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Document Version

Final published version

Citation (APA)

Grenko, B. (2026). *Dynamic Methanol Reforming in Fixed Bed Reactors: 2D unsteady modelling of shipboard hydrogen production*. [Dissertation (TU Delft), Delft University of Technology]. <https://doi.org/10.4233/uuid:f4c5a9ca-bbba-438c-92ac-b4965d65e8dc>

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DYNAMIC METHANOL REFORMING IN FIXED BED REACTORS

2D unsteady modelling of shipboard
hydrogen production

BOJAN GRENKO

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DISSERTATION

for the purpose of obtaining the degree of doctor
at Delft University of Technology
by the authority of the Rector Magnificus,
Prof.dr.ir. H. Bijl,
chair of the Board for Doctorates
to be defended publicly on
Friday 30th, October 2026, at 15:00 o'clock

by

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Rijksdienst voor Ondernemend
Nederland

This research is part of the MENENS project (Methanol als Energiestap Naar Emissieloze Nederlandse Scheepvaart). The project is funded by the Netherlands Enterprise Agency (RVO: Rijksdienst voor Ondernemend Nederland) under the grant number MOB21012.

Keywords: methanol steam reforming, fixed bed reactor, dynamic modelling, experimental, heat transfer, maritime, methanol, hydrogen

Printed by: Ridderprint

Cover design: Bojan Grenko

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ISBN 978-94-6518-454-8

An electronic copy of this dissertation is available at
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Cease, cows, life is short!

Aureliano Segundo
in *One Hundred Years of Solitude*
by Gabriel García Márquez

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Summary

This study concerns the dynamic operation of methanol steam reforming in fixed bed reactors for shipboard hydrogen production. The work is motivated by the need to reduce greenhouse gas emissions and harmful exhaust pollutants from the maritime sector, while also addressing the practical difficulty of storing hydrogen directly on board ships. Methanol is considered a promising alternative fuel and hydrogen carrier because it is liquid under ambient conditions, has relatively high energy density, is already handled at industrial scale, and can be used both in combustion-based transition technologies and in future fuel cell systems. In this context, methanol reforming offers a route to produce hydrogen on demand, avoiding some of the storage challenges associated with compressed or cryogenic hydrogen.

The dissertation focuses specifically on methanol steam reforming for polymer electrolyte membrane fuel cell systems. This reforming route is attractive because it provides a high hydrogen yield and comparatively low carbon monoxide selectivity. This is important because PEM fuel cells require pure hydrogen feed. The selected reactor type is a fixed randomly packed catalytic bed. This a configuration is widely used and commercially relevant for reforming applications.

The shipboard operation introduces requirements that are not prioritized in conventional land-based chemical plants. A ship power system must respond to changing loads, and therefore the reformer must be understood in transient operation, in addition to steady state operation. The central question of this dissertation is how fixed-bed methanol reformers behave dynamically, what limits their response time, and what modelling or experimental tools are needed for their reliable analysis.

The second chapter examines the broader problem of dynamic operation in fixed bed reactors. It shows that dynamic behaviour can arise from several motivations, including process flexibility, periodic operation, and on-demand production. These different cases require different performance metrics, modelling approaches, and measurement strategies. The dissertation points how dynamic reactor analysis cannot simply reuse steady state design priorities. Moreover, the objective of the transient analysis must first be clearly defined in each case. This chapter also reviews available numerical modelling approaches and analytical techniques for measuring changing gas compositions. A key point is that models of higher fidelity than 1D are often necessary for dynamic analysis, but not always readily available or computationally convenient. Likewise, transient experiments require instruments with suitable sampling rates, and often a combination of analytical techniques is more likely than using a single method.

To demonstrate the importance of model fidelity, this study develops and applies a dynamic 2D fixed bed reactor model for methanol steam reforming. A comparison with a 1D plug flow model shows that models may agree reasonably well at steady state but differ during transients, especially when predicting local temperature fields

and species selectivity. This is important because transient CO formation and hydrogen production are directly relevant to operation and control in fuel cell systems. The 2D model therefore becomes the central tool for the later chapters, which focus on origins of reformer response time.

The second major part of the dissertation, starting with chapter 3, investigates the internal heat transfer dynamics of the fixed bed reactor. Methanol steam reforming is endothermic, so reactor performance depends strongly on heat transport from the reactor wall into the catalyst bed. For this work, the model only deals with the internal packed bed behaviour by imposing changes directly in wall temperature and reactant throughput. Thus the limitations of the external heating system influence is excluded. This allows for an estimation of a theoretical lower limit for the reactor transient time. The results show that, for typical tube diameters of 2-3 cm, internal heat and mass transfer lead to transient times of up to about one minute. This suggests that internal radial heat transfer alone is unlikely to explain the much slower response times often associated with practical methanol reformer systems. The packed bed may only amplify slow external heat supply changes, but it is probably not the dominant source of long load-change durations.

Chapter 4 combines experiments and modelling to study external heat transfer effects and validate the dynamic reactor model. A laboratory fixed bed methanol steam reformer is used for gathering steady state and transient data, mainly consisting of internal bed temperatures and reformat carbon monoxide content. The model is adapted to include all detected experimental non-uniformities and heat transfer imperfections. This enables a complete comparison between simulated and measured reactor behaviour. The results show that the model can capture the main dynamic trends, but they also reveal a strong influence of practical heating details during transient operation. Important external factors include the heat capacity of the reactor and supporting structure, axial heat loss profiles, non-uniform axial heat supply, and instability in inlet reactant temperature. Among these, the heat capacity of the reactor assembly is especially influential because it stores and releases heat during load changes, thereby prolonging the transient response even in a relatively small and well-insulated laboratory reactor.

Overall, the conclusions of this study is that dynamic shipboard methanol reformer design requires a broader approach than conventional steady state reactor sizing. A comprehensive analysis includes definition of the cause and purpose of dynamic operation, selection of a model with sufficient spatial and temporal fidelity, and finally the use analytical instruments fast enough to validate transient predictions. From this study it is also concluded that the intrinsic internal dynamics of typical fixed bed reformer tubes are relatively fast compared with the load change times reported for practical systems. Therefore, future improvements in transient performance should focus strongly on the external heating arrangement, reactor thermal mass, heat integration strategy, and system level control. These findings are relevant not only for methanol reforming but also for other shipboard chemical reactors that may become part of future low emission maritime energy systems.

Samenvatting

Deze studie betreft de dynamische werking van methanol-stoomreforming in gepakt bed reactoren voor waterstofproductie aan boord van schepen. Het werk is gemotiveerd door de noodzaak om de uitstoot van broeikasgassen en schadelijke uitlaatgassen in de maritieme sector te verminderen, terwijl ook de praktische uitdagingen van directe waterstofopslag aan boord van schepen worden aangepakt. Methanol wordt beschouwd als een veelbelovende alternatieve brandstof en waterstofdrager omdat het onder omgevingsomstandigheden vloeibaar is, een relatief hoge energiedichtheid heeft, al op industriële schaal wordt verwerkt en zowel kan worden toegepast in transitietechnologieën die op verbranding zijn gebaseerd als in toekomstige brandstofcelsystemen. In deze context biedt methanolreforming een route om waterstof naar behoefte te produceren, waardoor een deel van de opslagproblemen van gecomprimeerde of cryogene waterstof wordt omzeilt. Het proefschrift richt zich specifiek op methanolstoomreforming voor brandstofcelsystemen die op polymeer elektrolyt membraantechnologie zijn gebaseerd. Deze route voor reforming is aantrekkelijk omdat zij een hoge waterstofopbrengst en een relatief lage koolmonoxideselectiviteit oplevert. Dit is belangrijk omdat PEM-brandstofcellen een zuivere waterstofvoeding vereisen. Het gekozen reactortype is een vast, willekeurig gepakt katalytisch bed. Dit is een configuratie die veel wordt gebruikt en commercieel relevant is voor toepassingen van reforming.

Gebruik aan boord van schepen stelt eisen die bij conventionele chemische installaties op land geen prioriteit hebben. Een scheepsenergiesysteem moet kunnen reageren op veranderende belastingen, en daarom moet de reformer niet alleen in stationaire toestand, maar ook tijdens transiënt bedrijf worden begrepen. De centrale vraag van dit proefschrift is dan ook hoe methanolreformers met gepakt bed zich dynamisch gedragen, wat hun responstijd beperkt en welke modellerings- of experimentele hulpmiddelen nodig zijn voor een betrouwbare analyse.

Het tweede hoofdstuk onderzoekt het bredere probleem van dynamisch gebruik in gepakt bed reactoren. Het laat zien dat dynamisch gedrag uit verschillende beweegredenen kan voortkomen, waaronder procesflexibiliteit, periodiek bedrijf of productie op aanvraag. Elk van deze afzonderlijke gevallen vereist verschillende prestatimaatstaven, modelleringsbenaderingen en meetstrategieën. In deze studie wordt benadrukt dat dynamische reactoranalyse niet simpelweg de ontwerpprioriteiten voor stationair bedrijf kan hergebruiken. Bovendien moet het doel van de transiënte analyse in elk geval eerst duidelijk worden gedefinieerd. Dit hoofdstuk bespreekt ook de beschikbare numerieke modelleringsbenaderingen en analytische technieken voor het meten van veranderende gassamenstellingen. Een belangrijk inzicht is dat modellen met een hogere nauwkeurigheid dan 1D vaak noodzakelijk zijn voor dynamische analyse, maar niet altijd direct beschikbaar of rekentechnisch praktisch

zijn. Op hun beurt vereisen transiënte experimenten instrumenten met geschikte bemonsteringsfrequenties, en is een combinatie van analytische technieken vaak waarschijnlijker dan het gebruik van één enkele methode. Om het belang van de betrouwbaarheid van het model aan te tonen, ontwikkelt en gebruikt deze studie een dynamisch 2D-model van een gepakt bed reactor voor methanolstoomreforming. Een vergelijking met een 1D-propstroommodel laat zien dat modellen in stationaire toestand redelijk goed kunnen overeenkomen, maar tijdens transiënten kunnen verschillen, vooral bij het voorspellen van lokale temperatuurvelden en componentselectiviteit. Dit is belangrijk omdat transiënte CO-vorming en waterstofproductie direct relevant zijn voor de werking en regeling van brandstofcelsystemen. Het 2D-model wordt daarom het centrale hulpmiddel voor de latere hoofdstukken, die zich richten op de achtergrond van de responstijd van de reformer.

In het tweede hoofddeel van het proefschrift, beginnend met hoofdstuk 3, wordt de interne warmteoverdrachtdynamiek van de gepakt bed reactor onderzocht. Methanolstoomreforming is endotherm, waardoor de reactorprestatie sterk afhankelijk is van warmtetransport van de reactorwand naar het katalysatorbed. Voor dit werk behandelt het model alleen het interne gedrag van het gepakte bed door veranderingen direct op te leggen aan de wandtemperatuur en de doorzet van reactanten. Zo wordt de invloed van beperkingen in het externe verwarmingssysteem uitgesloten. Dit maakt het mogelijk om een theoretische ondergrens voor de transiënte reactortijd te schatten. De resultaten laten zien dat, voor typische buisdiameters van ongeveer 2-3 cm, interne warmte- en massaoverdracht leiden tot transiënte tijden van hooguit ongeveer één minuut. Dit suggereert dat interne radiale warmteoverdracht alleen waarschijnlijk niet de veel langzamere responstijden kan verklaren die vaak worden geassocieerd met praktische methanolreformersystemen. Het gepakte bed kan trage veranderingen in de externe warmtetoevoer slechts versterken, maar is waarschijnlijk niet de dominante oorzaak van lange belastingsveranderingstijden.

