channel walls	$v_x = v_y = v_z = 0, T = T_w, \frac{\delta \omega_i}{\delta n} = 0$
Symmetry	$\frac{\delta v_x}{\delta n} = \frac{\delta v_y}{\delta n} = \frac{\delta v_z}{\delta n} = \frac{\delta T}{\delta n} = \frac{\delta \omega_i}{\delta n} = 0$
Free-fluid/catalyst interface	$\mathbf{V} = \langle \mathbf{V} \rangle, P = \langle P \rangle, T = \langle T \rangle, \omega_i = \langle \omega_i \rangle$

At the outlets of the respective microchannels, pressure conditions of 10 bar_g were used, and continuity in velocity, temperature and species fluxes across the outlet boundaries were imposed. At the microchannel walls, the axis-directional components of velocity were assumed to be zero (no slip condition), while local thermal equilibrium between the gas/catalyst and the reactor wall was imposed. The reactor wall acted as a physical boundary to the flow of gaseous species, and zero flux was imposed in the normal direction to the wall. At the interface between the free-fluid phase and the porous catalyst washcoat, continuity in velocity, pressure, temperature and species fluxes is apparent across the interface.

5.4.5 Transport and physical properties

Intermixing (binary diffusion) of gaseous species is assumed to occur according to the Fuller–Schettler–Giddings correlation (Eqn. 5.2) (Fuller *et al.*, 1966:21; Fuller *et al.*, 1969:3683). Reid *et al.* (1987:634) determined that this method of calculating the binary gas diffusion coefficients correlated well with experimentally determined diffusion coefficients. The

Bruggeman correlation (Eqn. 5.3) is further used to estimate the effective binary gas diffusion coefficients in the porous catalyst phase, accounting for local reaction temperatures (compared to the 293.15 K reference value) and the catalyst's porosity (Fuller *et al.*, 2009:336).

$$D_{ij} = \frac{10^{-3} T^{1.75} \left(\frac{1}{M_i} + \frac{1}{M_j} \right)^{\frac{1}{2}}}{P_{atm} \left[(\sum v_i)^{\frac{1}{3}} + (\sum v_j)^{\frac{1}{3}} \right]^2} \quad 5.2$$

$$D_{ij_{eff}} = D_{ij} \left(\frac{T}{T_0} \right)^{1.5} \varepsilon^{1.5} \quad 5.3$$

The temperature dependent thermal conductivities, specific heat capacities and viscosities of each of the gas components within the methanation microchannel (H₂, CO₂, CH₄ and H₂O) were obtained from the Korean Thermophysical Properties Data Bank (CHERIC, 2021). To approximate the effective properties of the gaseous mixture, the mole fraction weighted rule was used. In the case of the H₂ pre-heating stream, the pure component properties of H₂ were applied.

The catalyst layer is presumed to be uniform in its morphology, with a constant porosity (0.4) and permeability (1×10⁻¹² m²). Thermophysical properties of the porous catalyst washcoat are assumed constant for model simplification. Corresponding values for its density (2650 kg m⁻³), thermal conductivity (14.5 W m⁻¹ K⁻¹) and heat capacity (550 J kg⁻¹ K⁻¹) are used. These constants are calculated based on the mass fraction weighted rule (5 wt.% Ru/Al₂O₃) using the pure component properties of Ru and Al₂O₃. To take into account the porosity of the catalyst layer, the following approximation is used to calculate the effective properties within the porous catalyst phase (thermal conductivity as an example calculation):

$$k_{eff} = \varepsilon k_{gas} + (1 - \varepsilon) k_{cat} \quad 5.4$$

Similarly, the metal substrate (reactor wall, SS316Ti) is assumed to have the following values: density, 8000 kg m⁻³; thermal conductivity, 19.5 W m⁻¹ K⁻¹; heat capacity 550 J kg⁻¹ K⁻¹. In the cases of both the catalyst washcoat and the metal substrate, constants for their thermophysical properties were determined at the typical operating temperatures (400–500°C) at which methanation was observed to take place in the experimental investigation of the microchannel reactor (section 5.3.1).

5.4.6 Methanation reaction kinetics

In this work, a reversible elementary rate law first derived by Lunde (1974:228) and Lunde & Kester (1974:30) is used to describe the CO₂ methanation reaction. The general form of the global rate law is given by Eqn. 5.5:

$$-\frac{dp_{CO_2}}{dt} = A \exp\left(\frac{E_a}{RT}\right) \times \left[(p_{CO_2})^n (p_{H_2})^{4n} - \frac{(p_{CH_4})^n (p_{H_2O})^{2n}}{(K(T))^n} \right] \quad 5.5$$

$$r_{Sabatier} = \frac{1}{RT} \frac{dp_{CO_2}}{dt} \quad 5.6$$

In previous work by our research group (Engelbrecht *et al.*, 2017:851), values for the pre-exponential constant (A), activation energy (E_a) and empirical constant (n) were found to be 6.83×10⁶ bar^{-0.11} s⁻¹, 69.35 kJ mol⁻¹ and 0.222, respectively. In that work, the CO₂ methanation reaction was studied at isothermal conditions and at 10 barg, using an 8.5 wt.% Ru/Al₂O₃ catalyst and microchannels of 150 μm. Since the microchannel reactor studied in this work employs a 5.0 wt.% Ru/Al₂O₃ catalyst, as well as having catalytic plates sandwiching microchannels of 250 μm (ultimate channels of 500 μm, represented with symmetry planes in the model), the global rate law's pre-exponential constant, A, was adjusted to 1.65×10⁶ bar^{-0.11} s⁻¹ by comparing a set of model results to a set of isothermal experiments done at temperatures of 300–400°C, in 20°C increments. The heating cartridges were used to control the experimental reactor's temperature at the respective temperature setpoints, as low heat formation was attained (far from equilibrium). From the obtained results, the comparison of model and experimental gradients in CO₂ conversion fitted accurately, and so, the activation energy, E_a, and empirical constant, n, were left unchanged.

5.5 CFD MODELLING: RESULTS AND DISCUSSION

This section presents an extensive investigation into the heat and mass transport occurring within the thermally coupled microchannel reactor for CO₂ methanation. Unless otherwise specified, the total methanation flow that is used for the presentation of the CFD results is 5 NL min⁻¹, while the corresponding H₂ pre-heating stream is 4 NL min⁻¹. Note that throughout the presentation of reaction parameters and their subsequent discussions, the geometric aspect ratio of the microchannel system has been altered for ease of presentation, but the unit of width and length remains m (e.g. y and x coordinates in Figure 5.9: (left) with different axis magnitudes).

5.5.1 Thermal effects delineated by the model

As a result of the exothermic heat release of the CO₂ methanation reaction, it is expected that a significant temperature maximum will be obtained within the microchannel reactor, in the region where the methanation reaction rate is the highest. In Figure 5.9, the temperature distribution predicted by the CFD model is presented, firstly, in the two dimensional coordinate system of the axial (x) and transverse (y) coupling of the methanation reaction and the H₂ pre-heating stream (Figure 5.9: left). Secondly, the temperature in the central longitudinal plane of the solid metal wall is presented as a function of the x coordinate (Figure 5.9: right). From these distributions, it is clear that a temperature maximum of 458.7°C was obtained at axial location $x = 0.017$ m (Figure 5.9: right). Heat transfer mechanisms that govern the axial temperature profile are gaseous heat convection and conduction, as well as heat conduction in the solid metal wall. It is suspected that small Nusselt numbers is obtained for the methanation and H₂ pre-heating streams, which will confirm that the heat transfer is ultimately limited by convention (further discussed in section 5.5.3.3).

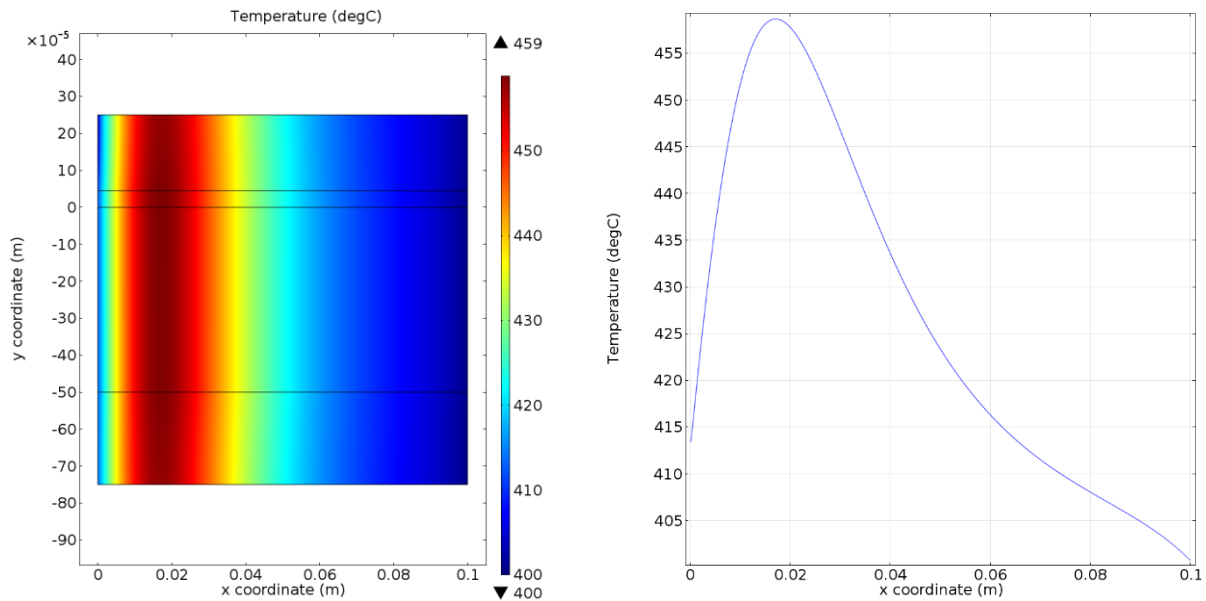


Figure 5.9: (Left) Temperature distribution in the thermally coupled microchannel reactor, and (right) temperature profile at the central longitudinal plane of the solid metal wall. The illustrations are displayed assuming the inlet of the methanation microchannel is at axial location $x = 0$ m.

A transverse temperature profile in the y direction of the thermally coupled microchannel reactor is presented in Figure 5.10, at axial locations of $x = 0$ m, $x = 0.001$ m and $x = 0.005$ m.

This illustration is a partial representation of the extreme inlet region of the CO₂ methanation microchannel (Figure 5.9: (left)). For the axial location of $x = 0$ m, the inlet temperature of 400°C for the methanation stream is evident at y coordinates of 45–250 μm (Figure 5.10). A strong temperature gradient manifested in the catalyst washcoat ($y = 0$ –45 μm), while some heat transfer from the H₂ pre-heating stream is apparent towards the solid metal wall. Across the reactor wall, there exists a temperature gradient of 3.9°C at this axial location. At $x = 0.005$ m, a near isothermal temperature gradient was obtained, with the CO₂ methanation stream having a gas temperature of 435.0°C at the microchannel symmetry plane ($y = 250$ μm), while the wall temperature is 436.6°C. This axial location represents the first twentieth of the total length of the microchannel. For the remaining section of the thermally coupled microchannel system ($x = 0.005$ –0.1 m), the magnitude of the transverse temperature profile decreases consistently; at the methanation outlet ($x = 0.1$ m), the CO₂ methanation stream has a gas temperature of 401.0°C at the microchannel symmetry plane ($y = 250$ μm), while the wall temperature is 400.7°C and the H₂ pre-heating stream enters at 400°C (not shown). The heat transfer via conduction seems very effective in the transverse direction, and the gas phase temperatures and the solid metal wall temperature is closely correlated for given axial locations, except for the inlet case of $x = 0$ m. This is attributed to sufficient thermal conductivities of the solid metal wall (19.5 W m⁻¹ K⁻¹) and the porous catalyst layer (14.5 W m⁻¹ K⁻¹), as well as the solid metal wall's small characteristic dimension (500 μm).

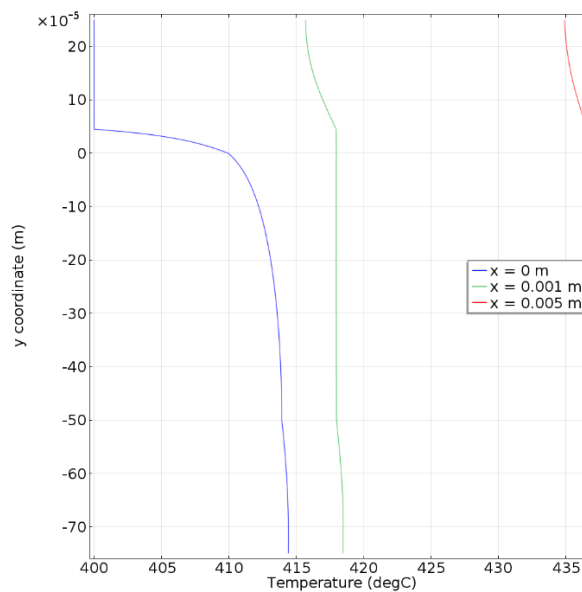


Figure 5.10: Transverse temperature profile (y direction) across the thermally coupled microchannel reactor at three axial locations: $x = 0$ m, $x = 0.001$ m and $x = 0.005$ m.