Hoofdstuk 4 combineert experimenten en modellering om externe warmteoverdrachtseffecten te bestuderen en het dynamische reactormodel te valideren. Een laboratoriumreactor voor stoomreforming van methanol met gepakt bed wordt gebruikt om stationaire en transiënte data te verzamelen, die voornamelijk bestaan uit interne bedtemperaturen en het koolmonoxidegehalte van het reformaat. Het model wordt aangepast om alle waargenomen experimentele niet-uniformiteiten en imperfecties in de warmteoverdracht mee te nemen. Dit maakt een volledige vergelijking mogelijk tussen gesimuleerd en gemeten reactorgedrag. De resultaten laten zien dat het model de belangrijkste dynamische trends kan beschrijven, maar tonen ook een sterke invloed aan van praktische verwarmingsdetails tijdens transiënt bedrijf. Belangrijke externe factoren zijn onder meer de warmtecapaciteit van de reactor en ondersteunende structuur, axiale warmteverliesprofielen, niet-uniforme axiale warmtetoevoer en instabiliteit in de inlaattemperatuur van de reactanten. Van deze factoren is de warmtecapaciteit van de reactorassemblage bijzonder invloedrijk, omdat deze tijdens belastingsveranderingen warmte opslaat en weer afgeeft, waardoor de transiënte respons zelfs in een relatief kleine en goed geïsoleerde laboratoriumreactor wordt verlengd.

Al met al is de conclusie van deze studie dat het dynamisch ontwerp van

methanolreformers aan boord van schepen een bredere benadering vereist dan conventionele reactordimensionering voor stationair bedrijf. Een volledige analyse omvat de definitie van de oorzaak en het doel van dynamisch bedrijf, de selectie van een model met voldoende ruimtelijke en temporele nauwkeurigheid, en ten slotte het gebruik van analytische instrumenten die snel genoeg zijn om transiënte voorspellingen te valideren. Op basis van deze studie wordt ook geconcludeerd dat de intrinsieke interne dynamiek van typische fixed bed reformerbuizen relatief snel is in vergelijking met de belastingsveranderingstijden die voor praktische systemen worden gerapporteerd. Daarom zouden toekomstige verbeteringen in transiënte prestaties zich sterk moeten richten op de externe verwarmingsconfiguratie, de thermische massa van de reactor, de warmte-integratiestrategie en de regeling op systeemniveau. Deze bevindingen zijn niet alleen relevant voor methanolreforming, maar ook voor andere chemische reactoren aan boord van schepen die deel kunnen gaan uitmaken van toekomstige emissiearme maritieme energiesystemen.

Nomenclature

Latin

Symbol	Unit	Description
A_{pe}	m^2	Interstitial area available for crossflow perpendicular to the bank of tubes at the widest point in the shell
$A_{t,in}$	m^2	Inner surface area of a single reactor tube
$A_{t,out}$	m^2	Outer surface area of a single reactor tube
C_i	$mol\ m^{-3}$	Concentration of species i
D_{er}	$m^2\ s^{-1}$	Effective radial dispersion coefficient
H_j	$J\ mol^{-1}$	Enthalpy of reaction j
$P_{el,in}$	W	Electric heater power
Q_{loss}	$W\ m^{-2}$	Normalized heat flux loss
S_c	$m^2\ kg^{-1}$	Catalyst surface (BET) area
T	K	Temperature
T_{fg}	K	Flue gas temperature
T_w	K	Reactor tube wall temperature
U	$W\ m^{-2}\ K^{-1}$	Overall (combined) heat transfer coefficient
V_t	m^3	Reactor tube (annulus) volume
$W_{cat.}/F_{CH_3OH}$	$kg\ mol\ s^{-1}$	Ratio of catalyst mass to methanol molar feed rate

Symbol	Unit	Description
$c_{p,f}$	$J\ kg^{-1}\ K^{-1}$	Fluid phase specific heat capacity
$c_{p,fg}$	$J\ kg^{-1}\ K^{-1}$	Flue gas specific heat capacity
$c_{p,s}$	$J\ kg^{-1}\ K^{-1}$	Catalyst specific heat capacity
$c_{p,w}$	$J\ kg^{-1}\ K^{-1}$	Reactor tube wall specific heat capacity
d_{in}	m	Reactor tube internal diameter
d_{lm}	m	Log-mean reactor tube diameter
d_p	m	Catalyst pellet diameter
d_{pore}	Å	Catalyst average pore diameter
$d_{t,out}$	m	Reactor tube outer diameter
h_s	$W\ m^{-2}\ K^{-1}$	Heat transfer coefficient of the shell side film
h_t	$W\ m^{-2}\ K^{-1}$	Heat transfer coefficient of the tube side film
k_w	$W\ m^{-1}\ K^{-1}$	Thermal conductivity of reactor tube wall
l_r	m	Reactor length
p	Pa	Pressure

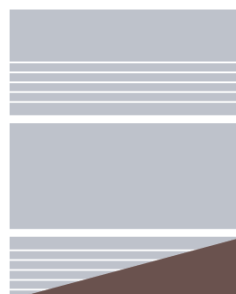
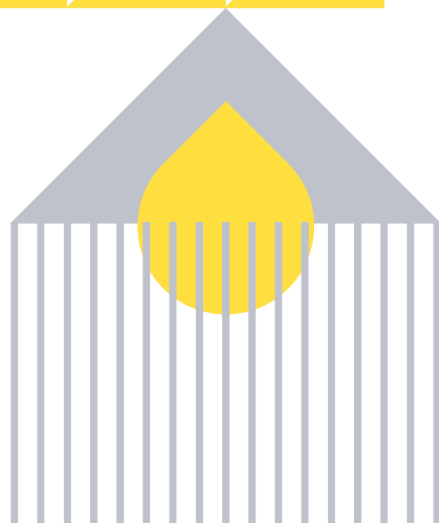
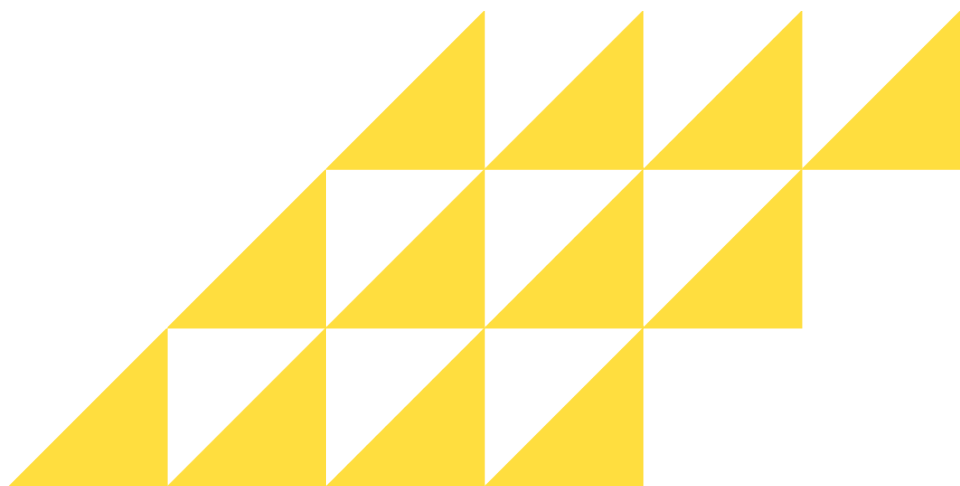
Symbol	Unit	Description
r_i	$\text{mol s}^{-1} \text{ m}^{-2}$	Area specific formation/consumption rate of component i
r_j	$\text{mol s}^{-1} \text{ m}^{-2}$	Area specific reaction rate of reaction j
s_w	m	Reactor tube wall thickness
t	s	Time
u_s	m s^{-1}	Superficial fluid velocity

Greek

Symbol	Unit	Description
ε	-	Reactor bed porosity
η_d	-	Trace heater wrapping density factor
η_j	-	Effectiveness factor for reaction j
λ_{er}	$\text{W m}^{-1} \text{ K}^{-1}$	Effective radial thermal conductivity
μ	Pa s	Dynamic viscosity
ρ	kg m^{-3}	Density
ρ_c	kg m^{-3}	Catalyst bulk density
$\rho_{c,f}$	kg m^{-3}	Fluid phase density
$\rho_{c,s}$	kg m^{-3}	Catalyst material solid density
ρ_{fg}	kg m^{-3}	Flue gas density
ρ_w	kg m^{-3}	Reactor tube wall density

Acronyms

Acronym	Description
ATR	Autothermal reforming (of methanol)
DAC	Direct air capture of CO_2
CCS	Carbon capture and storage (system)
GHG	Greenhouse gas
ICE	Internal combustion engine
IMO	International Maritime Organization
MCFC	Molten carbonate fuel cell
MSR	Methanol steam reforming
NOx	Nitrogen oxides
PEMFC	Polymer electrolyte (proton exchange) membrane fuel cell
PM	Particulate matter
POM	Partial oxidation of methanol
SOFC	Solid oxide fuel cell
SOx	Sulfur oxides
VOC	Volatile organic compounds



1

Introduction

Hitherto it is questionable if all the mechanical inventions yet made have lightened the day's toil of any human being.

John Stuart Mill

Maritime defossilization is motivated by climate commitments, energy-sector emissions, local port pollution, and IMO regulations. Hydrogen economy emerges as a potential answer. Methanol is a promising hydrogen carrier, and suitable for shipboard fuel-cell systems. The combination of methanol steam reforming in fixed-bed reactors for PEMFC applications is brought into focus. Research questions are defined based on dynamic operation, internal transient limits, and external heat-transfer limits.

1.1. Defossilization of energy

On 12 December 2015, in Paris, France, 195 countries agreed to limit the average global temperature increase to 2 °C, and ideally keep it below 1.5 °C. The participants signed a legally binding international treaty known as the Paris Agreement [1]. One of its aims is to quickly reach the peak emissions of greenhouse gases (GHG), with 2025 identified as a key year, and decrease them by 43% by 2030. Within the European Union, the emission cut plans are even stricter. The European Green Deal [2] approved in 2020 has the objectives of 50-55% reduction in GHGs by the year 2030 and climate neutrality by 2050.

The outcome of decided policies and actions remains to be seen. The leading reporting bodies on global temperature now observe a persisting and increasing trend [3–5]. The data are clear: the 1.5 °C goal is beyond our reach. Nonetheless, the plans in motion are not futile as the most catastrophic outcomes can still be averted [6, 7]. For this, urgency and consistency of global actions are key.

Approximately 75% of all GHG emissions are a by-product of the global energy consumption [8]. Fossil fuels are widely used in many applications because renewable electric energy cannot always be used directly. In response, studies suggest diverse large scale energy storage solutions such as mechanical, electrochemical, chemical, or thermal storage [9–11]. Among these, chemical storage through alternative fuels is identified as one of vital approaches for hard-to-abate sectors.

The most promising alternative fuel at present with demonstrated sustainable production is hydrogen [12]. Hydrogen can be used in combustion and electrochemical based energy extraction routes [13, 14]. However, hydrogen storage is problematic for applications with high energy density requirements. Its volumetric energy density is very low, resulting in storage solutions with cryogenic temperatures, extreme pressures, or both [15]. With storage tank weight included, the gravimetric energy density also becomes relatively low. One solution to hydrogen storage is again through chemical storage, otherwise known as hydrogen carriers [16, 17].

Hydrogen carriers are hydrogen-containing molecules able to release hydrogen in a controlled manner through chemical processes. The carriers can be in various states of matter. Examples include metal hydrides (solid adsorption-based storage), sodium borohydride (solid chemical storage), liquid organic hydrogen carriers (LOHC), or ammonia (gas at ambient conditions). The carrier choice depends on the required physico-chemical characteristics. Such renewable fuel future suggests not only a large variety of used fuels, but also a multitude of chemical processes for both fuel production and energy extraction [9, 13, 18].

There are two fundamental requirements for limiting global greenhouse gas emissions with alternative fuels: timely use of renewable energy, and process intensification. The current consumers of alternative fuels must rely on what is available prior to the full establishment of sustainable production chain. Today, the vast majority of energy carriers and feedstock for produced alternative fuels come from fossil fuels [19–21]. With this production pathway, the well-to-wheel/wake emissions are in fact higher than with direct use of fossil fuels [22, 23]. Establishing a renewable production globally is therefore even more urgent.

The intensification of (electro)chemical conversion processes is also vital due to high

energy requirements of alternative fuel production [24, 25]. Market competitiveness and wider adoption depend on technology maturity and efficiency. What is more, prior to efficiency optimization the known processes must first be adapted for renewable energy and feedstocks. The required adjustments can range from alternative operation strategies to novel reactor and heat exchange technologies, depending on the exact application [26]. Analyses of adaptation strategies are thus a key initial step and will expectedly differ based on the reaction specifics, target sector, and overall process purpose.