In Figure 5.11, the experimentally measured and model predicted temperature profiles for the 5 NL min⁻¹ flow condition is presented against the axial coordinate x . As in the case of the experimental evaluation of the methanation demonstrator, the counter-current flow configuration resulted in the temperature maximum being located near the inlet of the methanation microchannel. However, in the case of the model, this location is much closer to the inlet of the methanation microchannel, as compared to the maximum steady-state temperature measured in the experimental reactor ($x = 0.0325$ m, thermocouple position 4). Furthermore, although both gas streams were modelled as having inlet temperatures of 400.0°C, it is interesting to note that the reactor wall temperature at the methanation inlet is 413.4°C, while the wall temperature is 400.7°C at the methanation outlet ($x = 0.1$ m). In general for the 5 NL min⁻¹ methanation flow condition, the experimentally measured steady-state temperature gradient was less severe, with the methanation inlet being at 434.3°C, the maximum temperature of 444.8°C recorded at $x = 0.0325$ m, and near the outlet of the methanation microchannel ($x = 0.0925$ m) the temperature was measured as 419.0°C.

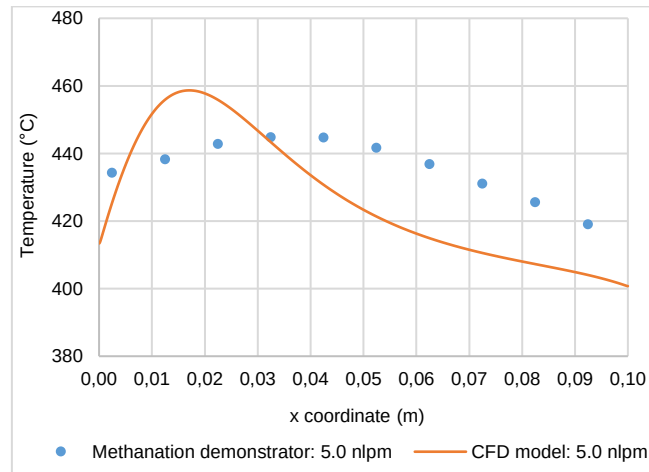


Figure 5.11: Comparison of the CFD model's temperature profile to the temperature profile of the methanation demonstrator, at the central longitudinal plane of the solid metal wall. The illustration is displayed assuming the inlet of the methanation microchannel is at axial location $x = 0$ m.

In Figure 5.12, the conductive heat flux at the fluid/wall interface of the H₂ pre-heating stream is quantified. This interface corresponds to the location of $y = -500$ μ m in Figure 5.9: (left). Firstly, the y component of the heat flux—associated with thermal conduction between the wall and the fluid—is discussed. As the H₂ pre-heating stream entered the microchannel at $x = 0.1$

m, a spike in the heat flux was observed, which reached a magnitude of 58.0 W m^{-2} in the direction of the fluid. This is due to the gas stream inlet having a lower temperature than the reactor wall, and the gas acted as a heat sink for a brief section of the microchannel. Some heat was further transferred to the H₂ stream at x locations of 0.01–0.06 m, where the corresponding CO₂ methanation reaction is believed to release the majority of its reaction heat (further discussed in section 5.5.3.2). Interestingly, the conductive heat flux in the y direction becomes positive (1.10 W m^{-2}) at the outlet of the pre-heating stream ($x = 0 \text{ m}$), which indicated that some heat was conducted from the H₂ gas back to the wall, as the methanation stream is heated from its 400.0°C inlet temperature. From the heat flux profile in the x coordinate (axial), it is evident that heat was conducted away from the region of highest wall temperature ($x = 0.017 \text{ m}$), towards the methanation inlet side (maximum 52.5 W m^{-2} at $x = 0.001 \text{ m}$) and downstream of the reactor (maximum 13.0 W m^{-2} at $x = 0.032 \text{ m}$).

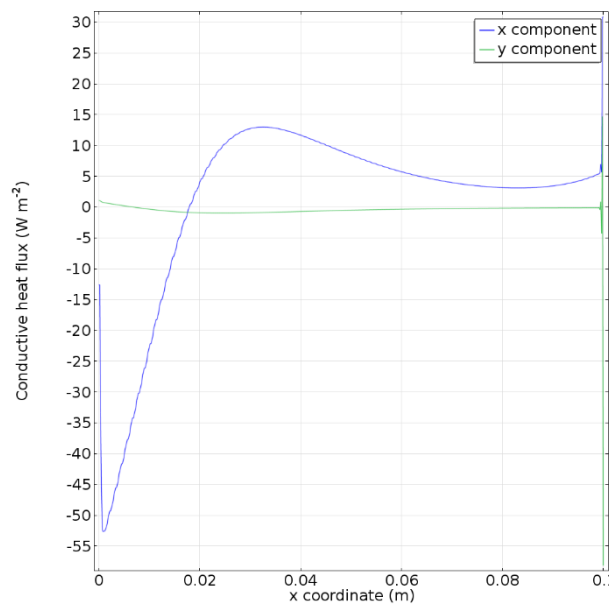


Figure 5.12: Directional (x and y) components of the conductive heat flux magnitude at the fluid/wall interface of the H₂ pre-heating stream ($y = -500 \text{ }\mu\text{m}$ in Figure 5.9: (left)). The illustration is displayed assuming the inlet of the methanation microchannel is at axial location $x = 0 \text{ m}$.

5.5.2 Catalytic activity and model comparison to experimental data

Molar concentrations of the product gas species are presented in Figure 5.13, as a function of the x coordinate for the 5 NL min^{-1} methanation flow condition. The H₂O component is not presented, and the H₂, CO₂ and CH₄ fractions were subsequently normalised. At the

microchannel outlet, the product gas mole fractions of H₂, CO₂ and CH₄ were predicted by the model to be 0.312, 0.078 and 0.609, respectively. These mole fractions are closely correlated to those determined at steady-state in the methanation demonstrator, which were 0.260 for H₂, 0.069 for CO₂ and 0.671 for CH₄. From the CFD model, the CO₂ conversion was calculated as 88.6%, while the experimental CO₂ conversion was determined to be 91.1%.

During both experimental investigations of the bench-top microchannel reactor and demonstrator for CO₂ methanation, it was determined that counter-current operation favoured high methanation reaction rates near the inlet of the reactor (with associated higher steady-state temperatures), while downstream reactor temperatures were typically lower, which contributed to equilibrium favouring conversions of CO₂ and H₂. It is evident from the CFD model (Figure 5.13), that indeed, a significant amount of CO₂ and H₂ was converted to CH₄ in the axial region $x = 0$ – 0.06 m, while some conversion was observed towards the outlet of the microchannel ($x = 0.06$ – 0.1 m), albeit at a lesser extent as the decreasing reactor temperature (Figure 5.9: right) follows the isotherm of thermodynamic equilibrium.

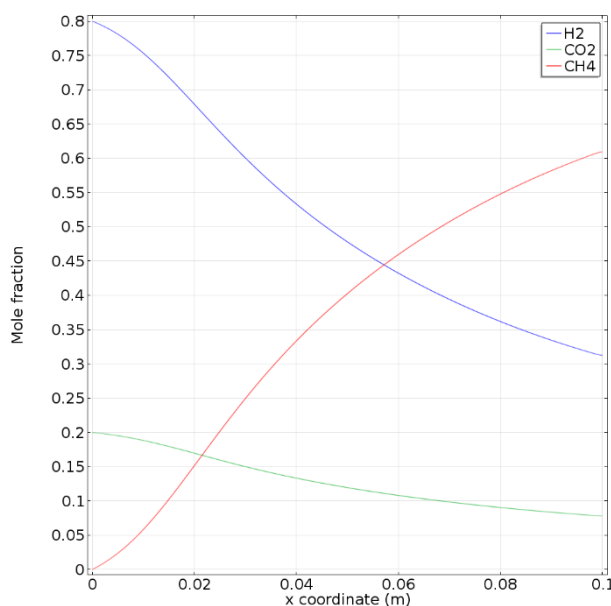


Figure 5.13: Profiles of the H₂, CO₂ and CH₄ mole fractions in the methanation microchannel, presented on a dry basis (H₂O component neglected for presentation purposes) and plotted against the axial coordinate x , for the following conditions: total methanation flow of 5.0 NL min⁻¹ and reaction pressure of 10 barg. The illustration is displayed assuming the inlet of the methanation microchannel is at axial location $x = 0$ m.

In Table 5.5, the steady-state methanation and thermal performance of the modelled microchannel reactor is compared to the methanation demonstrator for total methanation flow rates of 5–7 NL min⁻¹. As in the case of the 5 NL min⁻¹ flow condition, there is some deviation in the wall temperature at the respective methanation inlet and outlet for 6 NL min⁻¹, when comparing the CFD model to the experimental reactor. The inlet and outlet wall temperatures were calculated as 414.1°C and 401.0°C, respectively. It is obvious that the inlet temperature boundary conditions (400.0°C) for the methanation and H₂ pre-heating gas streams dictate the wall temperature. More so, this is evident at the outlet of the methanation reactor, where a low reaction rate is obtained. At the methanation inlet, some axial heat recirculation (Figure 5.12) from the main reaction zone resulted in the wall temperature being 14.1°C higher than the 400.0°C gas inlet. The CO₂ conversion was calculated as 86.9%, while the experimental CO₂ conversion was 90.5%. For the set of model comparisons presented, the initial assumption that the RWGS reaction—responsible for CO production—can be neglected, is justified when considering the very high selectivity towards CH₄ production (>99.89%) by the experimental microchannel reactor.

Table 5.5: CFD model validation to the performance of the methanation demonstrator, for the following conditions: total methanation flow of 5.0–7.0 NL min⁻¹ and reaction pressure of 10 bar_g.

Experiment/Model	Methanation flow (NL min ⁻¹)	Mole fraction				X CO ₂ (%)	S CH ₄ (%)	Inlet wall temp (°C)	Max wall temp (°C)	Outlet wall temp (°C)
		H ₂	CH ₄	CO	CO ₂					
Experiment	5.0	0.260	0.671	0.0004	0.069	91.1	99.94	434.3	444.8	419.0
Model	5.0	0.312	0.609	–	0.078	88.6	100.0	413.4	458.7	400.7
Experiment	6.0	0.273	0.654	0.0007	0.073	90.5	99.89	447.1	460.4	428.1
Model	6.0	0.344	0.570	–	0.086	86.9	100.0	414.1	468.1	401.0
Experiment	7.0	0.309	0.613	0.0000	0.078	88.9	100.0	461.7	476.0	437.3
Model	7.0	0.370	0.538	–	0.092	85.4	100.0	414.7	477.7	401.2

To some extent, the initial difference (13.9°C) in the maximum wall temperature for the 5 NL min⁻¹ flow condition is lowered when observing the 6 and 7 NL min⁻¹ methanation flows. The maximum wall temperature difference was as low as 7.7 and 1.7°C, respectively, for these higher methanation flow rates. On the other hand, the comparison of the inlet and outlet wall temperatures worsened considerably. It becomes evident that, with variable methanation flow rate, constant boundary conditions for the respective methanation and H₂ pre-heating inlet temperatures (400.0°C) was a questionable assumption. Due to the design and microscale dimensions of the microchannels, the gas inlet temperatures could not be practically verified in the experimental microchannel reactor; the measured wall temperature was the closest alternative to make assumptions regarding the inlet temperatures. For all the methanation flows considered here, the calculated CO₂ conversion was within a 3.6% deviation of the experimental conversions. It is possible that, if the reactor temperature could have been modelled more accurately—especially in the downstream, equilibrium favouring region (0.06–0.1 m)—the corresponding CO₂ conversions and CH₄ mole fractions in the product gas would fit even better to the experimental data.

5.5.3 Reaction coupled transport phenomena

This section describes heat and mass transport characteristics of the thermally coupled microchannel reactor for CO₂ methanation. In section 5.5.3.1, velocity distributions are presented within the respective microchannels for methanation and H₂ pre-heating. Section 5.5.3.2 is dedicated to the modelled reaction rate of the CO₂ methanation reaction in the porous catalyst layer. In section 5.5.3.3, five dimensionless numbers are calculated to describe and quantify convective, diffusive and reaction-coupled transport phenomena, which are not clearly apparent merely through axial profiles of mole fraction, velocity and reaction rate.