1.1.1. Renewable energy in the maritime sector

Waterborne transport has a large impact on the local air quality despite being among freight modes with least carbon intensity [27] (defined as carbon emissions per goods weight and distance travelled). Residents of port cities are exposed to increased concentrations of combustion products such as particulate matter (PM), Nitrogen Oxides (NO_x), Sulfur Oxides (SO_x), and Volatile Organic Compounds (VOC) [28, 29]. Around 10% of premature deaths in areas with high ship traffic are attributed to resulting lower air quality [30]. Consequently, the maritime sector is no exception to strict emission regulations.

Since 2005, the International Maritime Organization (IMO) enforces regulations on ship emission of NO_x, SO_x, VOCs, and ozone depleting substances [31]. The emission standards on sulfur were then further tightened in 2020, mandating a cap of 0.5% by mass in the fuel [32]. More recently, in 2025, the IMO drafted a net-zero path for ships over 5,000 gross tonnage that is aligned with the Paris Agreement [33]. This is especially important since international shipping was not covered by the Paris Agreement alone.

The most promising path to sustainable emission reduction in the maritime sector is through the use of renewable alternative fuels [34]. Multiple fuels and power conversion approaches are possible, depending on their characteristics. The path starts with short-term strategies. Immediate solutions include (blending) fuels lower in sulphur and carbon such as most biofuels or liquefied natural gas, and fitting exhaust after-treatment systems [35].

The mid-term plan introduces additional alternative fuels. Hydrogen, methanol, dimethyl ether, or ammonia used in (dual fuel) internal combustion engines (ICE) further reduce exhaust emissions. Each new fuel adds unique challenges to the combustion process, and some research is still needed before entering wider use [36]. Such efforts signify deliberate steps towards adoption of alternative fuels. This opens the market for sustainable fuel producers, and establishes the groundwork for other power converters in the long-term plan.

The long-term strategies for on-board power shift away from combustion based technologies [37]. Fuel cells have been drawing attention because they convert hydrogen into electrical energy through electrochemical reactions. They do not produce harmful combustion products, and their system noise and vibrations is significantly less than from ICE. The most promising fuel cell types for ships are polymer electrolyte membrane (PEMFC), solid oxide (SOFC), and molten carbonate (MCFC) fuel cells

[38]. Each fuel cell type requires specific hydrogen content and purity as inlet feed. Given the multitude of potential hydrogen carriers, this makes on-board fuel processing a key part of future power systems.

1.1.2. Challenges in shipboard power defossilization

The early adoption of alternative energy conversion systems relies on anticipating and addressing a wide range of emerging challenges. As this transition unfolds, many considerations and research directions surface. Advancements in shipboard energy systems draw on multiple fields of study and often require cross-discipline collaboration. The research relevance also goes far beyond technology progression. It is the basis for regulatory body directives, techno-economic assessments, crew training, and many more future aspects. Various ongoing and critical challenges within this landscape are highlighted in this section.

Bringing alternative fuels into the current engine room entails the most immediate analyses. First, a retrofit requires selection of a (potentially) sustainable fuel that is ideally compatible with both current and future solutions [39, 40]. The fuel storage and supply system must be adapted to the new fuel [41, 42]. The engine retrofit raises a whole set of questions on its adaptation ranging from fundamental understanding of combustion [43–45] to control and impact on operating strategies in steady and transient regimes [46, 47]. On top of everything, the shipowners must consider for the uncertainty in future technology developments and business case during the vessel lifetime [48–50]

In the fuel cell-based engine room the analysis takes another few turns. The risk management of hydrogen carriers and their processing on-board must be better understood [51, 52]. Even the physical behaviour of a hydrogen carrier sometimes requires attention. For example; sodium borohydride is a hygroscopic solid powder which chemically stores hydrogen and releases it upon contact with water. The powder cakes together during prolonged storage, and this behaviour is detrimental for storage and transport [53–55]. Then, since fuel cells produce low voltage DC electrical power, the system can be fully electrified. Such cases open up topics such as design, optimization, safety, and control of electrified energy systems [56–60].

The technology readiness level of fuel cells is seemingly high, but only on the account of a limited number of commercial solutions on the market [61–64]. The technology is still new for the operating customer. Operation capabilities and circumstances affect the fuel cell lifetime and operating strategy [65–68]. These effects in the long term might be unknown even to the manufacturer. What is more, installing fuel cell in the engine room requires a system tailored to it [69–72]. Various arrangements are explored through research, but practical experience is still needed for the better part.

The remaining part of this future landscape is the on-board chemical processing, such as hydrogen extraction and separation, or exhaust treatment. The chemical processes are not entirely familiar with shipboard environment and vice versa. The objectives, problems, tools, and methodologies for shipboard reactor design are presently underdefined. The exact involved processes and reactors depend heavily on

the processed chemical compounds. This work investigates the associated challenges to methanol, specifically in the context of its reforming to hydrogen for shipboard fuel cell systems

1.1.3. Methanol cycle for sustainable shipping

The methanol (CH_3OH or MeOH) is regarded as one of the most promising emerging alternative fuels for shipping [73]. Its advantages include: liquid state at atmospheric conditions, relatively high energy density, and wide availability due to chemical industry uses. As fuel, methanol can be used in dual fuel ICEs or reformed to hydrogen for fuel cell systems. It is therefore placed among mid and long term solutions for sustainable shipping [73].

The methanol production process is already well established, but is currently not sustainable for the most part [74, 75]. In short, the process sustainability depends on the source of input reactants: H_2 , and CO_2/CO . Renewable "e-hydrogen" can be produced via water electrolysis, in which energy intensity and production cost are currently a drawback [76]. Renewable carbon, in addition to energy intensity, also carries alternative sourcing as a yet open question. Unless methanol is synthesised with bio-based carbon, the carbon produced during methanol consumption must be captured somehow to close the carbon cycle.

The options for sustainable carbon supply are direct air capture (DAC), or on-site carbon capture and storage (CCS) systems. With DAC, the energy intensity is high due to low CO_2 concentration in the air (≈ 430 ppm by volume) [77]. Moreover, areas with plentiful renewable energy for DAC tend to have even lower CO_2 concentrations. On the other hand, on-site CCS from CO_2 -rich exhausts have problems with efficient separation, requiring bulky or (energy) expensive systems [78]. Besides with technological advances, the problem could be abated by relying on power generation with exhausts that contain high CO_2 concentration and easy-to-separate species.

The carbon capture systems are a vital component of the sustainable methanol lifecycle. A significant portion of its sustainability depends seemingly on the end user, and practical limitations may arise. The user must think of the additional energy required for CO_2 separation and liquefaction, as research suggests [79, 80]. CCS takes up valuable cargo space and weight, and is typically stored in liquid form under a combination of high pressure and low temperature (≤ 80 bar; $\geq -40^\circ\text{C}$). Economic factors such as the feasibility of selling captured CO_2 back to methanol producers may also play a role. These challenges could be detrimental to the integration of methanol into the renewable energy economy.

1.2. Methanol reforming to hydrogen

As a hydrogen carrier, methanol is fully or partially reformed on-site to produce on-demand feed for fuel cells or ICE. Reforming within only fuel cell system scopes are considered further in this section. Such system consists of many elements and is tailored around two key components: methanol reformer and a fuel cell. Depending on the reforming method, the reformer can have characteristic reactant and product

composition, catalyst, and associated thermochemistry. Similarly, the fuel cell type dictates the required inlet feed composition, operating temperature, and waste heat available for recovery. Additional system components simply manage the required heat and feed composition inputs to the reformer and fuel cell.

The reforming reactor is frequently a fixed, randomly-packed bed catalytic reactor [81, 82]. Due to reaction thermochemistry, these reactors are built as heat exchangers in shell-and-tube configuration. Figure 1.1 shows this arrangement. The required process temperature is maintained with the shell side fluid, which is typically hot flue gas.

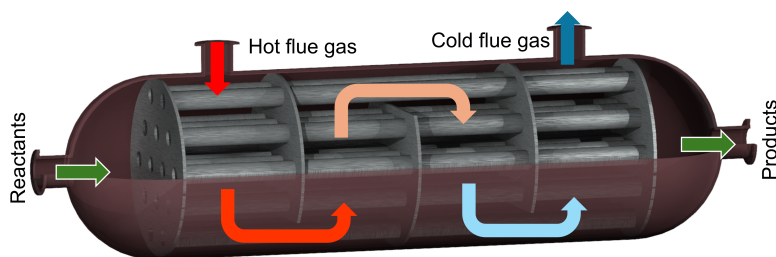


Figure 1.1.: Shell-and-tube reactor arrangement heated with flue gas

1.2.1. Reforming methods and reactions

Evaluating the pairings between reforming methods and fuel cell types requires understanding of the involved processes. Three methods of reforming methanol to hydrogen are often mentioned in fuel cell pairing context: methanol steam reforming, partial oxidation of methanol, and autothermal reforming.

Methanol steam reforming (MSR)

Methanol and steam are converted to H_2 and CO_2 in a direct methanol steam reforming reaction:



An alternative, simultaneous pathway with the same effect is through the methanol decomposition (MD):



followed by the water-gas shift (WGS):



The reaction is overall endothermic. The catalyst is most often copper-based, with $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ composition being readily available commercially [83]. The process temperatures on a copper-based catalyst range from 473–573 K (200–300 °C).

The MSR reaction has the highest yield of H_2 per mole of CO_2 since it extracts H_2 from water as well. Moreover, MSR has the best CO selectivity. The mild reforming temperatures limit the reverse-WGS reaction, and in practice the reformat contains 1–2 % molar of CO [81].

MSR is well suited for pairings with PEMFC because of its low CO selectivity. High-temperature PEMFC tolerate up to 3% CO by volume, and minimal reformat processing is required [84]. On the other hand, low-temperature PEMFC require high purity H_2 with ≤ 0.2 ppm CO by volume. Palladium membranes are typical for such separation of CO_2 and CO [85, 86]. Any hydrogen separated with the by-products can then be combusted and used in the reaction heat supply.

The reforming process, and consequently pairing with the fuel cell, are influenced by the catalyst material. The process temperature with copper based catalysts is capped at ≈ 573 K due to material stability issues [81, 83]. Higher process temperature would be beneficial since it accelerates reaction rates and results in smaller reactors. Researchers found better stability in noble metal based catalysts such as palladium and platinum [87], which operate at $T \leq 623$ K. However, these catalysts and elevated temperatures were both found to increase selectivity towards CO. This increases the separation energy intensity in couplings with PEMFC. The noble metal catalysts are today found mainly in research, partly also due to expensive materials.

By prioritizing the process selectivity, researchers also investigate low temperature catalysts [83, 88]. The active material can be copper or noble metals, while the novelty is in support structures, preparation methods, and reaction-promoting additives. The process temperatures can be reduced down to 373 K (100 °C), which produces very little CO and allows lower grade heat in the system. The industry might find these development interesting for heat integration with HT-PEMFC, which operate at temperatures up to 473 K (200 °C) [84, 89].

The most popular active catalytic materials are generally used in all reforming methods [90]. The difference is mostly in additives and preparation methods. Moreover, MSR is the most commonly researched and used method of methanol reforming. In the following paragraphs, the method performances are described briefly and mostly in reference to MSR.

Partial oxidation of methanol (POM)

In presence of oxygen instead of steam, methanol converts to hydrogen through the exothermic partial oxidation reaction:

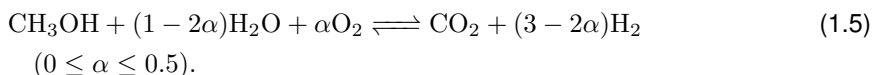


This pathway has multiple benefits over steam reforming [91]. First, the reaction is exothermic. The response to load changes is thus fast, which is very beneficial for transport purposes. Then, the systems are more compact due to reduced heat recirculation. Finally, air can be used to supply oxygen so only methanol storage is required. This benefit is situational since it introduces N_2 as a dilutant into the process. The product dilution can adversely affect fuel cell performance if not addressed [92, 93].

There are several disadvantages of POM. Reactor cooling is needed to maintain process temperature and prevent thermal runaway. The temperature in the reactor with a highly exothermic process can be difficult to control, making safety an added concern. Finally, the ratios of CO_2/H_2 and CO/H_2 in the product are higher compared to MSR [90, 91].

Autothermal reforming (ATR)

Autothermal reforming, sometimes described as combined methanol reforming, integrates both steam reforming and partial oxidation. The exothermic POM supplies the heat for endothermic MSR, according to the following reaction:



As a mix between MSR and POM, this method balances the external heat management and CO_2/H_2 ratio in the product. When $\alpha \approx 0.1$ in eq. 1.5, the overall process becomes isoenergetic. In practice, the process is made slightly exothermic due heat losses and easier control [90, 94]. This, however, lowers the maximum theoretical H_2 output. An important obstacle of ATR is in the local variations of reaction rates and temperature. The POM is dominant in the inlet region, which produces heat and supplies it for the downstream MSR reaction. The resulting local hot spots foster catalyst sintering and reduce its lifetime.

Aqueous phase methanol reforming

In recent years, aqueous phase methanol reforming has been gaining attention as a method for fuel cell supply [95–98]. The reactions are the same as in MSR (eqs. 1.1-1.3), and the method differs in reactant phase. Higher pressures in the reactor (15-50 bar) allow for the reactants to stay in liquid phase under reforming temperatures of $\leq 523 \text{ K}$ (250°C). In this way, the reactant evaporation is not needed and the process is more energy efficient. Furthermore, the products remain gaseous at used pressures and are separated from the reactants naturally during the reforming process. This also benefits selectivity since it limits the CO production through reverse-WGS reaction.

The research in this reforming method chiefly focuses on the improving the reaction rates [96, 97]. The reaction rates are slower than in MSR with current methods and materials, and improving them would make the reactors more compact. In addition to work on catalytic material activity and hydrothermal stability, researchers also point out mass transfer limitations as a key issue. The rate of H_2 vacating the porous catalyst surface can limit the reaction rate, which is common in such three-phase reforming systems [99]. Despite all, the method is seen as a promising addition to future methanol reforming systems.

1.2.2. Alternative reactor types and heating

Other reactor types besides fixed-bed (Figure 1.1) can also be used for methanol reforming. One alternative is a fluidized bed reactor, which is a reactor tube filled with powdery catalyst particles that are suspended due to the continuous upwards

reactant flow. The catalyst-reactant mixture behaves like a fluid, which improves the internal heat and mass transfer [83]. This reactor type enables heat management strategies such as heating/cooling coils within a single large reactor tube, in addition to classic multitube heat exchanger configurations. The disadvantage of this reactor is in maritime conditions, namely ship inclinations during operation. The reactor slanting affects the velocity, trajectory, and shape of the bubbles flowing upwards, which creates a slug regime with a high degree of gas bypass [100]. Inclination is a problem in other bubbling reactors too, for example the bubble column reactor [101]. Such reactors are thus not often used for maritime purposes.

Wall-coated reactors have also been shown as an effective alternative in many applications [83, 102]. In this approach a catalytic slurry (washcoat) is used and applied onto any surface, often with impregnation method, making it catalytically active. These reactors take novel shapes optimized for certain flow characteristics. The resulting benefits include often low pressure drop and possibility for rapid changes in operating temperature, both due to absence of catalytic pellets. The most common application is in a monolith reactor, which consists of dense honeycombed structure with square or triangular channels [103, 104]. Microreactors also make use of wall-coating, especially when facing space constraints in system integration [105, 106]. Finally, catalyst coating is used on ceramic or metallic foams as another way of creating a structured catalyst with enhanced internal transport properties [107, 108].

Heating type is another significant choice in fixed bed reactor design. Flue gas heating is frequent because often it is a system product, but it is not necessarily the only option. Other heating media may be considered such as oil or condensing steam. Additionally, innovative heating approaches are emerging in research. Heating elements may be inserted directly in the catalyst bed [83, 109]. Electrical heating is also gaining attention as a part of chemical plant defossilization plans. Heat generation in the reactor walls can be achieved through induction or resistive heating elements [104, 110]. The catalyst bed may be heated directly through microwave heating, significantly reducing heat transfer limitations [111]. All alternative technologies affect the reactor configuration, and many are still in research stages at present time.

1.2.3. Shipboard methanol reforming systems

Methanol reforming for maritime purposes has been receiving an increasing amount of attention in recent years [12, 73]. As a still evolving technology, the system concepts differ in practice and research. Commercial solutions must focus on providing a functional unit compliant with maritime regulations. Research, on the other hand, explores the viability of new concepts. This subsection gives recent examples of functional systems and discusses their characteristics.

Commercial solutions

At the time of writing, commercial reformers are constructed as independent and self-sustaining hydrogen production units. Figure 1.2 shows the most simple example of such methanol reforming setup. Examples from the market include methanol based hydrogen generators from e1 Marine, who offer M- and S-series specifically

for maritime purposes [61]. Moreover, it is possible to order a reformer-PEMFC integrated unit under the name M2PWR-FC. The units with integrated PEMFC are also developed by a number of other companies such as Freudenberg [63], PowerCell [64], M-Reformer [62], and Blue World Technologies [112].

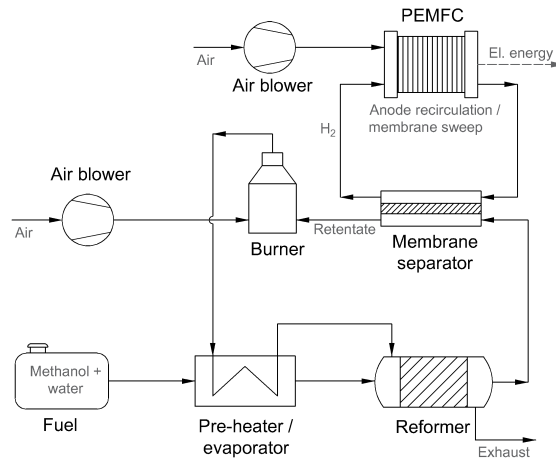


Figure 1.2.: Self sufficient reformed methanol system for a LT-PEMFC

The manufacturers seemingly wish to offer a modular product, ready to use directly off the shelf. This is very beneficial for the transition to new technologies in the maritime sector. In this way the manufacturer takes most of the burdens such as process design and control, or safety certification. This greatly helps the ship architects who are already dealing with plenty of new considerations in replacing the internal combustion engine. The modular units are possibly the most viable start to on-board alternative power generation.

In the long term, the modular approach has several obvious downsides. First is the space and weight efficiency. When multiple modules are needed, all units must have their own service space around them. The same applies to weight – piping, pumps, or heat exchangers all weigh less if there is one instance of each. Another downside is the adaptability of the reforming system to evolving technology. Higher process intensification is possible in custom systems through the ability to modify components such as reactor geometry, catalytic materials, or control schemes in the newest build. Shipbuilders also learn from the building process, and often make according changes to the following projects. This is possible if the reforming system is custom-built. Finally, such custom-built systems allow for heat integration with other on-board thermal processes, such as high temperature fuel cells. This would improve the overall energy efficiency. These concepts are currently found only in research, and represent a set of ideas for the way forward.

Reforming systems in research

In the future, the reforming systems will expectedly undergo developments in terms of efficiency and adaptability, but also complexity. Several technology additions and research directions are envisioned based on the prioritized objectives. A single change can impact the entire system layout, which is the cause of plentiful research and optimization opportunities on the system level.

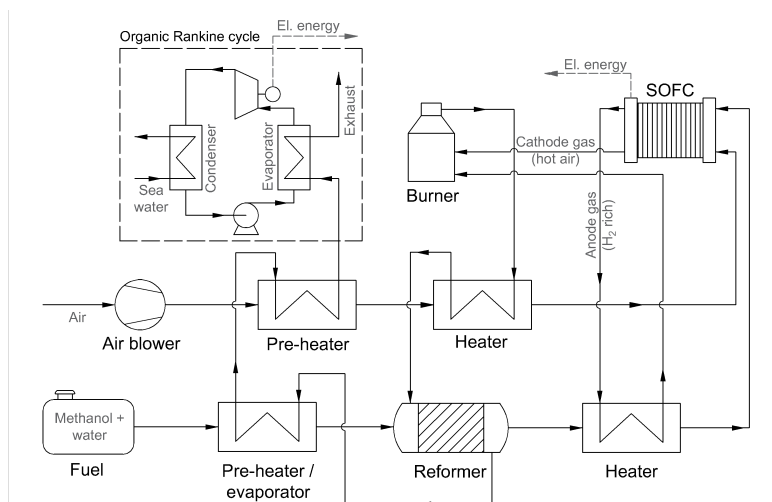


Figure 1.3.: Schematic of a steam reformed methanol SOFC system with organic Rankine cycle. Reproduced from [113].

Integration with different fuel cell types is frequently investigated for their effect on overall system characteristics. A PEMFC-based system is simpler to integrate, but often requires costly separation of CO, CO₂, H₂O, and CH₃OH from the reformat [85, 86]. High temperature fuel cells do not require separation and high quality waste heat may be used to sustain the reforming reaction, but heat management becomes more complex [89, 114]. Figure 1.3 shows an example of a reformed methanol SOFC system paired with an organic Rankine cycle. Despite the complexity, system efficiency can be much higher with SOFC. Reformed methanol PEMFC system efficiency typically ranges between 20-35% [115]. SOFC systems have an efficiency range of 50-80% [113, 116–118], consisting of combined heat and power. The efficiency range is wider than for PEMFC, since the exact value depends on system aim and architecture.

The system arrangement can also be adapted to novel and emerging technologies. Adaptations can be caused by reforming method [119–121], reactor type [121, 122], heating type [123, 124], hydrogen separation method [125], or included thermodynamic cycles [126, 127]. For example, Figure 1.4 shows a PEMFC system with a membrane reforming reactor. This results in a better (decreased) CO selectivity, but much higher material replacement cost according to Bernardinelli et al. [128]. The resulting system benefits are best applied in specialized cases.

Hybrid systems combine multiple technologies with fuel cell technology such as

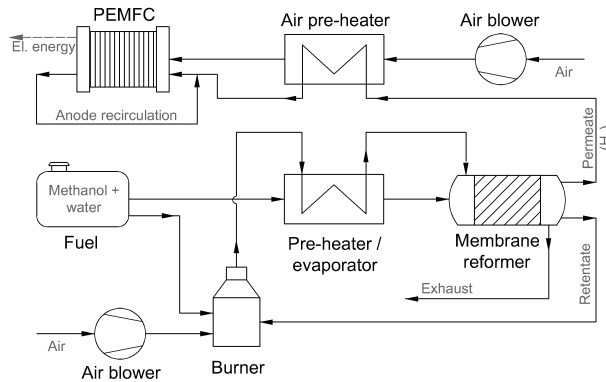


Figure 1.4.: Schematic of a steam reformed methanol LT-PEMFC system with a membrane reactor. Reproduced from [128].

ICEs [129, 130], gas turbines [131], or batteries and supercapacitors [132]. Such systems may even use more than one fuel [133]. Components in the hybrid system complement each other so that each one may operate close to its optimal conditions. This improves the energy efficiency, accelerates transient response, and increases component lifespan. The system disadvantages include complexity in design, control, maintenance, and often non-compactness, making the hybrid approach circumstantial.

All energy systems are designed based on included components, and modifications to any single component are often reflected on the entire system. As seen from the literature, many systems are situational due to their unique advantages and disadvantages. Exploring various technologies within a system context is therefore essential to the future system designer.

1.3. Research objectives

1.3.1. MENENS project

The following work is a part of MENENS project – Methanol als Energiestap Naar een Emmissieloze Nederlandse Scheepvaart; or in English – Methanol as an energy step towards emission-free Dutch shipping. The project focused on transition to methanol as ship fuel, and ran from November 2021 to February 2026. The Netherlands Enterprise Agency (RVO: Rijksdienst voor Ondernemend Nederland) supported the project with 24.3 million euro under the grant number MOB21012.