5.5.3.1 Velocity profiles

For the modelled 5 NL min⁻¹ methanation flow condition, it was calculated that the linear inlet velocity in a single microchannel is 0.115 m s⁻¹, at corresponding reaction conditions of 400.0°C and 10 bar_g. In Figure 5.14: (left), the developed velocity profile in the methanation microchannel is illustrated as a function of the x coordinate. It was found that a fully developed flow profile quickly developed near the microchannel inlet ($x = 0.017$ m). It is also in this region, and at the symmetry plane in the microchannel (furthest from the catalyst layer, 250 µm on the y-axis), that the maximum linear velocity of 0.174 m s⁻¹ was calculated. This

maximum velocity is determined by two reaction effects: (i) higher reactor temperature (subsequent lower density and faster flow), and (ii) proximity to the inlet of the microchannel where the stoichiometry of the methanation reaction has not yet significantly contributed to a decrease in the local molar flow rate (five moles of reactant produces three moles of product). In the downstream section of the microchannel ($x = 0.06$ – 0.1 m) the opposite of both these effects, namely lower reactor temperatures and an already significant conversion of CO₂ and H₂, contributed to a much lower linear velocity in the microchannel (maximum 0.111 m s^{-1} at the $x = 0.1$ m and $y = 250 \text{ }\mu\text{m}$). In the porous catalyst layer (0 – $45 \text{ }\mu\text{m}$ on the y coordinate) convective transfer was determined to be limited, where linear velocities close to 0 m s^{-1} were observed. On the contrary, diffusive mass transport becomes more important in the catalyst layer, and is further discussed in section 5.5.3.3, together with the quantification of the Damköhler number.

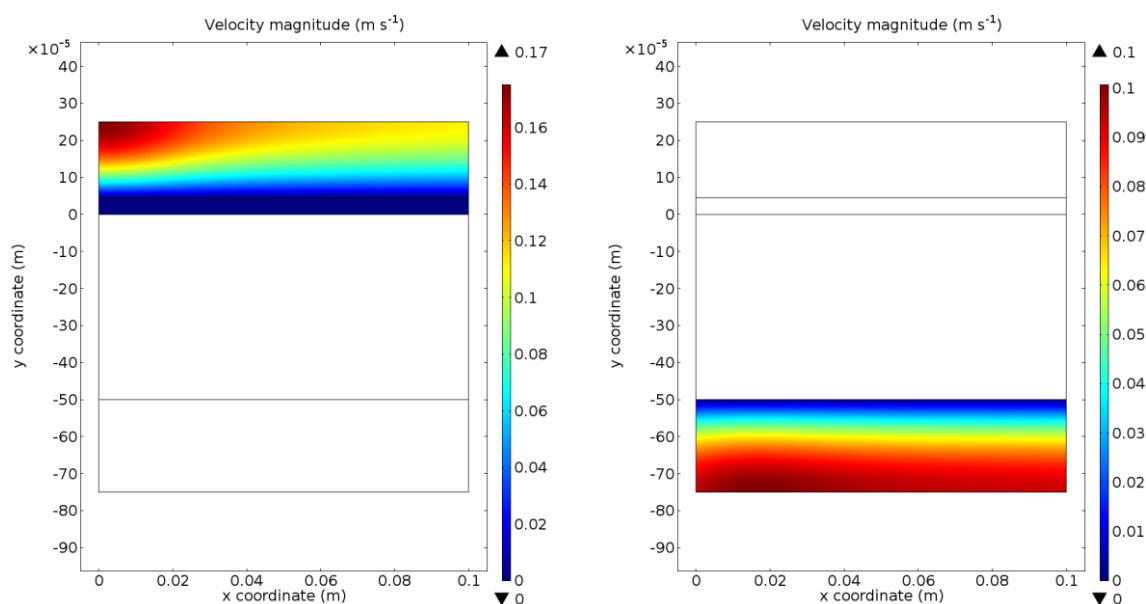


Figure 5.14: Velocity field magnitude in (left) the methanation microchannel, and (right) the counter-current H₂ pre-heating microchannel, plotted against the axial coordinate x . The illustrations are displayed assuming the inlet of the methanation microchannel is at axial location $x = 0$ m.

The velocity profile in the microchannel dedicated for H₂ pre-heating is presented in Figure 5.14: (right). Importantly, the inlet of this particular microchannel is at $x = 0.1$ m, resulting from the counter-current flow operation applied to the microchannel reactor. For the 4 NL min^{-1} H₂ flow that is pre-heated in this microchannel, it was calculated that the linear inlet velocity

is 0.0617 m s⁻¹ at reaction conditions of 400.0°C and 10 bar_g. As in the case of the methanation microchannel, a fully developed flow profile was obtained; however in this case, the maximum linear velocity (0.101 m s⁻¹) was located near the outlet of the microchannel ($x = 0.017$ m) where the reactor was observed to be at its highest temperature. Near the reactor wall, the linear velocity approached 0 m s⁻¹; the no slip boundary condition is evident.

5.5.3.2 Reaction rate profiles

The axial reaction rate of CO₂ methanation for the 5 NL min⁻¹ flow condition is presented in Figure 5.15: (left). On first observation, it is clear that the reaction rate reached a maximum value of 1790 mol m⁻³ s⁻¹ at an x coordinate of 0.01 m. From the inlet of the microchannel ($x = 0$ m), the reaction rate increased considerably to this maximum, from an initial rate of 1010 mol m⁻³ s⁻¹ and at the reactor inlet temperature of 400.0°C. The corresponding heat released by the CO₂ methanation reaction (Figure 5.15: right) had a specific density of 1.97×10^5 kW m⁻³ at axial location $x = 0.01$ m within the catalyst layer. In the downstream direction from the rate maximum ($x = 0.01$ – 0.1 m), the reaction rate was observed to decrease considerably to a value of 77.8 mol m⁻³ s⁻¹ at the methanation outlet. The decrease in reaction rate is attributed to a combination of kinetic limitations associated with lower reactor temperatures and decreased partial pressures of H₂ and CO₂, as well as increasing effects of equilibrium limitation near the outlet of the microchannels.

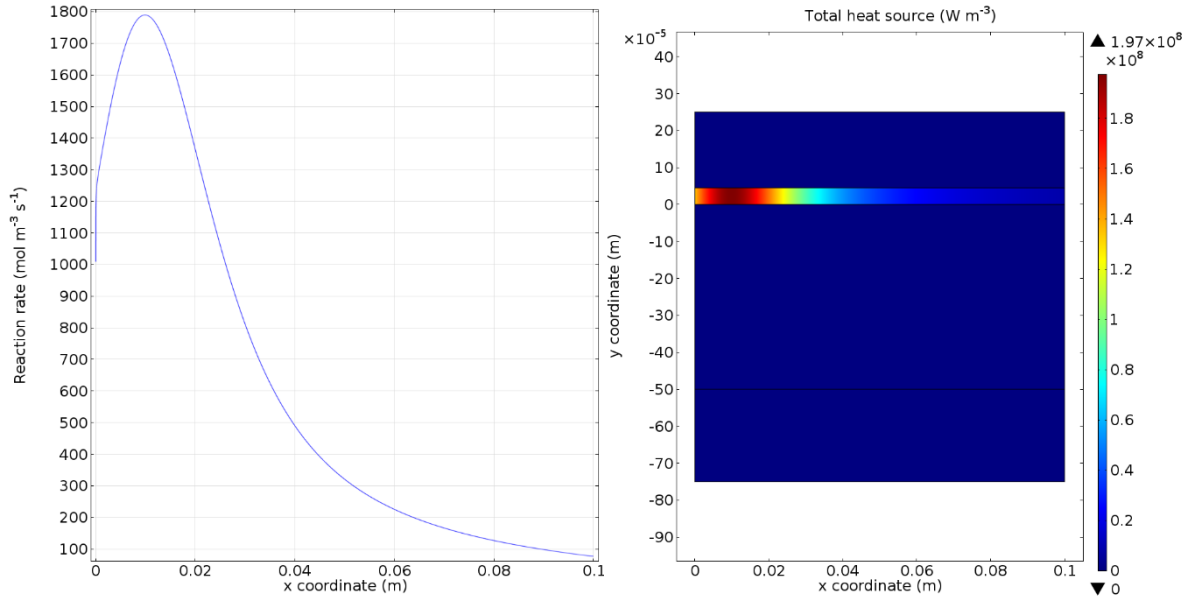


Figure 5.15: (Left) Methanation reaction rate at the central longitudinal plane of the methanation catalyst layer, and (right) heat generation density plotted against the axial coordinate x . The illustration is displayed assuming the inlet of the methanation microchannel is at axial location $x = 0$ m.

5.5.3.3 Quantification of dimensionless numbers to describe convective and diffusive mass transport, and thermal characteristics

The Reynolds number given in (Eqn. 5.7) describes a fluid's inertial forces in relation to its viscous forces, and is the primary dimensionless number to characterise laminar and turbulent fluid flow regimes. It is commonly accepted that a $Re \geq 2100$ is associated with a transition zone, and at which pure laminar flow ceases to occur.

$$\text{Reynolds number} = \frac{\rho v_x D_H}{\mu} \quad 5.7$$

The corresponding Reynolds number was calculated at the central longitudinal plane of the methanation microchannel, and is illustrated in Figure 5.16 as a function of the axial coordinate x . At the microchannel inlet ($x = 0$ m), the Reynolds number was calculated to have a magnitude of 15.7. This confirms the initial model assumptions of steady and laminar flow within the microchannel. Typically, these values are characteristic of microchannel systems. The further decrease in the Reynolds number along the axial coordinate is primarily due to the decrease in the fluid velocity, v_x , associated with the reduction in the volumetric flow rate as

the CO₂ methanation reaction progresses. The Reynolds number of the H₂ pre-heating stream was in the range of 2.25–2.45.

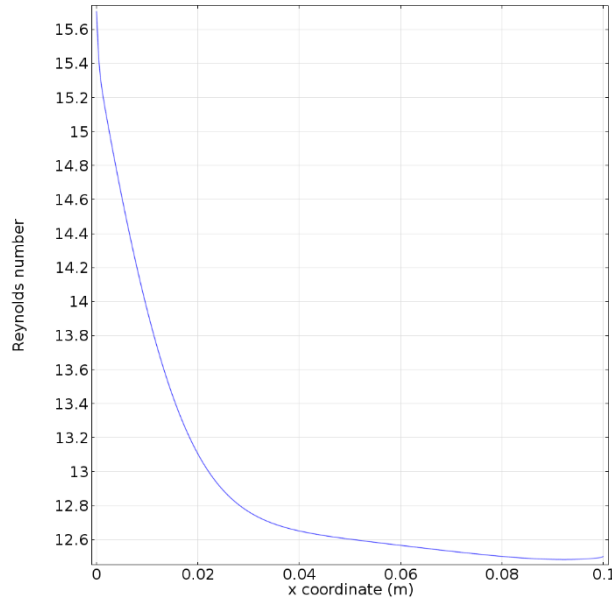


Figure 5.16: Calculated Reynolds number (Eqn. 5.7) at the central longitudinal plane of the methanation microchannel, plotted against the axial coordinate x . The illustration is displayed assuming the inlet of the methanation microchannel is at axial location $x = 0$ m.

The momentum Fourier number (Eqn. 5.8) relates two time scales of mass transfer, and is used to determine whether the mean fluid residence time (τ) is sufficient to allow for diffusion (τ_D) to take place in the characteristic dimension (D_H) of the microchannel. In this instance, the effective diffusion of CO₂ (D_{CO_2}) was considered, as it is the consumed species with the lowest diffusivity. Fourier numbers $\gg 1$ are typical of microchannel systems with high aspect ratios (L/D_H).

$$\text{Fourier number} = \frac{\tau}{\tau_D}, \quad 5.8$$

$$\text{where } \tau_D = \frac{1}{D_{CO_2}} \cdot \frac{D_H^2}{4} \quad 5.9$$

At the microchannel inlet ($x = 0$ m), the Fourier number was calculated as 2966 (Figure 5.17). Although the linear velocity decreases in the axial direction from the methanation inlet—which would mean an increasing Fourier number—it was observed to decrease as a result of the predominant, effective reduction of CO₂'s diffusion in the gas mixture. The reduced diffusion

of CO₂ has two origins; (i) the consumption of CO₂ species from the gas mixture, and (ii) lower reaction temperature towards the microchannel outlet.

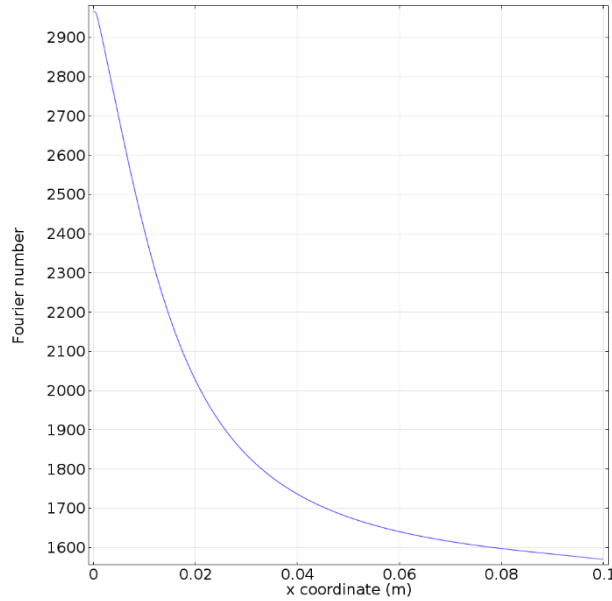


Figure 5.17: Calculated momentum Fourier number (Eqn. 5.8) at the central longitudinal plane of the methanation microchannel, plotted against the axial coordinate x . The illustration is displayed assuming the inlet of the methanation microchannel is at axial location $x = 0$ m.

The Damköhler number (Eqn. 5.10) is defined here as the external diffusion time (τ_D) in the characteristic dimension of the microchannel (D_H) compared to the chemical reaction time (τ_r). A reaction system with a Damköhler number $\ll 1$ has a negligible diffusion time so that the chemical reaction remains the rate controlling factor. Typically, with increasing microchannel diameters, the system will lean more towards being diffusion controlled. It is also possible to calculate an internal Damköhler number using the catalyst washcoat's characteristic pore dimensions.

$$\text{Damköhler number} = \frac{\tau_D}{\tau_r}, \quad 5.10$$

$$\text{where } \tau_D = \frac{1}{D_{CO_2}} \cdot \frac{D_H^2}{4} \quad 5.11$$

$$\text{and } \tau_r = \frac{C_{CO_2 in}}{r_{Sabatier}}. \quad 5.12$$

In this case, the Damköhler number associated with the methanation microchannel did not exceed 0.006 (Figure 5.18). The maximum value for the Damköhler number was obtained at

the axial location ($x = 0.015$ m) between the point of the maximum reaction rate ($x = 0.01$ m) and the maximum wall temperature ($x = 0.017$ m). However, from the magnitude of the Damköhler number, it is evident that external, binary gas diffusion did not have a significant effect in limiting mass transport from the bulk fluid phase towards the catalyst layer. This is in part due to the characteristically small microchannel hydraulic diameter ($D_H = 410$ μm) employed in this reactor.

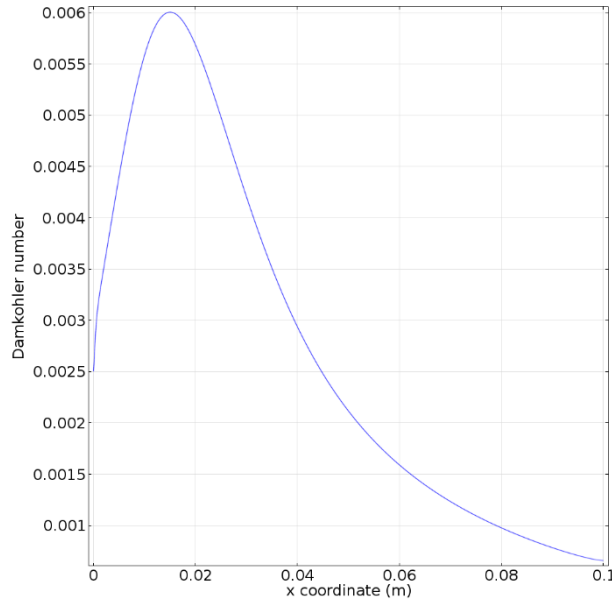


Figure 5.18: Calculated Damköhler number (Eqn. 5.10) at the central longitudinal plane of the methanation microchannel, plotted against the axial coordinate x . The illustration is displayed assuming the inlet of the methanation microchannel is at axial location $x = 0$ m.

Unlike any of the dimensionless numbers discussed here, the Prandtl number (Eqn. 5.13) describes a purely fluidic property without the inclusion of a length scale such as the microchannel's hydraulic diameter. It compares the fluid's momentum diffusivity (kinematic viscosity) to its thermal diffusivity. For instance, it is generally accepted that air at room conditions has a Prandtl number of 0.7.

$$\text{Prandtl number} = \frac{\mu_{\text{gas}}/\rho_{\text{gas}}}{k_{\text{gas}}/c_{p_{\text{gas}}}/\rho_{\text{gas}}} = \frac{\mu_{\text{gas}}c_{p_{\text{gas}}}}{k_{\text{gas}}} \quad 5.13$$

Due to the extent of the methanation reaction in the axial direction of the microchannel reactor, the Prandtl number was observed to have some variation in its magnitude in the length scale of the microchannel. The Prandtl number (Figure 5.19) increased from 0.225 at the microchannel inlet to 0.576 at the outlet, as the ratio of the reactants and methanation products varied.

Hydrogen, which accounted for 80 vol.% at the microchannel inlet, has a high thermal conductivity yet relatively low specific heat capacity. On the other hand, at the microchannel outlet, CH₄ and H₂O have relatively high specific heat capacities and lower thermal conductivities, hence the change in the Prandtl number (according to Eqn. 5.13).

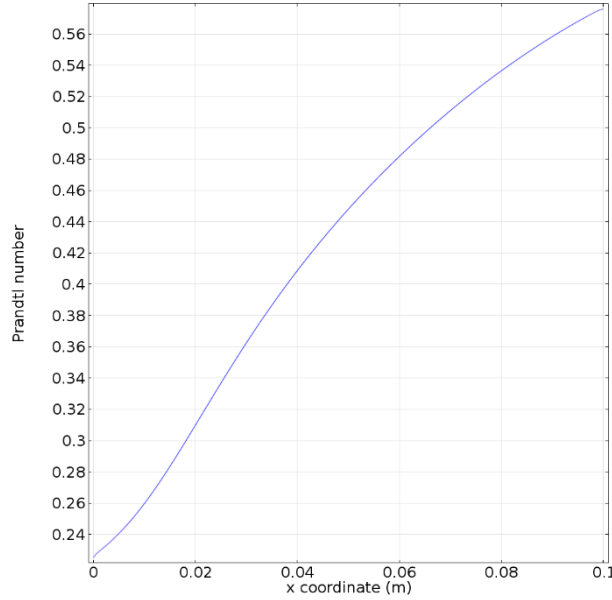


Figure 5.19: Calculated Prandtl number (Eqn. 5.13) at the central longitudinal plane of the methanation microchannel, plotted against the axial coordinate x . The illustration is displayed assuming the inlet of the methanation microchannel is at axial location $x = 0$ m.

The Nusselt number (Nu) describes fluidic heat transfer, and is defined as the ratio of convective to conductive heat transfer (Eqn. 5.14). It has a general direct correlation to the Reynolds number and the Prandtl number. Small Nusselt numbers ($Nu < 1$) are characteristic of laminar flows (where convective transfer is limited), while larger numbers ($Nu > 10$) are associated with turbulent flows (convection dominates overall heat transfer).

$$Nusselt\ number = \frac{h_{gas} D_H}{k_{gas}} \quad 5.14$$

$$\text{or } Nusselt\ number = 1.5 \times \left(\frac{w C_{p_{gas}}}{k_{gas} L} \right)^{0.4} \quad 5.15$$

Because the heat transfer coefficient, h_{gas} , is unknown for both the methanation stream and the pre-heated H₂, a correlation from McAdams (1954:238) was used to estimate the Nusselt number (Eqn. 5.15). Importantly, the correlation uses American units for the gas mixture's mass flow rate, w (lb hr⁻¹), specific heat capacity, $C_{p_{gas}}$ (BTU lb⁻¹ °F⁻¹), thermal conductivity,

k_{gas} (BTU ft hr⁻¹ ft⁻² °F⁻¹), and microchannel length, L (ft). This equation is valid for laminar flows ($\text{Re} < 2100$), high aspect ratio channels ($L/D_H \gg 1$), and negligible fluid buoyancy effects which could be caused by, among other factors, excessive local temperature and density gradients or large channel diameters (Grashof number).

The Nusselt number for the methanation stream (Figure 5.20: left) varied from 2.69 near the microchannel inlet to 3.59 at the microchannel outlet. This variation can be explained by the slightly higher specific heat capacity and lower thermal conductivity downstream in the microchannel, as was the case in the calculation of the Prandtl number. It was observed that the Nusselt number for the H₂ pre-heating stream (Figure 5.20: right) did not vary significantly (2.13–2.18) throughout the microchannel, and can be ascribed to H₂'s relatively constant thermal properties in the temperature range of 400.0–460.0°C.

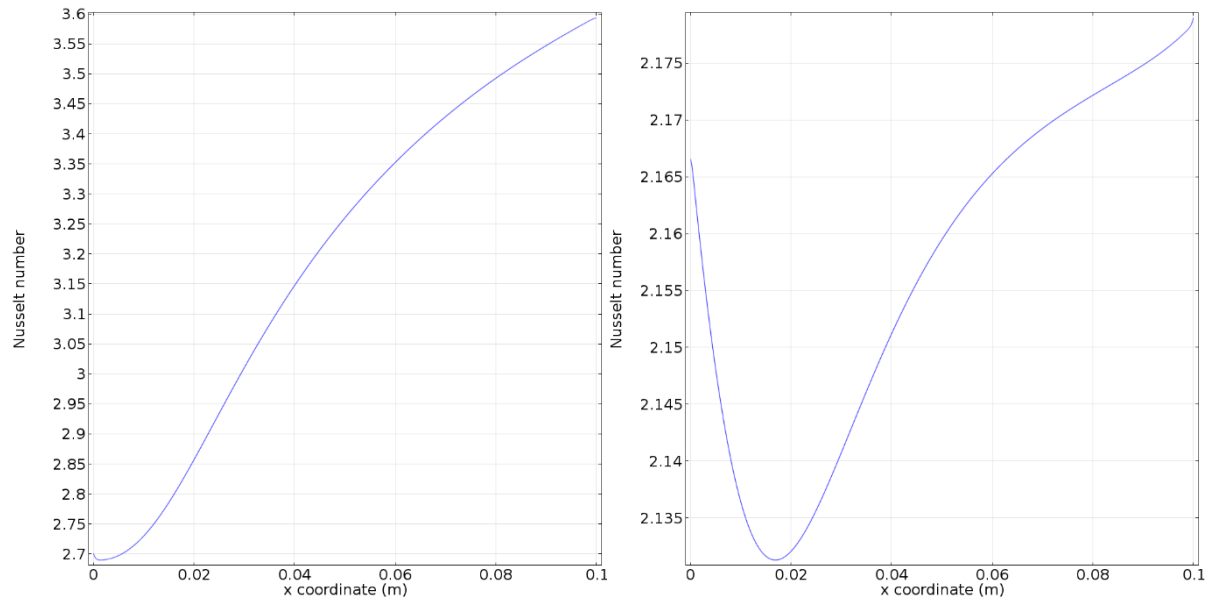


Figure 5.20: Calculated Nusselt number (Eqn. 5.15) at the central longitudinal plane of: (left) the methanation microchannel, and (right) the counter-current H₂ pre-heating microchannel, plotted against the axial coordinate x . The illustrations are displayed assuming the inlet of the methanation microchannel is at axial location $x = 0$ m.

From the formal definition of the Nusselt number (Eqn. 5.14), the convective heat transfer coefficient of the two gas streams can then be calculated (Figure 5.21). Firstly, the methanation stream's heat transfer coefficient was at a maximum of 1742 W m⁻² K⁻¹, and decreased to 908 W m⁻² K⁻¹ at the microchannel outlet (Figure 5.21: left). In the H₂ pre-heating stream, the coefficient varied in a range of 1384–1431 W m⁻² K⁻¹ (Figure 5.21: right). It is believed that

microchannel heat transfer coefficients have been calculated to be even higher than the values recorded with this reactor's case (Anxionnaz *et al.*, 2008:2032; Hessel & Löwe, 2003:393; Mielke *et al.*, 2017:769). Factors that could yield higher heat transfer coefficients are the microchannel's hydraulic diameter (smaller diameters are often associated with improved heat transfer), and more turbulent flows, compared to what is reported here.