MENENS involved 21 partners from the entire Dutch maritime sector and including shipyards, naval architects, equipment manufacturers, suppliers, and knowledge institutes. The project scope was divided into seven work packages, which in short are: methanol power generation (WP1), safe storage (WP2), system design and integration (WP3), lab testing including power and energy management and control (WP4), and board realisation by retrofits, full-scale measurements and validation feedback

(WP5-7).

Research on methanol reforming was conducted within WP1: methanol power generation. The majority of WP1 focused on methanol powered internal combustion engines. However, the potential for future methanol-fuelled fuel cells was within its scope. This topic was researched primarily at Delft University of Technology.

1.3.2. Scope and research questions

This research focuses on shipboard methanol reforming for fuel cell feed purposes. Herein the fuel cell scope is narrowed down to PEMFC-based systems. The PEMFC system is more rigid in terms of integration, and sets clearer requirements for reactor performance. Namely, PEMFC have strict requirements for inlet feed composition, which naturally provides an objective for the reactor operation. Manufacturers specify limits of 0.2 ppm CO in line with standard ISO 14687-2 [134, 135]. The process CO selectivity is thus a clear objective since it makes H₂ purification and separation easier. Additionally, the transient response of PEMFC is relatively fast, even on the scale of several seconds in laboratory conditions [136, 137]. The reformer transient time becomes a target metric since it is potentially limiting to the system transient response.

The chemical processing scope is limited to methanol steam reforming on a copper based catalyst in a fixed randomly packed bed. This combination is chosen foremost because of its continued relevancy. The MSR method is versatile in fuel cell pairings and includes previously selected PEMFC due to its good CO selectivity. The MSR-PEMFC combination is already recognized in the industry, as seen from the commercially available modules. These existing solutions are a good basis for expansion into custom designed systems of the future.

The scope is also based on practical reasons. The research literature provides a good basis for reactor and system level modelling studies. Several validated kinetic models for copper based catalyst are available in the literature. Moreover, the combination is easiest for experimental studies. This is first facilitated by the commercially available copper based catalysts. It is also easier to implement heating and control of an endothermic system. The experimental component is thus possible within the present PhD time frame.

With the defined scope, the study is centred on maritime requirements for the reformer systems and design tools. Namely, the focus is placed on the dynamic operation requirement. Reactor operation and its characterization are currently well established only for land-based systems. The reactor transient capabilities, together with adequate tools to quantify it, are not known nor firmly defined in their requirements. The identified gap in literature leads to the definition of research questions in this dissertation:

RQ.1 What are the emerging considerations in analysis and prediction of dynamically operated fixed bed methanol reforming reactors, compared to steady state operation?

The extent of additional factors that should be considered in dynamic operation is unknown. As a first step, the appropriate numerical and analytical tools must

be used in design of such reactor. The current toolbox of a chemical engineer is heavily oriented towards systems in steady state. The evaluation of available tools and operation circumstances is needed prior to examining the operation itself.

RQ.2 What is the theoretical minimum for transient time of a fixed bed methanol reforming reactor?

The reforming process is limited by heat transfer, and achieving new steady state expectedly takes more time compared to internal combustion engine systems. Moreover, the reformer can be the limiting component during load transients in a PEMFC power production system. The minimum transient time of a fixed bed reactor depends on heat transfer within the catalytic bed, under the assumption of fast external heat supply. The transient time may dictate the size of a hydrogen buffer tank in the system. The lowest transient time is therefore a useful metric in future system design.

RQ.3 What are the limiting external factors to the transient time of a fixed bed methanol reforming reactor?

The external heat supply factors cannot be disregarded in practice. Understanding their influence on the transient time is necessary for hydrogen buffer size, but also system design. The external factors could be the deciding factor on the reactor type and heat supply system.

The research questions are applicable to many on-board chemical processes, and particularly ones in fixed bed reactors. The objectives, problems, tools, and methodologies outlined in this dissertation are not specific to a single process. The shipboard power defossilization relies on many processes, and methanol reforming to hydrogen is a single but powerful example.

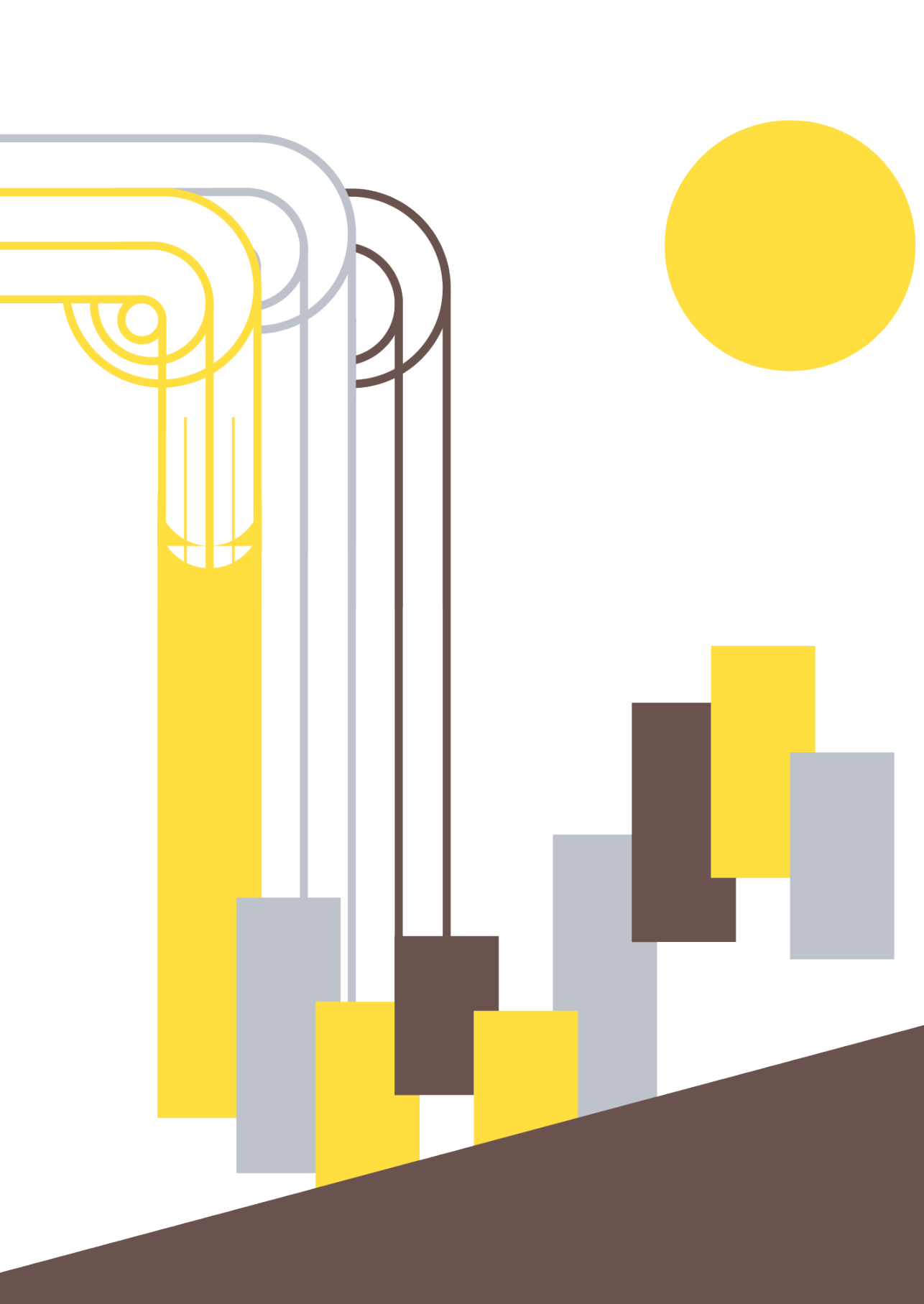
1.3.3. Dissertation structure

The chapters following the introduction address the research questions in order. **RQ.1** is central to Chapter 2, in which different motivations and types of dynamic reactor operation are presented. The available modelling tools are then examined in terms of popularity, accuracy, and computational intensity. The analytical instruments are also discussed, but the analysis is limited to gaseous species found among common products in petrochemical processes. The chapter finally demonstrates a modelling case study on prediction differences between dynamic 1D plug flow reactor model, and a newly developed dynamic 2D fixed bed reactor model. This chapter demonstrates the variety of reasons and tools found in dynamic reactor operation, and illustrates the required numerical tools for dynamic reactor design.

In Chapters 3 and 4, the developed dynamic 2D fixed bed reactor model is used to address remaining research questions. Chapter 3 focuses on heat and mass transfer inside of the fixed bed within the scope of **RQ.2**. The changes to reactant throughput and reactor wall temperature are directly controlled in the simulation, thus disregarding external influences on them. The resulting transient response results from internal bed

transport limitations, and is analysed for theoretical minimum time. Chapter 4 expands the analysis towards external heat transfer factors. In this chapter, **RQ.3** is addressed both experimentally and numerically. The experimental work also serves as validation for the developed dynamic model. This chapter presents several external practical limitations such as reactor and reactant heaters or local heat sinks. Their effect on the experiments and potential practice consequences are discussed.

The final chapter first draws the overall conclusions from the conducted research. The research is placed in broader context by connecting it back to maritime setting. The technology outlook for shipboard reformers and adjacent technologies is discussed. Finally, the next steps for future research directions are proposed.



2

Analysis of dynamic operation in fixed bed reactors

This chapter focuses on the situations in which fixed bed reactors may need to operate dynamically and the reasons for these requirements. Available models and analytical techniques are reviewed for their suitability in evaluating dynamic operation. Finally, the concluding case study shows that 1D and 2D models can agree at steady state but differ significantly during transients, especially for selectivity predictions.

Chapter published as: **Grenko, B.**, de Jong, W., van de Ketterij, R. and van Biert, L. *Analytical and numerical aspects of dynamic industrial chemical process analysis in fixed bed reactors* (2026). *Chemical Engineering Science*

2.1. Introduction

Dynamic operation of chemical reactors appears in recent research within a variety of topics. In periodic processes the fluctuations could be inherent to the process, or intentionally introduced for intensification. Furthermore, deviation from optimized steady state operation is becoming more common in the context of electrified chemical plants as a way of decarbonizing the chemical industry – the third largest source of industrial greenhouse emissions in 2019 [139]. Variations of renewable power share in the grid can be followed for plant sustainability goals [140, 141], and in Power-to-X processes for chemical energy storage and renewable fuel production [142, 143]. The chemical plant in these cases requires quick responses to the energy supply. The same operations are also used when the electrified chemical plant has economic targets with electricity prices as the variation driver. Last, the variations can also be caused by variable product demand.

In applications with dynamic operation in design conditions, the reactor transient characteristics have to be evaluated and included alongside the traditional design process. However, it is standard practice to design the chemical reactors by optimizing steady state operations, while reactor dynamics are a minimization task for the control system [144–146]. The design approach for dynamic operation first requires standard definitions of important transient characteristics and metrics of performance. Additional numerical or analytical tools are also possibly required for a complete evaluation. The growing applications for dynamically operated chemical reactors suggest additional optimization targets in the design process [147, 148], while at present it is uncertain whether the traditional steady state design techniques are optimal, or even sufficient for the task [149, 150].

This chapter presents an outlook of dynamic chemical processes in terms of emerging problems in the unsteady regime, important dynamic characteristics, their quantification, and their inclusion in the design process. The outlook consists of: a classification of dynamic operation by type or motivation, assessment of important operation characteristics, comparison of required model characteristics against common literature models, a review of suitable analytical techniques for process monitoring and model validation, and finally a conducted numerical case study of methanol steam reforming which compares performances of a 1D with a 2D model. The chapter focus is placed on fixed bed reactors due to their expectedly high uncertainty during transient performance caused by the combined effects of high bed heat capacity, reaction heat consumption or production, and convective heat and mass transport.

The study concludes that comparable metrics between various processes are not obvious, and for the moment it is best to use process-specific variables. This study reveals that the 1D unsteady models, which are commonly used in literature, inherently produce a substantial error compared to 2D models. The comprehensive evaluation of dynamic operation adds considerable complexity to used analytical and modelling techniques since it requires multiple models and analytical instruments that can follow the process dynamics.