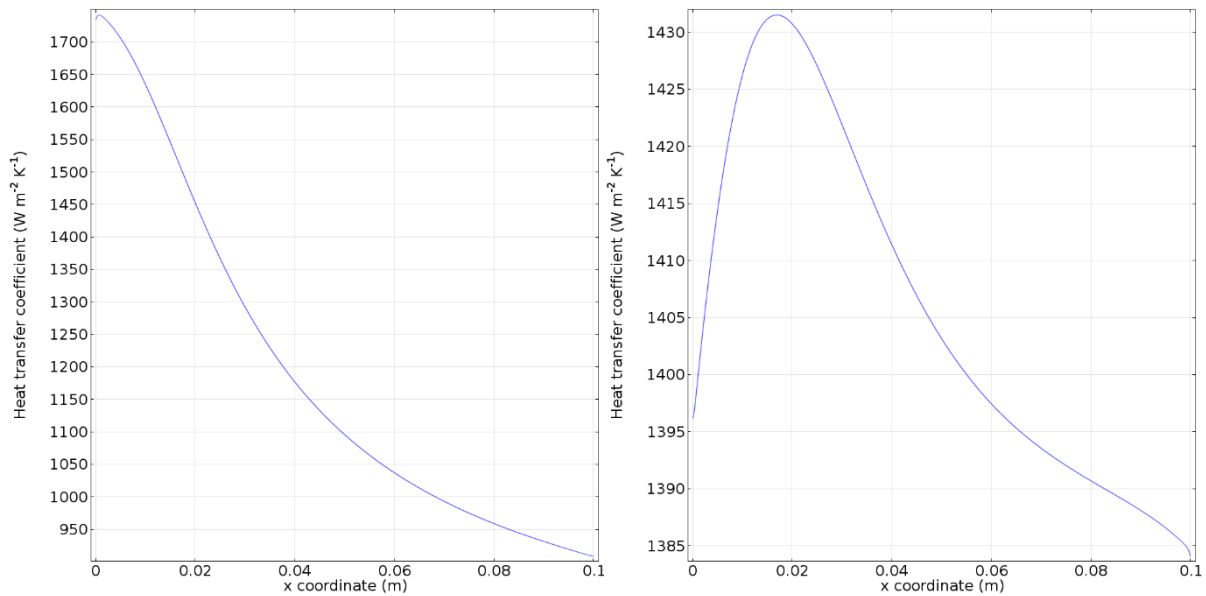


Figure 5.21: Calculated convective heat transfer coefficients (Eqn. 5.14) at the central longitudinal plane of: (left) the methanation microchannel, and (right) the counter-current H₂ pre-heating microchannel, plotted against the axial coordinate x . The illustrations are displayed assuming the inlet of the methanation microchannel is at axial location $x = 0$ m.

5.5.4 CFD modelling: Parametric sensitivity analysis

In Table 5.6, a sensitivity analysis is presented on parametric constants that are considered important during CFD modelling, and their effect on the microchannel reactor's steady-state thermal and methanation performance. These parameters were varied one-by-one from the base case model, and include: the catalyst thermal conductivity, wall thermal conductivity, heat loss coefficient, the inlet temperatures for the methanation and H₂ pre-heating gas streams, and the number of mesh elements used during the discretisation of the model geometry.

Table 5.6: Sensitivity analysis on important parametric constants during CFD modelling.

Parameter	Value (Base value in brackets)	CH ₄ mole fraction	X CO ₂ (%)	Max reaction rate (mol m ⁻³ s ⁻¹)	Inlet wall temp (°C)	Max wall temp (°C)	Outlet wall temp (°C)
Base model		0.609	88.6	1 790	413.4	458.7	400.7
Catalyst thermal conductivity (W m ⁻¹ K ⁻¹)	11.0 (14.5)	0.611	88.7	1 820	415.8	459.6	400.7
	18.0 (14.5)	0.608	88.6	1 768	411.8	458.0	400.8
Wall thermal conductivity (W m ⁻¹ K ⁻¹)	18.0 (19.5)	0.611	88.8	1 828	413.3	460.4	400.7
	21.0 (19.5)	0.608	88.6	1 755	414.5	457.1	400.7
Heat loss coefficient (W m ⁻² K)	12.0 (15.0)	0.636	89.8	2 063	416.4	473.2	400.7
	18.0 (15.0)	0.586	87.7	1 609	411.4	448.3	400.7
Inlet temperature: Methanation stream (°C)	380.0 (400.0)	0.533	85.2	1 329	391.0	436.2	399.5
Inlet temperature: H ₂ pre-heating stream (°C)	380.0 (400.0)	0.538	85.4	1 488	409.5	441.3	381.8
Mesh elements	27 000 (45 600)	0.609	88.6	1746	411.7	457.6	400.7
	68 400 (45 600)	0.610	88.7	1 801	414.4	459.0	400.8

Firstly, the catalyst thermal conductivity was varied from the base case value of 14.5 W m⁻¹ K⁻¹, to a lower (11.0 W m⁻¹ K⁻¹) and a higher (18.0 W m⁻¹ K⁻¹) value. In the case of the lower catalyst thermal conductivity, the wall temperature at the methanation inlet increased slightly, from a temperature of 413.4°C to 415.8°C. It is envisioned that some heat was recirculated in the solid metal wall towards the inlet location of $x = 0$ m (a slightly pronounced effect as discussed for Figure 5.12). With the lower catalyst thermal conductivity, conductive heat transfer to effectively heat the incoming and colder methanation feed (400.0°C) was hindered, hence the higher wall temperature at the inlet. Minor increases in the maximum reaction rate, maximum wall temperature, CO₂ conversion and CH₄ product fraction were observed.

For the case of the higher catalyst thermal conductivity of $18.0 \text{ W m}^{-1} \text{ K}^{-1}$, slightly better heat transfer between the methanation gas stream and the solid metal wall was obtained. The wall inlet temperature reduced to 411.8°C , while the maximum temperature dropped 0.7°C to 458.0°C , compared to the base case model. The CO₂ conversion was unaffected by the increase in the catalyst thermal conductivity, and remained at 88.6%. It is envisioned that variations in the catalyst thermal conductivity will be more pronounced in microchannel reactors employing thicker catalyst layers ($>45 \mu\text{m}$), very fast kinetic processes (e.g. oxidation and partial oxidation reactions), and in cases where the solid metal wall has a thermal conductivity much higher than the catalyst layer, i.e. the catalyst layer provides thermal resistance as the limiting conductive heat transfer factor.

Compared to the catalyst thermal conductivity, the thermal conductivity of the solid metal wall affected the maximum wall temperature more than it did the wall inlet temperature. From the base value ($19.5 \text{ W m}^{-1} \text{ K}^{-1}$), the wall thermal conductivity was first lowered to $18.0 \text{ W m}^{-1} \text{ K}^{-1}$. The maximum wall temperature increased by 1.7°C to 460.4°C , which resulted in a slightly higher reaction rate ($1\,828 \text{ mol m}^{-3} \text{ s}^{-1}$ compared to $1\,790 \text{ mol m}^{-3} \text{ s}^{-1}$) and CO₂ conversion (88.8% compared to 88.6%).

Increasing the wall thermal conductivity to $21.0 \text{ W m}^{-1} \text{ K}^{-1}$ had exactly the opposite effect, as the maximum wall temperature decreased 1.6°C to 457.1°C . The CO₂ conversion remained 88.6%. In general, the wall inlet and outlet temperatures remained practically unchanged with the variations in the wall thermal conductivity. Typically, the wall thermal conductivity governs axial temperature profiles within the reactor (reviewed extensively in section 2.3.1); for very high thermal conductivities, isothermal operation can be achieved, while lower wall thermal conductivities provide excessive temperature profiles and may contribute to improved equilibrium effects of exothermic reactions.

During the sensitivity analysis, the heat loss coefficient (base value of $15 \text{ W m}^{-2} \text{ K}^{-1}$) was observed to have a great effect, particularly on the maximum wall temperature. When heat loss was lowered, with a corresponding coefficient of $12 \text{ W m}^{-2} \text{ K}^{-1}$, the wall temperature increased from 458.7°C to 473.2°C . The kinetic effect of the higher maximum wall temperature was clear, as increases in the CO₂ conversion (89.8%) and the CH₄ product fraction (0.636) were observed.

Contrastingly, when the heat loss from the reaction system was enhanced, using a coefficient of $18 \text{ W m}^{-2} \text{ K}^{-1}$, the maximum wall temperature decreased to 448.3°C , and the corresponding CO₂ conversion was slightly lower at 87.7%. Reflecting on the heat loss coefficient's effect on the reactor's steady-state axial temperature profile and the resultant methanation performance at 5 NL min^{-1} , the coefficient of $15 \text{ W m}^{-2} \text{ K}^{-1}$ is deemed to have provided a suitable balance in the modelled axial temperature profile compared to the experimental measurements (Figure 5.11), although the gradients of the profiles (and the subsequent maximum wall temperatures) differed somewhat.

Lowering the methanation inlet temperature from 400.0°C to 380.0°C had obvious negative effects on both the thermal behaviour, as well as the methanation performance of the modelled microchannel reactor. Firstly, the wall inlet temperature was calculated as 391.0°C , while the maximum reactor wall temperature decreased from 458.7°C to 436.2°C . Obvious kinetic limitations are associated with this lower maximum wall temperature, as the methanation reaction rate decreased from the base value of $1\,790 \text{ mol m}^{-3} \text{ s}^{-1}$ to $1\,329 \text{ mol m}^{-3} \text{ s}^{-1}$. The CO₂ conversion was 3.4% lower at a value of 85.2%.

Similarly, the reduction in the H₂ pre-heating stream's inlet temperature to 380.0°C is not desirable. The wall temperature at this location ($x = 0.1 \text{ m}$) corresponded closely, with a temperature calculated of 381.8°C . The maximum wall temperature and reaction rate was slightly higher compared to the case of a lower methanation inlet temperature, as values of 441.3°C and $1\,488 \text{ mol m}^{-3} \text{ s}^{-1}$ were respectively calculated. Yet, the CO₂ conversion remained poor at 85.4% due to an overall lower temperature profile as compared to the base case model.

Lastly, the discretisation of the mesh was varied from the base case of 45 600 elements. It is concluded that the mesh used for the base case model was generated with an acceptable degree of accuracy, as lowering the element number to 27 000 was mainly noticeable in the wall inlet temperature, as it was only 1.7°C lower than calculated for the base case. When the meshing elements were increased to 68 000, the wall inlet temperature consequently rose by 1.0°C . For both cases of varying the number of mesh elements, negligible effects on the CH₄ product fraction, CO₂ conversion and maximum reaction rate were noted.

5.5.5 Conclusions

A non-isothermal CFD model was developed, evaluated and compared to the thermally coupled microchannel reactor for CO₂ methanation (methanation demonstrator). Suitable governing equations, boundary conditions and model assumptions (as far as reasonably possible) were established to describe momentum and species transfer within the respective microchannels, as well as the thermal coupling effect between the fluidic microchannels and the solid microchannel wall separating them. For the 5 NL min⁻¹ flow condition, the axial wall temperature predicted by the CFD model was more pronounced than the experimentally observed temperature profile, with a 58.0°C difference from the temperature maximum—located at axial position 0.017 m—towards the outlet of the microchannel reactor. In the case of the methanation demonstrator, the temperature difference was 25.8°C. Nonetheless, both experimental and modelled temperature profiles showed a characteristic decrease in reactor temperature towards the methanation outlet, as a result of the counter-current flow configuration employed. From a practical perspective, the number of thermocouples that can be used to measure temperatures within the experimental microchannel reactor was limited. The CFD model provided valuable insight into transverse temperature gradients in the thermally coupled microchannel system (Figure 5.10), which was typically not measured in the methanation demonstrator. It became apparent that transverse temperature gradients were insignificant, except for at axial location $x = 0$ m, where the incoming CO₂ methanation feed was rapidly heated from its 400°C inlet temperature.

Prediction of the CO₂ conversion was very accurate: the 88.6% of CO₂ conversion in the model correlated well with the experimental conversion of 91.1%. It emerged that the thermal behaviour was more difficult to accurately predict with the CFD model compared to the methanation performance (CO₂ conversion). This became evident through a sensitivity analysis, and originates from a number of factors, including constants used for the thermal conductivities of materials, the inlet temperature assumptions, and the heat loss coefficient, among other less important parameters (section 5.5.4). The quantification of dimensionless numbers for heat and mass transport in section 5.5.3.3 provided an understanding into the characteristic operation of the microchannel reactor for thermally coupled CO₂ methanation. To conclude, these dimensionless numbers can be used to scale microchannel reactors towards larger fuel processors, taking into account microchannel geometries, typical aspect ratios of microchannel systems and reaction rates.

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CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

CHAPTER OVERVIEW

In this thesis, the application of microchannel reactor technology, capable of autothermal operation, was demonstrated for two thermo-catalytic processes: (i) the decomposition of NH_3 for H_2 production, intended for fuel cell power applications, and (ii) the CO_2 methanation process, as a renewable energy storage pathway, via the production of synthetic CH_4 . In Chapters 2–4 of this thesis, specific conclusions were made with regard to reactor operation and performance testing. In the present chapter, a broader view of concluding remarks is presented (in line with the specific objectives stated in the introductory chapter). Some technological recommendations towards the further development of process intensifying reactor technologies for renewable H_2 processing applications are also included.

6.1 CONCLUSIONS FROM THIS WORK

In recent years, there has been a rapidly growing trend in research and development programs, industrial activities and academia alike that focuses on systematic efficiency enhancements and intensification of chemical processes in the energy industry. To a certain extent, these activities are currently driven by improved process economics. However, addressing concerns related to decarbonisation and the reduction of associated emissions has led to substantial renewable energy integration in power sectors—factors that are largely driven by political initiatives in line with the Paris Agreement of 2015. Furthermore, global averages for solar photovoltaic (PV) and onshore wind power have recently achieved cost competitiveness with new installations of fossil fuel power plants (IRENA, 2019:12). There remains, however, one key challenge linked to renewable energies—at least for solar PV and wind power: the favourable geolocations that support their deployment are often remote—significant power transmission distances are necessary (coupled with associated energy losses), while their natural fluctuation places major strain on power grids at increased deployment capacities.

It is evident that opportunities exist for energy storage and regenerative power techniques to advance renewables integration in energy sectors. Green (renewable) H_2 production via water electrolysis seems an important energy conversion pathway to address global demand for a clean energy that is storable, transportable, and has power regeneration applicability in smaller-scale and off-grid fuel cell (FC) applications, as well as in industrial (MW)-scale FCs, and recently through H_2 ready utility scale gas turbines. Hydrogen has numerous other industrial applications for the synthesis of liquid fuels and specialty chemicals, as a chemical reduction agent and as a heat transfer fluid. Besides H_2 , NH_3 and CH_4 are energy carriers that have been known, produced, and used in the chemical industry for decades.

In this thesis, the respective processing of renewable H_2 from NH_3 , and towards CH_4 production, was investigated using microchannel reactor technology—chemical processing apparatus that is characteristically suited for compact and modular systems, and which supports dynamic operation, often at significant down-turn ratios. These aspects are imperative, as supplying H_2 to FCs is subject to the downstream power demand, while fluctuations in green H_2 supply dictate synthetic CH_4 production.

- I. In Chapter 2, a thorough review of the literature revealed that the autothermal operation of microchannel fuel processors, via the thermal coupling of exothermic and endothermic reactions, could offer numerous process advantages. These included the following: (i) improved efficiencies via design-specific heat transfer and waste heat recuperation, (ii) they may support single fuel requirements as both the heat source and renewable H_2 carrier (case in point, NH_3), and (iii) offer attractive physical characteristics of the fuel processor with regard to compactness, thus promoting high power densities and overall multifunctional use as stand-alone chemical conversion and integrated heat exchanger devices.
- II. In Chapter 3, an autothermal microchannel reactor was evaluated for H_2 production via NH_3 decomposition, while catalytic NH_3 oxidation was used to provide the heating requirements of the slightly endothermic decomposition reaction. An NH_3 conversion of 99.8% was achieved at the recommended steady-state operating point, while the H_2 throughput corresponded to 8.92 NL min^{-1} (equivalent to a FC power output of 0.71 kW_e). During experimentation, the microchannel reactor was evaluated in start–stop cycles. Through assessing the dynamics of reactor operation from hot-standby mode (start-up), the microchannel reactor was able to produce H_2 in relatively short response times ($<1 \text{ h}$), typically associated with variable FC power demand. An overall ammonia-to-hydrogen process efficiency of 75.9% was achieved—this appears impressive, given the scale of the microchannel reactor.
- III. In Chapter 4, an almost identical microchannel reactor was used to carry out the exothermic and pressurised CO_2 methanation (Sabatier) process, with the necessary cooling requirements provided for using H_2 as a cooling fluid. Extensive thermal and methanation performance analyses revealed that equilibrium favouring axial temperature profiles are possible when the methanation reactor is operated in the counter-current flow configuration. At the recommended operating point, a total methanation flow of 7 NL min^{-1} was converted towards synthetic CH_4 at a CO_2 conversion rate of 90.5%. The CH_4 output was as high as $19.8 \text{ NL g}_{\text{cat}}^{-1} \text{ h}^{-1}$, while the overall process efficiency was noted as 76.6% (including 4.7% in heat recuperated from the exothermic process). Converting renewable H_2 towards synthetic CH_4 therefore seems appropriate to address challenges of large-scale renewable energy storage, by exploiting natural gas networks with GWh-scale energy storage capacity.

- IV. In Chapter 5, the autothermal microchannel reactor for CO₂ methanation was converted into a compact, presentable and semi-automated methanation demonstrator. The design of the demonstrator was such that improved thermal insulation and some internal recirculation of reaction heat (via a H₂ pre-heating stage) contributed to the autothermal operation of the processing unit at a recommended total methanation flow of 5 NL min⁻¹. Although a trade-off in terms of a slightly lower thermal efficiency of 74.2% was noted, the advantage of autothermal microchannel reactor technology was clearly demonstrated in a compact and stand-alone CO₂ methanation processing unit. Furthermore, a dynamic response test (over a continuous period of 24 h) was carried out at methanation flows of 5 and 7 NL min⁻¹. The methanation demonstrator exhibited unrelenting thermal adaptation to variable methanation throughput, without any reduction in methanation performance, which would otherwise typically be associated with catalyst degradation.
- V. Chapter 5 included a description of the development and characterisation of an advanced 2D CFD model to describe the thermally coupled CO₂ methanation reactor. The performance characteristics of the experimentally evaluated methanation demonstrator were used to validate the CFD model, while a comprehensive assessment of heat and mass transport within the axial dimension of the microchannels proved valuable in characterising these aspects of the microchannel reactor. It was concluded that the CFD model can be used to select operating conditions and further scale autothermal microchannel reactor technology for catalytic H₂ processes—in this case CO₂ methanation—provided that accurate experimental data on the reaction kinetics, microchannel inlet temperatures and heat loss are known. It is generally these parameters that dictate the thermal characteristics of the microchannel reactor and its subsequent H₂ processing rate.

6.2 CONTRIBUTIONS TO THE CURRENT KNOWLEDGE BASE

Autothermal microchannel reactor technology presents numerous opportunities in chemical processing devices that support inherent characteristics associated with their compactness, process intensifying heat and mass transfer properties, and multifunctional use as reactors and heat-exchangers. These aspects warrant the use of microchannel technology for catalytic processes such as reforming and methanation that require efficient heat management, dynamic

operation and high production throughput—it is especially attractive for applications of variable renewable H₂ processing for energy conversion and chemical synthesis (power-to-X).

- I. The literature overview, presented in Chapter 2, detailed various microchannel design aspects that contributes to the autothermal operability of microchannel fuel processors. Not only were literature accounts presented of both experimental and modelling evaluations, Chapter 2 serves as a platform for further research opportunity, as some limitations and other important design considerations were presented for the enhancement and scalability of thermally coupled processes in microchannel reactors.
- II. Autothermal microchannel reactor technology has been demonstrated for the processing of renewable H₂ via two important thermo-catalytic processes, namely: NH₃ decomposition and CO₂ methanation, respectively in Chapters 3 and 4. These experimental investigations have proved valuable in expanding the current knowledge base on reactor operability, thermal efficiencies, and achievable throughput of microchannel fuel processors in the kW scale.
- III. The design, assembly and operation of a CO₂ methanation demonstrator was undertaken, and documented in Chapter 5, in order to demonstrate the compact and modular characteristics that advocate the use of microchannel reactors in H₂ fuel processors. The development of the 2D CFD model proved to be useful in obtaining a non-isothermal model that could be later used for methanation reactor upscaling (given some model refinement), and typically not often seen in the literature at the scale of this microchannel reactor. The model further outlined characteristic heat and mass transport within the reactor that was not quantifiable during the experimental investigation, as well as presented a parametric sensitivity analysis on the reactor's steady-state thermal behaviour and methanation performance.

Overall, the design of future, and typically larger, microchannel fuel processors is now possible, emerging from known mass transport rates and catalyst productivities of smaller microchannel reactors and fabrication techniques available now. The processing of H₂ via chemical energy vectors such as NH₃ and CH₄ will change the future landscape of converting, storing, transporting and using renewable energy in industries, worldwide.

6.3 RECOMMENDATIONS FOR THE FURTHER DEVELOPMENT OF MICROCHANNEL REACTORS FOR HYDROGEN-BASED GAS PROCESSING

Although the autothermal microchannel reactor for NH_3 decomposition is now able to achieve a steady-state conversion of 99.8% at the recommended operating point—which seems impressive—the 680 ppm of NH_3 present in the H_2 -rich product gas stream will be problematic for low temperature FCs for power generation, especially using proton exchange membrane technology, which require NH_3 impurities to be <1 ppm. Additional investigations in the following areas are recommended for the further development of autothermal NH_3 decomposition technology: (i) the use of reaction temperatures as high as 800°C , to reduce the equilibrium limited residual NH_3 present in the product gas (personal communication with G Kolb), (ii) the development of highly active and durable Ru catalyst formulations on either basic (CaO) or acidic (Al_2O_3) supports, while using alkali dopants (Sayas *et al.*, 2020:5027), to extend the performance time at the high decomposition temperature mentioned above, and (iii) to integrate NH_3 fuel processors into systems supporting pressure swing adsorption (PSA) technology for H_2 purification, and to test the operation of decomposition reactors at slightly pressurised conditions, to thus allow for the integration with PSA technology (Sayas *et al.*, 2020:5034).

An interesting prospect is the partial reforming of NH_3 into H_2 , and the use this fuel mixture in modified internal combustion engines, not necessarily FC applications. Factors that promote this pathway as a first adaption to NH_3/H_2 applications are: (i) reduced reforming heat demand; the engine's hot exhaust gas may be used to drive the reforming reaction, (ii) improved combustion characteristics that H_2 provide; the flame speed of pure NH_3 combustion is generally considered low, and (iii) robustness of the traditional internal combustion engine once it is designed and tuned to reduce residual NO_x and N_2O . This technology pathway will probably be followed not only in high duty vehicles, but also marine vessels, and for stationary power generators/turbines burning NH_3/H_2 mixtures.

From the experimental investigation of the autothermal microchannel reactor for NH_3 decomposition, it became apparent that the NH_3 oxidation (combustion) reaction is prone to the formation of NO_x and N_2O (severe pollutants and greenhouse gases). Besides the catalytic NH_3 oxidation reaction presented herein, NO_x and N_2O formation are also problematic in gas turbine combustion, when using NH_3 fuel—it has attracted much attention from both the

scientific community and industrial gas turbine manufacturers, with efforts made to curb these emissions (Patel, 2021). Specifically, for the flameless catalytic NH_3 oxidation reaction, further strategies to investigate lean and rich NH_3 fuel mixtures are recommended, as well as the improvement of such catalysts that may favour the selective catalytic reduction of the NO_x and N_2O towards atmospheric N_2 at specific reactor temperature conditions (Valera-Medina *et al.*, 2018:94).

With regards to thermally coupled CO_2 methanation, axial temperature gradients that are associated with improved methanation equilibrium were demonstrated here in both the bench-top investigation, as well as in the methanation demonstrator. Nonetheless, the near-equilibrium limited CO_2 conversion of 91.1% at the demonstrator's recommended operating point resulted in a CH_4 content in the product gas (67.1% CH_4), which currently does not conform to the requirements for direct injection into natural gas pipelines (>90% CH_4). Strategies, some of which are already industrially implemented, are recommended to separate the CH_4 from the product gas mixture, while the unreacted H_2 and CO_2 can be recycled back to the methanation reactor. The implementation of a low temperature methanation reactor (<300°C) in series may improve the overall CO_2 conversion; however, at the desired 90% CH_4 fraction in the product, the H_2 fraction may still be ~8%, such that current standards of natural gas quality do not allow significant H_2 to be injected into natural gas pipelines—a reality that emanates from material embrittlement and natural gas end-user restrictions with regard to H_2 (Altfeld & Pinchbeck, 2013:5–10). A product gas separation step therefore seems mandatory.

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APPENDIX A

The P&I diagrams of the respective experimental setups for autothermal ammonia decomposition (Chapter 3) and CO₂ methanation (Chapter 4) are presented in Appendix A. In the case of ammonia decomposition, a secondary P&I diagram is provided to indicate the flow rate and composition measurement of the ammonia oxidation flue gas. In the case of CO₂ methanation, the main P&I diagram is presented for the co-current flow configuration, while a secondary P&I diagram is given to present counter-current flow configuration.