2.2. Types of dynamic reactor operation

Dynamic operation of chemical reactors, also described as forced, transient, or unsteady operation, appears in multiple chemical engineering applications. The motivation for dynamic operation is often case specific and multifold. The present work recognizes three main motivators for repeated and continuous dynamic operation: process flexibility, process periodicity, and on-demand production. The most common examples in each category of dynamic operation are considered in this section, with their important characteristics. A summary of reviewed literature with respective simulated timescales, events, and methods is shown in Table 2.1.

Table 2.1.: Summary of timescales, events, and simulation methods for dynamic reactor operation in recent literature

Operation category	Reference	Dynamic event timescale	Simulation method	Simulated events
Plant flexibility (plant scale)	Tiggeloven et al., 2023 [151]	> 8 h	Mixed integer linear programming (MATLAB)	Start-up, shut-down, load following
	Tiggeloven et al., 2025 [142]	> 10 h	Mixed integer linear programming (MATLAB)	Start-up, shut-down, load following
	Giannikoupoulos et al., 2022 [152]	> 25 h	Mixed integer linear programming	Load following
	Foslie et al., 2024 [153]	> 150 h	Mixed integer linear programming (Julia)	Load following
	Caspari et al., 2019 [154]	> 48 h	1D plug flow model (Aspen plus)	Load following
	Chen et al., 2021 [143]	-	1D plug flow model (Aspen plus)	Yearly operation with pre-defined steady states
	Klüh et al., 2024 [140]	-	1D plug flow model (Aspen plus)	Yearly operation with pre-defined steady states
Forced periodic operation (reactor scale)	Bielefeld et al., 2024 [141]	-	Linear programming	Yearly operation with pre-defined steady states
	Leipold et al., 2025 [155]	36 s > t > 1 h	1D unsteady plug flow (Julia) + multi objective optimization	Multiple oscillations periodic
	Leipold et al., 2024 [156]	> 1 h	1D unsteady plug flow (Julia) + multi objective optimization	Multiple oscillations periodic
On-demand (system scale)	Nikolic et al., 2016 [157]	> 45 min	Unsteady CSTR (Julia) + nonlinear frequency response method	Multiple oscillations periodic
	Hollmann et al., 2023 [158]	> 3 min	1D plug flow model (MATLAB Simulink)	Load following
	van Biert et al., 2019 [159]	> 1.5 h	1D isothermal plug flow model (MATLAB simulink)	Start-up, load following

2.2.1. Process flexibility

The flexibility of a chemical plant is its ability to react and adapt to changing system environment for economic benefits or carbon intensity reduction, mainly in the context of renewable energy application. The definition includes several types of flexibility, as concluded independently by Bruns et al. [160] and Luo et al. [161]. First, the

capacity or volume flexibility is the ability to cope with varying throughput rates. Then, feedstock and product flexibility describe the plant resilience towards feed composition and product type using the same feedstock, respectively, both of which can be used to combat market volatility. Finally, operational flexibility is defined as response readiness to any uncertainties in operational parameters. Luo et al. are more specific in this definition, and distinguish between scheduling flexibility and production flexibility. Scheduling flexibility refers to quick start of the production cycle, while production flexibility denotes fast alternation between different production schemes. Both authors agree that one of the main causes for future process flexibility is the increasing relevance and intermittence of renewable energy supply. Chemical plants might need to increase competitiveness by adapting to the fluctuating cost and carbon intensity of both energy and sustainably produced feedstock.

The benefits of plant flexibility are recognized in the reviews of Bielefeld et al. [147] and Cegla et al. [148]. They find that electrified plants can most easily adapt to renewable energy supply. However, both also highlight the current high uncertainty in payoff. Bielefeld et al. mention lack of established methodology and practical knowledge in design and operation of a flexible plant. Cegla et al. express similar opinions on development and integration of complex computer based tools on a broader industrial scale. The uncertainty is logical since there are multiple types of process flexibility, and many can be used to increase plant competitiveness. Consequently, the benefits of plant flexibility must be evaluated on a case-by-case basis.

Case studies expectedly vary in their conclusions about the benefits of plant flexibility, due to specific boundary conditions and motivations of the studies. Tiggeloven et al. [151] investigated ethylene production from electrified naphtha cracking in three scenarios with different energy sources: grid based, grid and battery based, and plant's own renewable energy supply such as using photovoltaics and wind turbines. The high dependence on electricity prices, compared to conventional crackers, resulted in a conclusion that the operating envelope has the largest impact on production cost in electrified systems. However, cost savings up to 57.9% could be achieved with flexible operation. The same research group extended their analysis on ammonia-ethylene clusters [142] in the context of emission reduction by comparing pathways such as electrification, green H₂ supply, and carbon capture and storage (CCS). This study focused on emission reduction, and concluded that the use of batteries impacts emission flexibility more than the operating strategy of electric crackers. The study also suggests that near term zero-emission goals of such plants are not realistic. Chen and Yang [143] investigated flexible methanol production with variability in renewable energy supply and concluded a consistent cost reduction between 21-25% in all investigated scenarios. The authors found that flexibility is achieved by oversizing the process units and storage units for intermediates, and that long term economic gains outweigh the initial investment. Klüh et al. [140] also had positive findings for flexible methanol production plant via electrified biomass gasification. Their analysis showed an increase of 43.4-94.9% in carbon efficiency, which they define as a ratio of carbon in the targeted product and biomass. A difference in methanol production price between -12% and 8.9% was also reported. The analysis of existing petrochemical processes

in the Netherlands by Bielefeld et al. [141] showed a 6% cost increase in flexible electrified systems with various energy and product intermediate storage solutions, but also the potential to completely eliminate direct (scope 1) plant CO₂ emissions.

The varying conclusions of case studies on chemical plant flexibility can be attributed to many factors. First, processes are inherently different in production scope, energy intensity, and available equipment. Then, all studies take different flexibility approaches. The timescales for process changes are specific and rarely discussed. The authors use process flexibility for different objectives. The energy and reactant prices are also location specific. At present it is hard to estimate which circumstances lead to most benefit from system flexibility. However, the topic relevance is steadily increasing, and dynamic plant operation for flexibility purposes could lead to significant benefits in the renewable energy based future.

2.2.2. Periodic processes

Periodic or cyclical processes refer to any operation of chemical reactors in which input process variables change according to regular intervals. Kiefer et al. [162] provide an experimental example of a sorption-enhanced methane synthesis process in a fixed bed reactor. The added sorbent material in the reactor removes steam from the products, positively shifting the equilibrium of the Sabatier reaction. The sorbent is periodically regenerated by purging after it gets saturated. The authors remark how the dry state of regenerated sorbent highly influences on product quality, and consequently heat management, operation strategy, and reactor design. Similarly, Li et al. [163] experimentally investigated sorption enhanced methanol steam reforming for hydrogen production. By using CO₂ sorbent materials, they obtained a product with up to 99.3% hydrogen content consistently over 10 cycles, which is a large improvement from the typical value of 75%. The reported regeneration period is 2 hours per 30 minutes of reforming.

Another type of periodic operation is found in reverse flow reactors, in which flow direction is periodically reversed. The main added benefit of this system is heat regeneration as the locations of hot/cold zones in the reactor periodically alternate, managing the overall heat management. In their review, Barresi et al. [164] highlight the benefits of this reactor type in treatment of lean mixtures of volatile organic compounds with air. Furthermore, the review of Marín et al. [165] discusses the mass regeneration in reversed flow operation. In this scenario, sorbent materials at the reactant inlet remove the unwanted species from the inlet reactant flow, while the sorbent at the outlet is simultaneously regenerated. The sorbent zones swap roles when the flow is reversed. The same authors summarize the available literature and report that the range of flow switching times in methane catalytic combustion is between 15 and 1800 seconds.

Conceptually similar to reverse flow are loop reactors, which are a network system of reactors in series. These systems enable dynamic switching of feed positions within the loop. Similar to reverse flow reactors, Barresi et al. [164] note that loop reactors can better exploit the catalyst heat capacity. Both Barresi et al. [164] and Sheintuch et al. [166] observe significantly decreased by-products in loop reactors designed for

processing of volatile organic compounds, but at the cost of a complex control system.

The dynamic analysis of periodic processes occurs on the reactor scale, in contrast to process flexibility analysis which considers the full plant scale. However, it is likely impossible to apply the same approach among different cases due to wide variation of key performance indicators. The motivation, characteristics, and typical time scales of periodic processes are found to be highly case dependant.

2.2.3. On-demand production

The motivation for on-demand production stems from the need to minimize the system size and weight by minimizing product or energy buffers in the system. On-demand production is currently uncommon in the chemical processing industry, but a growing relevance is observed for large transport applications (ships, buses, trucks, forklifts), stationary backup power for critical infrastructure (telecommunications, hospitals), and portable power systems in military or private use. A variety of chemical reactors facilitate on-site conversion of hydrogen carriers into hydrogen, which is then used in fuel cells to generate electrical power with low emissions. In this way, storage of hydrogen and/or electricity is minimized. For simplicity and clarity, this section discusses a single application of on-demand production. Maritime applications are focused on in this section due to power demand fluctuations, high industry interest, and system scale which is closer to a full-scale chemical plant than to microreactor scale.

In shipboard systems, power generation pathways with hydrogen carriers are proposed [167] in response to strict emission regulations for ships [31], and problematic on-board hydrogen storage systems [168]. A multitude of hydrogen carriers and conversion processes are researched due to different fuel requirements for each fuel cell type, storage and safety compliance of each carrier [169]. For example, partial or complete methane reforming is most common for solid oxide fuel cell systems [170]. Alternatively, systems with proton exchange membrane (PEM) fuel cells can be paired with methanol reforming, ammonia cracking, sodium borohydride dehydrogenation, or processes including liquid organic hydrogen carriers [169].

Such shipboard systems are medium sized in comparison with traditional chemical plants [127, 171, 172], and represent unique challenges. For example, the entire reactor and downstream equipment volume is often more important than only the reactor areal footprint because of deck height space limitations. The choice of heat supply system might also be restricted due to necessary integration with other on-board systems. Finally, decreasing reactor transient times also reduces the necessity for intermediate storage, either in the form of hydrogen tanks or batteries, decreasing the overall system size.

Novel commercial solutions such as M2H2 [173], Mreformer [62], and Amogy genset [174] are a testament to maritime industry's interest in on-board hydrogen production. Implementation intents are seen in projects such as the reformed methanol powered Hydrogen One tugboat [175], and shipbuilder orders for hydrogen generators [176]. The relevance for on-demand operation is seemingly growing fast out of necessity. Moreover, a feasible and compact solution could potentially find uses in other large transport vehicles such as trains or trucks.

Dynamic modelling of chemical reactions in on-demand systems is currently most often related to control. Proof-of-concept system studies generally use steady state simulations in a sensitivity analysis fashion to display the validity over required load range [127, 129]. Fuel cell control studies, however, often use dynamic process model for in their systems. Methane reforming namely can be found prior to the fuel cell, and on the anode of solid oxide fuel cell. For this purpose, the literature has been recommending simplistic 0D continuously stirred tank reactor models or 1D plug flow models [177], which studies use to this day [158, 159].

2.3. Current state of unsteady reactor modelling

The model choice in chemical reactor simulations is often made by the available numerical tools. The convenience of popular commercial software often causes bypassing of a critical question: *what are the required model characteristics for the task at hand?* This section addresses the capabilities of available common models for steady and unsteady reactor simulations, and discusses how they are reflected among the recent unsteady modelling case studies.

2.3.1. Model characteristics

The reactor model characteristics vary based on the academic literature type, and publication date. Books on chemical reaction engineering tend to describe idealized approaches, mainly for reactor sizing using a steady state design approach. For example, Jakobsen [178] shows only the simplest steady state approaches in the context of chemical reaction engineering, despite covering complex reactive flow models in great detail. Conesa [179] describes 1D unsteady state models for different reactor types, namely for start-up and shut-down procedures, but does not discuss the sizing implications in these regimes of reactor operation. Admittedly, books focus on models with wide applicability and long-lasting relevancy, and simple 0D or 1D models such as plug flow represented in Figure 2.1 are used extensively. More complex models and their applications for chemical reaction engineering are seldom described.