A.1 PIPING AND INSTRUMENTATION (P&I) DIAGRAM OF AN AUTOTHERMAL PROCESS FOR AMMONIA DECOMPOSITION

A piping and instrumentation (P&I) diagram of the experimental setup for the autothermal process for ammonia decomposition is illustrated in Figure A.1—the notations used in the presentation of the P&I diagram are defined in Table A.1.

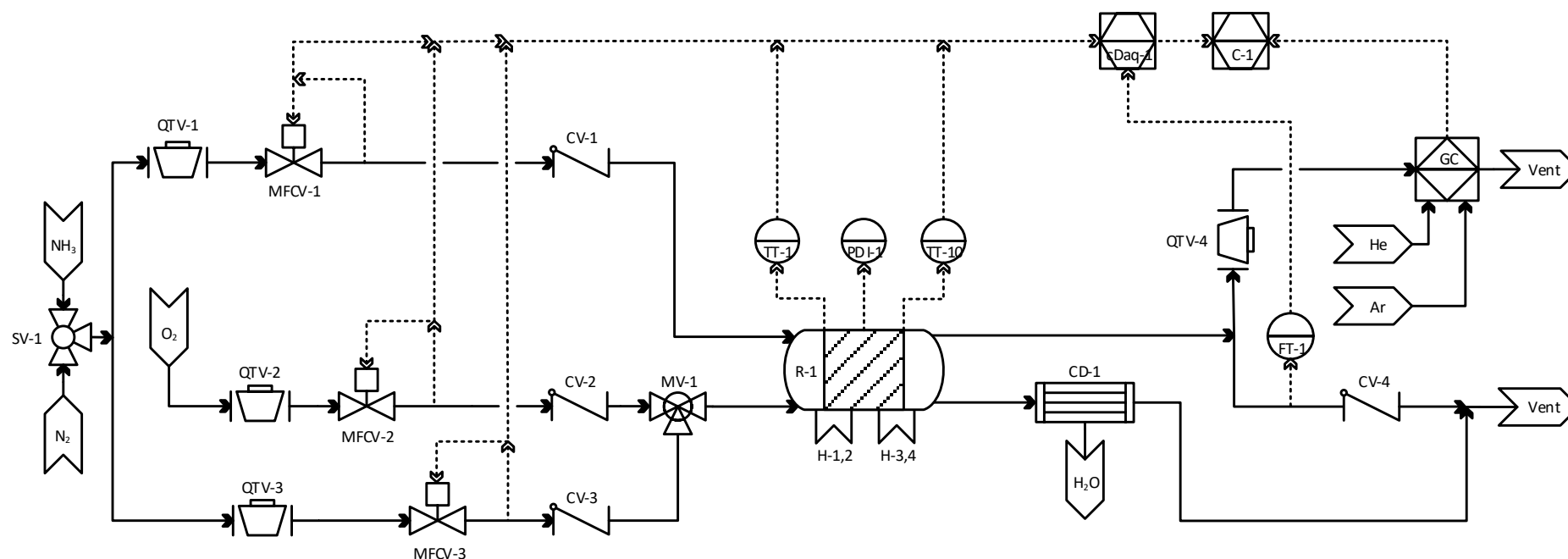


Figure A.1: P&I diagram of the autothermal process for ammonia decomposition (notations defined in Table A.1).

Table A.1: Notations used on the P&I diagrams presented in Figure A.1 and Figure A.2.

Process stream	Description	Equipment notation	Description	Instrument notation	Description
Ar	Argon, 10 mL min ⁻¹	CD	6 m pipe condenser (¼ pipe) and water knock-out pot	C	Computer
He	Helium, 20 mL min ⁻¹	CV	Check valve	cDaq	Compact Daq
H ₂ O	Water condensate, 100 mL h ⁻¹	H	Temperature-controlled heater	FT	Flow transmitter
N ₂	Nitrogen, 1 NL min ⁻¹	MFCV	Mass flow control valve	GC	Gas chromatograph
NH ₃	Ammonia, 6.0 NL min ⁻¹ for decomposition and 2.34 NL min ⁻¹ for oxidation	MV	Mixing valve	PDI	Pressure drop indicator
		QTV	Quarter-turn valve	TT	Temperature transmitter
O ₂	Oxygen, 1.66 NL min ⁻¹	R	Reactor		
Vent	Product gas vent, 12 NL min ⁻¹ for decomposition, 1.15 NL min ⁻¹ for oxidation and 25 mL min ⁻¹ via the GC sample loop	SV	Three-way ball valve		

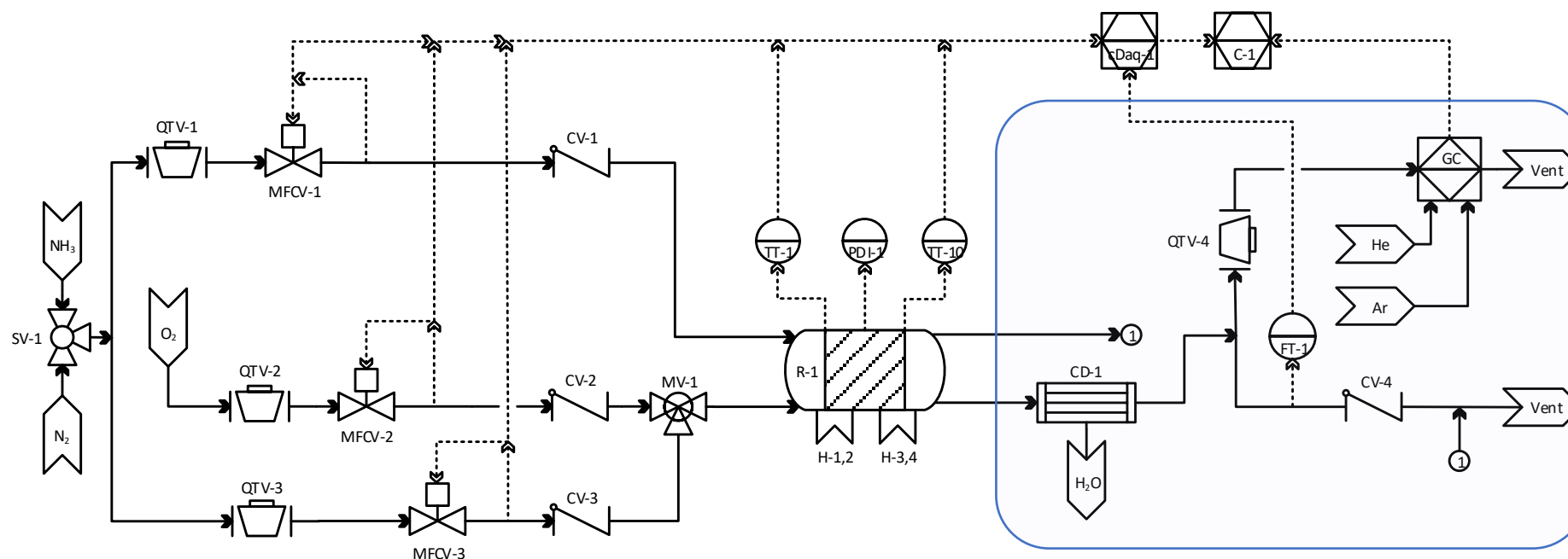


Figure A.2: P&I diagram of the autothermal process for ammonia decomposition (notations defined in Table A.1). The shaded region on the P&I diagram indicates the alternative piping configuration used for the quantification of the NH_3 oxidation flue gas stream.

A.2 PIPING AND INSTRUMENTATION (P&I) DIAGRAM OF AN AUTOTHERMAL PROCESS FOR CO₂ METHANATION

A piping and instrumentation (P&I) diagram of the experimental setup for the autothermal process for CO₂ methanation is illustrated in Figure A.3—the notations used in the presentation of the P&I diagram are defined in Table A.2. The P&I diagram presents the CO₂ methanation process in a co-current flow configuration.

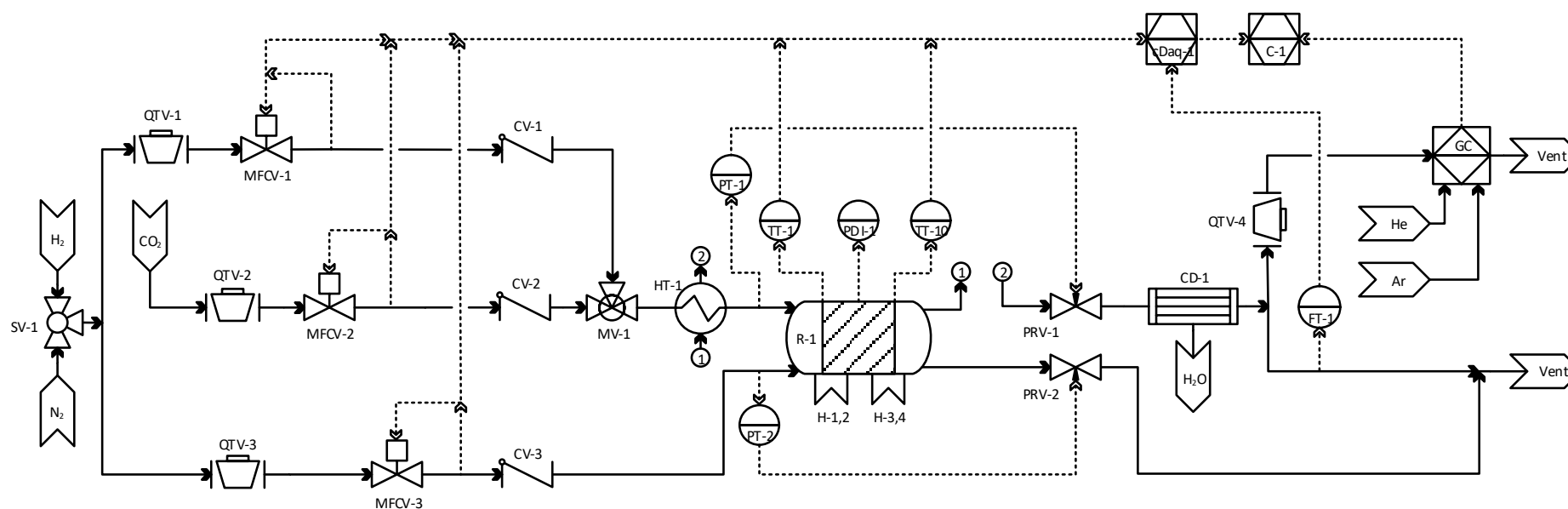


Figure A.3: P&I diagram of the autothermal process for CO₂ methanation in a co-current flow configuration (notations defined in Table A.2).

Table A.2: Notations used on the P&I diagrams presented in Figure A.3 and Figure A.4.

Process stream	Description	Equipment notation	Description	Instrument notation	Description
Ar	Argon, 10 mL min ⁻¹	CD	1 m pipe condenser (¼ pipe) and water knock-out pot	C	Computer
CO ₂	Carbon dioxide, 1.4 NL min ⁻¹	CV	Check valve	cDaq	Compact Daq
He	Helium, 20 mL min ⁻¹	H	Temperature-controlled heater	FT	Flow transmitter
H ₂	Hydrogen, 5.6 NL min ⁻¹ for methanation and 5.2 NL min ⁻¹ for cooling	HT	Heat exchanger	GC	Gas chromatograph
		MFCV	Mass flow control valve	PDI	Pressure drop indicator
H ₂ O	Water condensate, 75 mL h ⁻¹	MV	Mixing valve	PT	Pressure transmitter
N ₂	Nitrogen, 1 NL min ⁻¹	QTV	Quarter-turn valve	TT	Temperature transmitter
Vent	Product gas vent, 2.0 NL min ⁻¹ for methanation, 5.2 NL min ⁻¹ for cooling and 25 mL min ⁻¹ via the GC sample loop	PRV	Pressure relief valve		
		R	Reactor		
		SV	Three-way ball valve		