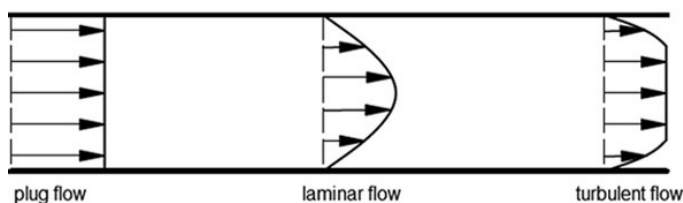


Figure 2.1.: Plug flow graphical representation. Reprinted from [180] with permission of Wiley, Copyright 2019.

Scientific publications review model requirements for chemical engineering, often thoroughly exploring only one aspect. Zagoruiko et al. [181] concluded that the models for industrial catalytic processes must account for non-uniformities of flow

heat transfer and concentration distribution in axial and radial direction, especially in unsteady models. They reason that lab scale uniformity is lost on industrial scales, and that direct scale-up is not appropriate without accounting for dynamic interactions in large systems. Tesser et al. [182] also advocate for capturing the macroscopic and microscopic gradients in the models depicted in Figure 2.2, arguing that all processes interact with each other. They also find that internal diffusion limitations strongly influence process selectivity.

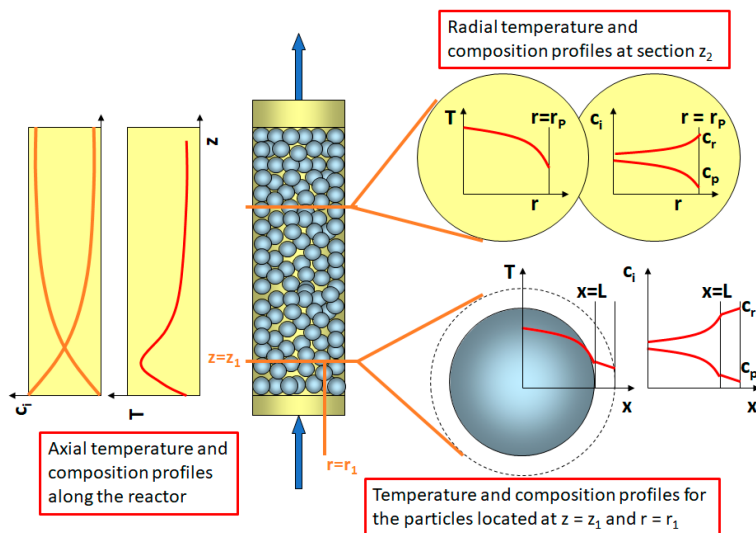


Figure 2.2.: Interparticle and intraparticle gradients of heat and concentration within a packed bed reactor. Reprinted from [182] with permission of MDPI, Copyright 2020.

Stegenhake et al. [149] and Fabrik et al. [183] both use holistic approaches for reviewing fixed bed model requirements, and agree that the model capabilities should be determined by simulation objectives, available resources, and model accuracy. Both authors identify assumptions and various coefficients as a cause for increased deviations from reality. In simpler 1D models, the error sources are often assumptions like constant density, simplified catalyst particle shapes, and empirical correlations for effective heat transfer parameters. Stegenhake et al. also point out that empirical correlations can be based on invasive measurement methods which considerably influence the reactor behaviour, resulting in a fundamentally inaccurate correlation. On the other hand, higher fidelity models use less assumptions but require more parameters and experimentally measured data as input. For example, even 2D heterogeneous models for fixed bed reactors require much more data on the used catalyst since they distinguish between fluid and solid phases in the reactor.

The required amount of data for higher fidelity models can become an obstacle in some fields. For example, Harkou et al. [184] note in their review of CFD methods of modelling fuel production from CO_2 hydrogenation that kinetic data is very limited for

certain reactions. The flexibility of high fidelity methods then becomes limited by data availability.

Furthermore, the main issue of highest resolution methods such as CFD in chemical engineering is computational efficiency. In their review of CFD methods for reactive flows at surfaces, Micale et al. [185] indicate that 70-90% of the computational effort is spent on solving the high non-linear reaction kinetic equations when microkinetics are involved. Full resolution 3D CFD models are known to be unfeasible for most objectives in industrial chemical engineering. For listed reasons, many authors [149, 183–185] propose hybrid approaches as best application of CFD, such as combining experiments and CFD, or hierarchical modelling where correlations for simpler models are derived from higher fidelity simulations.

2.3.2. Unsteady fixed bed reactor modelling in case studies

Unsteady 1D models for fixed bed reactors have been used in recent literature for load-flexible operation analyses of processes such as CO₂ methanation [144, 145, 186], CO₂ hydrogenation to methanol [146], or ammonia synthesis [187]. The studies advise that the reactor dynamics should be included during the design optimization, but the same studies do not entirely adopt this suggestion. In listed works, unsteady models are employed after the design is optimized for the required range of steady states, and often only for the most extreme transient events. The unsteady modelling results, such as one shown in Figure 2.3, act only as a final inspection of reactor performance in time, and do not serve as input to design optimization. The required model accuracy and characteristics for design in dynamic regime are not discussed. The study of Wentrup et al. [150] claimed that the commonly used 1D models are mainly useful in qualitative analyses, and not accurate enough for detailed quantitative insight. This study reviewed the models for dynamic operation of Fischer-Tropsch reactors in process intensification and Power-to-X applications. One of their main concerns is the lack of unsteady model tuning and validation data, which is caused by low accessibility of experimental techniques for high-resolution transient product analysis. They also extend their conclusions to other fixed bed reactors.

Giglio et al. [189] demonstrated a qualitative analysis with a study on intermittent power-to-gas in methanation reactors. The authors used a 1D unsteady model analysis to prevent overheating during startup, and for CO₂ staging strategy for load flexibility. Quantitative analyses are mostly performed with CFD, like in the study of Karpilov et al. [188] who simulated the performance of a preheated packed bed for steam methane reforming. The study simplified the reactor geometry to 10 catalytic pellets in a tube, as commonly done in CFD reactor studies. The authors presented a detailed dynamic temperature field, as shown in Figure 2.4a and predicted the molar fraction reduction of produced hydrogen from 0.377 to 0.249 in 15 seconds of operation, as shown in Figure 2.4b. Moreover, they quantified that the catalyst bed reheating is 1.5 times slower than its cooling due to reforming. However, the geometry simplification is significant, which limits the industrial applicability of this approach.

In chemical looping applications, unsteady models were also identified as a research gap in the reviews of Kataria et al. [190] and Peltola et al. [191]. Kataria et al. stated

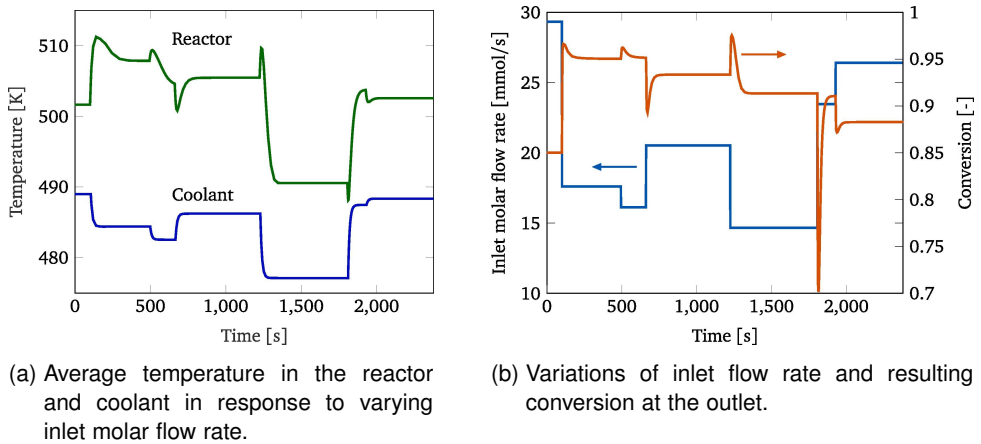


Figure 2.3.: 1D unsteady simulation of CO_2 methanation in a wall-cooled fixed bed reactor with varying inlet molar flow rate. Reprinted from [144] with permission of Elsevier, Copyright 2020.

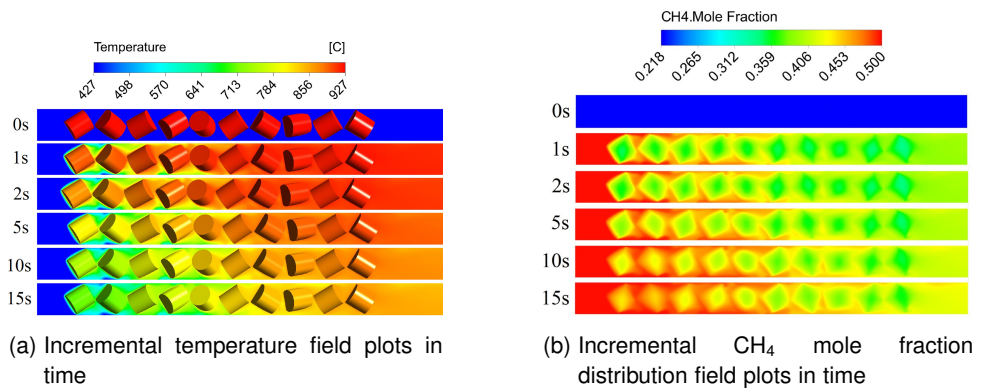


Figure 2.4.: Unsteady 3D steam methane reforming simulation of a single reforming cycle after hot stand-by in a simplified packed bed geometry. Reprinted from [188] with permission of Elsevier, Copyright 2023.

that capturing transient behaviour is critical for design of large scale plants, while Peltola et al. claimed that resolving unsteady simulations is potentially the final barrier for commercialization of high purity hydrogen production via chemical looping. The case study of Argyris et al. [192] on this topic presented a newly developed 1D and 2D unsteady model of a chemical looping reforming reactor, validated with experimental results. The study showed a local temperature underestimation by 2.5% and the average bed temperature by 1% in the 1D model due to its inability to resolve radial gradients. The 2D model followed the temperature closely. The authors conclude that the 1D model is more practical, unless detailed local temperature data is required. The

1D model was 21 times more computationally efficient, but the exact computational time or hardware were not specified so the applicability of the 2D model for industrial applications cannot be objectively assessed.

2.3.3. Development and performance of 2D models

Some interest is found in the literature on the development of 2D fixed bed reactor models, and predominantly on a case-by-case basis instead of systematic reviews. Fischer et al. [193] compare 1D to 2D model, with both heterogeneous and pseudo-homogeneous phase treatment on a methanation reactor in dynamic conditions. A custom solver is implemented in AMPL programming language. They conclude that pseudo-homogeneous models reach steady state significantly faster when transport resistances are non-negligible. However, they also show that 2D models often predict runaway conditions much sooner than the 1D model. Argyris et al. [192] also compare dynamic 1D and 2D pseudo-homogeneous models for oxidation, reduction, and reforming reactions in a chemical looping reactor. The models are implemented in C++. The authors find better agreement of 2D model with the experimental data, but deem the 1D sufficient. They then use 1D model for validation predominantly because of lower computational time. Fatahillah et al. [194] even more strongly conclude that 1D is sufficient for total methane oxidation in a fixed bed reactor. However, this study is in steady state with high throughputs, both of which diminish the influence of radial effects. The simulations were performed with Ansys Fluent.

In comparison to 3D particle resolved CFD models, the 2D pseudo-homogeneous offers significant advantage in computational efficiency. However, the accuracy difference can also be non-negligible. Steady state studies of Moghaddam et al. [195] shows inaccuracies in predicted temperature profiles, notably due to effective heat transfer parameters and their dependence on reactor length. They also conclude that high resolution numerical experiments can be used to improve the parameters in pseudo-homogeneous approach. More recently, Weng et al. [196] confirmed that hypothesis and successfully showed a methodology for parameter estimation based on particle resolved simulation data. Highly accurate predictions of temperature field in a dry methane reformer were achieved at < 1% computational time compared to the particle resolved simulation.