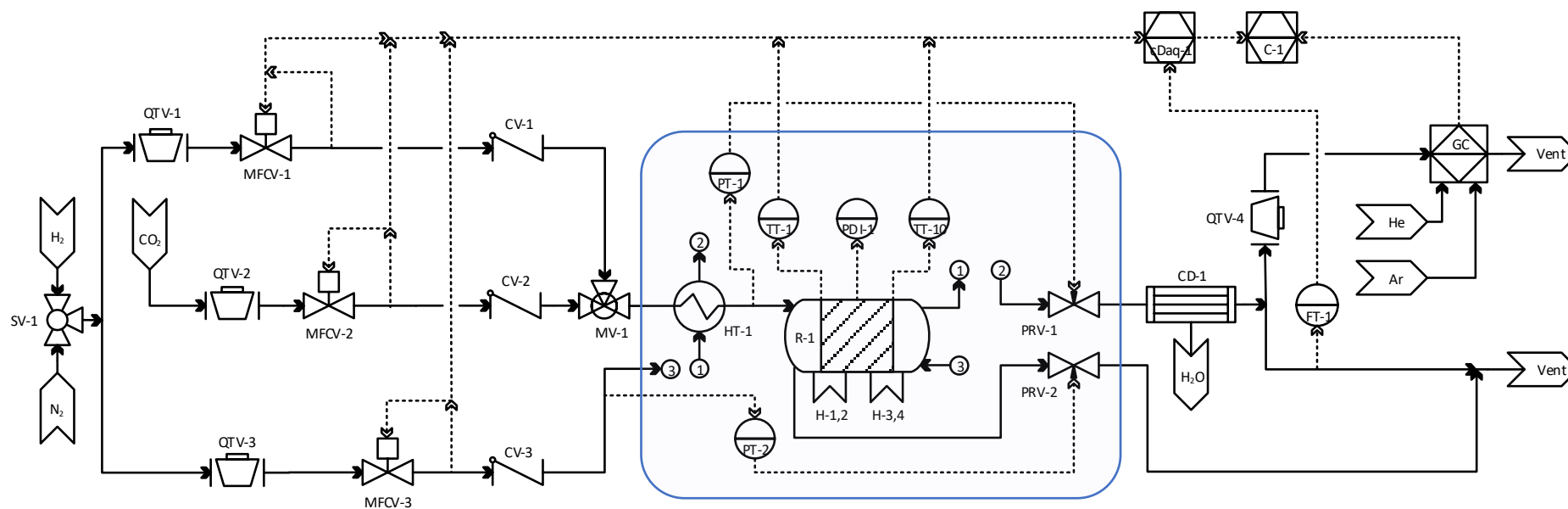
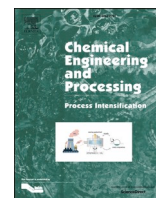


Figure A.4: P&I diagram of the autothermal process for CO₂ methanation (notations defined in Table A.2). The shaded region on the P&I diagram indicates the alternative piping for CO₂ methanation in a counter-current flow configuration.

APPENDIX B

The front pages of the research articles related to this thesis are provided in Appendix B. In addition, a summary of other articles and conference presentations related to microchannel fuel processors the author contributed to during the course of this study, is presented.



Microchannel reactor heat-exchangers: A review of design strategies for the effective thermal coupling of gas phase reactions

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Hydrogen production

ABSTRACT

The thermal coupling of endothermic and exothermic reactions is an important pathway for integrated thermal management within chemical reactors, which supports process intensification. Microchannel reactors are unique in the sense that they provide various design and operational characteristics that benefit high throughput and millisecond contact time chemical conversions. These include high microchannel aspect ratios, improved heat transfer (via thin and thermally conductive reactor substrates), and enhanced mass transfer (due to limited diffusional effects). In this review of experimental and simulated microchannel reactors, focus is put on improved designs and operating strategies to support thermal conduction across microchannel walls, yet keep chemical products from the respective reactions separate using spatially-segregated reaction chambers. Three common flow configurations (counter-current, co-current and cross-flow designs) are critically discussed as a result of their abilities to distribute – and in some cases recirculate – reaction heat, the steady-state temperature profiles established within them as a result of flow direction, and reactant conversions/product yields as a result of their thermal characteristics. Special attention is devoted to microchannel design aspects, including wall thermal conductivity, channel dimensions, catalyst positioning and other design strategies (distribution manifolds and heat recirculative reactor designs) to improve heat and mass flows within microchannel reactors.

1. Introduction

The natural intermittency of renewable energy sources have led to the exploration of various energy storage methods, including chemical energy storage. Compressed gas and liquid fuels (e.g. hydrogen, methane, ammonia, methanol and ethanol) have a superior energy density and storage capacity compared to battery, fly-wheel and compressed air energy storage systems. Stationary power generators based on chemical fuel conversion (e.g. fuel reformers coupled with fuel cells or alternatively gas turbines) can operate continuously, while mobile units (e.g. automobiles) can be refuelled within minutes. Moreover, the combination of fuel processors and fuel cells intended for on-board/mobile applications eliminate the need for on-board hydrogen storage vessels [1]. Perhaps the biggest restriction of chemical energy storage methods are their relatively low round-trip energy efficiencies and high initial capital cost [2]. Power-to-power efficiencies are generally in the

order of 33–45 % for methane and methanol fuels [3]. The biggest energy loss can be ascribed to the electrolyser and fuel cell [4], while the fuel processors can have efficiencies above 90 % when incorporating combined-heat and power systems.

Traditionally, fuel processing is performed for two reasons: (i) for power generation purposes, and (ii) the processing thereof towards chemicals of higher monetary value. Both these processes can benefit from micro-engineered reactor technologies (e.g. microchannels or monoliths), which in essence supports the concept of *process intensification* [5]. In the case of steam reforming, a portion of the fuel that is being reformed, is combusted to provide heat for the endothermic heat requirements [6], while cooling is applicable for reforming through partial oxidation and synthesis reactions. These reactions are thermally coupled in spatially segregated microchannels to provide intimate heat transfer, resulting in a plate heat-exchanger like design. These reactors support increased catalytic productivity compared to similar-sized conventional fixed-bed or fluidised-bed reactors. This is a result of

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A highly efficient autothermal microchannel reactor for ammonia decomposition: Analysis of hydrogen production in transient and steady-state regimes

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HIGHLIGHTS

- A scale-up of an autothermal microchannel reactor design for H₂ production.
- Effective thermal coupling between NH₃ decomposition and NH₃ oxidation reactions.
- Reactor performance assessed in transient and steady-state operating regimes.
- Improved reactor thermal efficiency of 75.9% and H₂ production rate of 0.71 kW_e.
- Combustible fuel-oxygen equivalence ratio identified to yield high N₂ product yield.

ARTICLE INFO

Keywords:

Ammonia decomposition
Ammonia oxidation
Autothermal reactor design
Microchannel reactor
Hydrogen generation
Fuel cell

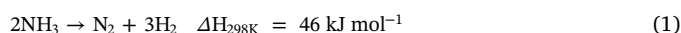
ABSTRACT

The experimental evaluation of an autothermal microchannel reactor for H₂ production from NH₃ decomposition is described. The reactor design incorporates an autothermal approach, with added NH₃ oxidation, for coupled heat supply to the endothermic decomposition reaction. An alternating catalytic plate arrangement is used to accomplish this thermal coupling in a cocurrent flow strategy. Detailed analysis of the transient operating regime associated with reactor start-up and steady-state results is presented. The effects of operating parameters on reactor performance are investigated, specifically, the NH₃ decomposition flow rate, NH₃ oxidation flow rate, and fuel-oxygen equivalence ratio. Overall, the reactor exhibits rapid response time during start-up; within 60 min, H₂ production is approximately 95% of steady-state values. The recommended operating point for steady-state H₂ production corresponds to an NH₃ decomposition flow rate of 6 NL min⁻¹, NH₃ oxidation flow rate of 4 NL min⁻¹, and fuel-oxygen equivalence ratio of 1.4. Under these flows, NH₃ conversion of 99.8% and H₂ equivalent fuel cell power output of 0.71 kW_e is achieved. The reactor shows good heat utilization with a thermal efficiency of 75.9%. An efficient autothermal reactor design is therefore demonstrated, which may be upscaled to a multi-kW H₂ production system for commercial implementation.

1. Introduction

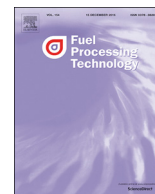
Recently hydrogen (H₂) received extensive consideration as a clean energy source through fuel cell applications [1–4]. However, global capacity relating to H₂ storage and distribution infrastructure is not yet established; it remains one of the greatest factors impeding the development of a H₂ energy economy [5,6]. Hydrogen also supports a low volumetric energy density. Hydrogen dense energy carriers such as ammonia (NH₃), methanol (CH₃OH) and ethanol (CH₃OH) are thus suitable for transport and on-site H₂ generation [1–4,6–9]. On the other hand, a recent universal trend has shaped to distance from fossil fuels and carbon-containing compounds for power generation [10,11]. As a

carbon-free energy carrier, NH₃ is a particularly attractive option for H₂ generation as it supports a hydrogen density of 108.5 kg m⁻³ at 8.57 bar_a (saturated liquid at 20 °C) [12]. Also, NH₃ has a large global production capacity of 100 million tons y⁻¹ [5]. The process of NH₃ decomposition (often called reforming) produces H₂ through a slightly endothermic reaction (reaction 1). This reaction takes place over a suitable catalyst (Ru or Ni) at temperatures of 500–700 °C [13].



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Thermal management and methanation performance of a microchannel-based Sabatier reactor/heat exchanger utilising renewable hydrogen

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ABSTRACT

Power-to-methane is a concept that offers the storage and utilisation of renewable energy, while recycling industrial CO₂ emissions, for carbon-based fuel production. An experimental microchannel reactor, that supports self-sustained operation, was evaluated for the Sabatier (methanation) reaction, using renewable hydrogen from a solar-to-hydrogen storage facility. Hydrogen, a common heat transfer medium, also provided the reactor's cooling requirements. Particular focus was placed on evaluation of the flow configuration within the reactor (co- and counter-current flow), because improved thermal management may offer enhanced CO₂ methanation reaction equilibrium. The effects of the following, within specified ranges, were determined, in terms of the reactor's thermal behaviour and the resulting methanation performance: the total methanation flow (4–7 NL min⁻¹), coolant flow (0.8–5.6 NL min⁻¹) and reaction pressure (5 and 10 bar_g). The counter-current flow configuration provided a decreasing temperature profile, with improved methanation performance and heat recovery. The recommended operating point was found to be under the following experimental conditions: a methanation flow of 7 NL min⁻¹, coolant flow of 5.2 NL min⁻¹ and reaction pressure of 10 bar_g. A CO₂ conversion of 90.5% and CH₄ power output of 667.1 W were achieved, while an overall methanation process efficiency of 76.6% was attained.

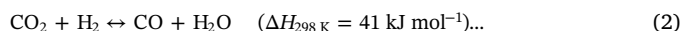
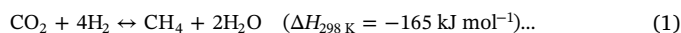
1. Introduction

Solar and wind energy are probably the most abundant sources of renewable energies, worldwide; in some economies they already constitute large portions of the power generated. The use of renewables limits CO₂ emissions, and allows countries to conform to the 2016 Paris Climate Change Agreement. However, the fluctuations in solar and wind energy, due to their natural intermittency, are a cause for concern, making these sources of renewable energies difficult to integrate into national power grids as baseload power [1–3]. The power-to-gas (PtG) concept was proposed in efforts to utilise excess renewable power during peak supply and to generate hydrogen (H₂) via water electrolysis [4]. However, H₂ has a low volumetric energy density, which presents difficulties in terms of H₂ transportation and storage [5]. The processing of H₂ to produce other energy carriers, e.g., methane (CH₄) or energy-dense liquids (methanol and dimethyl ether), has strengthened the concept. When there is an increase in the demand for power, the energy stored in these chemicals (energy carriers) can be converted back to generate electricity—hence providing power grid balancing.

High purity synthetic natural gas (SNG (containing mainly CH₄)) is

an attractive option for PtG; it has an enormous storage capacity in natural gas pipelines [6]. Other compounds such as C_{2–4} hydrocarbons can be blended to synthetic CH₄, should natural gas pipeline standards necessitate it. Furthermore, CH₄ also supports various other applications in the transport and chemical industries [6–8]. For example, in South Africa, in 2018, the country's Department of Energy announced that the country's energy matrix will diversify and increase the share of natural gas for power generation [9]. In turn, this will bring substantial development to the country's gas industry. There is also a global trend towards natural gas for power and fuel production because it results in lower process emissions, compared with the use of coal and oil.

The production of synthetic CH₄ (by methanation) follows a reaction pathway referred to as the Sabatier reaction (Eq. (1))—it involves the direct catalytic conversion of H₂ and CO₂. A secondary (and undesirable) catalytic reaction, which yields CO, is the well-known reverse water–gas shift (RWGS) reaction (Eq. (2)).



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B.1 LIST OF OTHER RESEARCH ARTICLES THE AUTHOR CONTRIBUTED TO THAT FEATURE MICROCHANNEL REACTOR TECHNOLOGY FOR HYDROGEN-BASED GAS PROCESSING

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B.2 LIST OF CONFERENCE PRESENTATIONS THE AUTHOR CONTRIBUTED TO DURING THE COURSE OF THIS STUDY

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Engelbrecht, N. & Bessarabov, D.G. 2018. Catalytic combustion assisted ammonia reforming in a microchannel reactor for hydrogen production. Oral presentation at the 29th Annual Conference of the Catalysis Society of South Africa (CATSA), 11–14 November, Legend Golf & Safari Resort, Limpopo, South Africa.