For dynamic industrial design tasks, it is apparent that 1D is not sufficient when safety is in question. Extra computational time must not be an obstacle in that case. Hierarchical approach such as shown by Weng et al. [196] could be the path forward for the industry. Parameter estimation from the literature data might also be possible in some cases. It might not be necessary for mid-fidelity models to be as accurate as the CFD simulations. However, the accuracy requirements are not obvious to deduct for the general case.

2.3.4. Challenges of increasing model fidelity in the industry

At present time, the models in the literature are chosen on two grounds: study objective, and computational efficiency. Dynamic regime and timescales do not affect

the chosen methodology, which is supported by Table 2.1. Instead, the available models affect the simulated domains and timescales, which is seen in CFD studies [188]. This is a severe limitation for dynamic design objectives with realistic transient times.

Measuring and characterizing internal reactor phenomena is a complex and time intensive task. Dixon [197] shows with an example of radial heat transfer in packed bed how even experiments can produce wrong trends due to biased measurements. The same study also mentions how parameter estimation with particle resolved CFD can suffer from length effects. Avoiding them requires larger simulated reactor domain, which further increases computational times. The resulting (empirical) measurements are potentially non-transferable between models and/or cases. Wide adoption of mid-fidelity models which rely on them is thus even more difficult.

Finally, extending a low fidelity model with correlations requires some programming skill and time. Appropriate commercial tools for mid-fidelity are limited, even general solvers for partial differential equations. At present time, the only open source tool for chemical processes known to the authors is Cantera. This suite of tools is not specifically focused on mid-fidelity, and most examples are kept simple. Even in this case the user must adapt the tool with own programming. With all listed challenges it is clear how 0D and 1D models remain the most used despite their known shortcomings.

2.3.5. Design speed-up with data driven approaches

Data driven approaches have been gaining popularity for many applications. They have large potential use, considering the recent insights from Power-to-X review papers [198, 199]. Robust digital tools for dynamic process design and control are specifically identified as a critical required tool for sustainable energy supply in the future. Physics-based models are rapidly advancing, but the rift between over-simplicity and enormous computational expense is still quite large. Data driven approaches can hence be used in two main ways: hybrid modelling, and efficient design space exploration.

In hybrid modelling there are multiple pathways. First, model order reduction simplifies a complex technique, such as CFD, into a fast mathematical representation. Bizon et al. [200] display the approach on a steady-state fixed bed reactor for design optimization and report computational time in order of seconds. Second, there are physics-informed neural networks. This machine learning technique has directly embedded physical constraints in the form of partial differential equations into the training function. Wang et al. [201] use such method for extraction of small-scale transport parameters in a packed bed reactor, namely diffusion coefficients in their case.

If physics based models are the only option, Bayesian optimization could still be used for the most efficient exploration of the design space. The technique is very popular with expensive CFD models. Examples from the literature optimize yield [202], temperature gradients [203], but also multiple simultaneous objectives [204].

The data driven approaches are still relatively new, and the full extent of their applicability in design is yet to be explored. Hybrid and full machine learning

approaches first raise questions on their robustness within and outside of their training data. Moreover, the required amount of data is unclear, as well as the expense of its gathering. In Bayesian optimization on CFD models there is still a lower limit of computational expense that might be too high for industrial design.

It is likely that combination of all listed approaches is used for best practices in industrial design. For example, an accurate and efficient 2D model can be created with parameters estimated through Bayesian optimization on CFD particle resolved data. For later control purposes, fast reduced order model can be based on data from 2D or 3D particle resolved original models.

2.4. Instrumental analytical techniques for dynamic chemical processes

Chemical analysis is needed in industrial applications for process monitoring, while in research it provides data for novel process and material characterization or model validation. Most experimental analyses are done for steady state operation and many popular techniques are suited only for that. In dynamic processes, the additional requirement is that the samples must be analysed quickly and accurately in time, which places constraints on certain techniques. Two papers analysed in the previous section [149, 150] identify the necessity for reliable and high resolution product analysis for model validation and better understanding of transient phenomena. This section discusses the challenges and suitability of popular instrumental analytical techniques for dynamic chemical processes. Moreover, only non-invasive product gas analysis techniques are explored.

The petrochemical industry, ammonia production, and processing of renewable fuels and energy carriers are taken as reference applications for fixed bed reactors. Most common species found in them are H_2 , N_2 , O_2 , CO , CO_2 , NH_3 , steam, and hydrocarbons such as methane or vaporized methanol. These gases are used for rating the detection capabilities of analytical techniques. The section summary is shown in Table 2.2.

2.4.1. Gas chromatography

Gas chromatography (GC) is the most common commercial gas analysis technique. Inherently a batch sampling type analysis method, it is capable of quantifying concentrations of all listed species. Its suitability for continuous analysis is highly dependant on utilized detectors and column characteristics. The column length determines the analysis run time, which can take up to 20-40 minutes per sample in longer columns. Column length is usually chosen based on expected analytes in the sample in order to produce a sufficient resolution in the chromatogram. The run time can be reduced to several minutes, and potentially even further with state-of-the-art equipment and sensors. Fialikov et al. [205] demonstrated analysis cycle time below 1 minute by using low pressure GC and low thermal mass resistive heating for the capillary column. Ultimately, the suitability of gas chromatography varies on a case

Table 2.2.: Overview of relevant instrumental gas analysis techniques for characterizing dynamic chemical processes

Technique	Analysis timescale	Advantages	Limitations	Note	Ref.
(micro-)GC	2-40 min	Detection versatility, multitude of available additional detectors	Potentially long analysis times, inherently batch type analysis, potential sample conditioning	Column type, length and analysis times depend on required resolution of analyzed species	[205, 206]
MS	Real time with DIMS	High sensitivity	Complexity, cost, required operator skill, difficulty detecting H_2 , CH_4 , $\ddot{a}$ and most air components	Often used as complementary technique to GC	[207–210]
FTIR	Real time	Fast in-line analysis, no sample preparation	Lower sensitivity than GC and MS, cannot detect H_2 , N_2 , and O_2	Often used as complementary technique to GC	[211, 212]
NDIR	mili(second) range	Fast analysis, lower cost and complexity than FTIR	Cannot detect H_2 , N_2 , and O_2	Most often requires one sensor per specie	[213–215]
Raman	1 min	No sample preparation, fast analysis, high amount of acquired information	Lower sensitivity, cannot detect monoatomic gases	Features may differ depending on exact advanced Raman technique	[216–219]
TDLAS	(mili)second range	No sample preparation, fast analysis, high potential sensitivity	Weak detection of H_2 and N_2 , may need a sensor per detected specie	Sensitivity and analysis time are correlated	[220–225]

GC: gas chromatography, MS: mass spectrometry, FTIR: Fourier transform infrared spectroscopy, NDIR: non-dispersive infrared spectroscopy, TDLAS: tunable diode laser absorption spectroscopy

by case basis, since it also depends on the time-scale of the characterized transient event.

2.4.2. Mass spectrometry

Mass spectrometry (MS) is most often used together with GC, in which case the GC run time is the limiting factor. Direct injection MS (DIMS) is also possible which enables real time analysis. Two types of DIMS are gaining scientific interest in previous years: selected ion flow tube-mass spectrometry (SIFT-MS), and proton transfer reaction-mass spectrometry (PTR-MS) [207]. These techniques are mostly used for analyses of breath or volatile organic compounds in the air [208]. Applications in chemical industry are scarce but present, with an example given by Ren et al. [209] who devised a novel MS method for natural gas leakage detection. Detectable species in MS depend on the used precursor ion, and most common ions such as H_3O^+ , NO^+ , or O_2^+ do not react with hydrogen, methane, and species in ambient air [210]; making them undetectable with this type of MS. The main strength of MS is its sensitivity, so it is potentially useful as a complementary technique for detecting traces of some targeted species. The current limitations of MS are its cost, complexity, and often required operator skill level.

2.4.3. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy is a technique suitable for in-line real time analysis of solids, liquids, or gases. Its relevant uses include catalyst characterization studies under operating conditions [211], and analysis of hydrocarbon fuels and exhaust gas emissions [212]. Gas analysis with infrared (IR) techniques is generally less popular than with GC and MS because of lower sensitivity. On the other hand FTIR analysis is possible in real time, which increases its relevance in dynamic process analysis. An additional strength of IR techniques is qualitative detection of unexpected species via specific spectral characteristics. However, a significant limitation in the present context is its inability to directly detect H_2 , N_2 , and O_2 , since they do not have dipole moments. In some cases, this method may still be used in combination with mass balancing to calculate the exact product composition. Otherwise, FTIR may be best used in combination with other techniques.

2.4.4. Non-dispersive infrared spectroscopy

Non-dispersive infrared (NDIR) spectroscopy is another technique that measures infrared absorption of the sample. However unlike FTIR, the infrared radiation source in NDIR emits a wavelength range characteristic for one species, meaning that NDIR sensors typically measure a single species in the sample. NDIR is therefore not as versatile as FTIR, but it is less complex to operate and less costly. Most common usages include detection and quantification of CO_2 levels in the air, breath, or emission monitoring systems [213]. Quantification of gas concentrations is in the ppm range, and the analysis time can vary between millisecond and second scale [214]. Multi-species detection systems with NDIR are possible, but better performing systems tend to be bulky and with high acquisition and maintenance costs [214, 215]. Same as in FTIR, the main limitation of NDIR for present purpose is the inability to detect gases without dipole moments.

2.4.5. Raman spectroscopy

Raman spectroscopy is a technique used in wide array of sciences including forensics, archaeology, diagnostics, and various branches of chemical industry since it offers a non-destructive and rapid analysis of samples in all states of matter without sample preparation [216]. In gas analysis, Raman is often used to complement IR techniques because it offers more specific chemical information, but the measured Raman effect is weak and the sensitivity is lower than IR. Raman techniques detect all species of present interest and struggle only with monoatomic gases, which lack the vibrational modes necessary for Raman scattering. Raman is not as widespread as GC in commercial applications potentially due to a multitude of different advanced Raman sub-techniques which all offer quite specific advantages [217]. Raman has been recognized to be suitable for on-line natural gas analysis [218, 219], and several commercial solutions and implementation for natural gas analysis with run times of around 30 seconds are already on the market [217]. The technique is able to identify

species of interest in fast analysis, making Raman spectroscopy a suitable analysis technique candidate.

2.4.6. Tunable diode laser absorption spectroscopy

Tunable diode laser absorption spectroscopy (TDLAS) is generally used for in-situ detection of very low concentration limits, measuring up to ppb range. The fastest analyses are produced in the (mili)second range, while measurement of extremely low concentrations can take up to several minutes. Sensitivity of this method is species dependent, and is lowest for gases with weak adsorption lines such as H_2 and N_2 . Hydrogen TDLAS sensors are still challenging in accuracy and detection time, but some researchers deem it suitable for usage in industrial environment for safety monitoring [220, 221]. In principle, each TLDAS sensor can detect only one species, but researchers have achieved multi-species gas detection with a single diode by scanning multiple adsorption line profiles [222, 223]. Successful demonstration of TLDAS in practice has been shown for processes with natural gas and typical accompanying species at low weight and instrumentation cost [224, 225]. TLDAS therefore appears very useful for a multitude of dynamic process contexts.

2.4.7. Other notable techniques

Spectroscopy techniques are plentiful and particularly fitting for dynamic processes because of the fast analysis times. In addition to the listed ones, a notable example is also photoacoustic spectroscopy, based on the photoacoustic effect. It can detect complex gas mixtures in the ppb range. Drawbacks include system size and cost, noise interference, and maintenance of long term stability [226]. Another example is terahertz spectroscopy. This highly sensitive and selective technique detects unique molecular rotation fingerprints. However, detection is limited to polar molecules. Additional limitations include water vapour interference and potentially source bandwidth range [227].

Apart from (product) gas detection, there is also value in experimental characterization of catalyst and reactor behaviour. For catalysts, relevant methods include steady-State isotopic transient kinetic analysis (SSITKA), and temporal analysis of products (TAP). Despite its name, SSITKA characterizes catalyst kinetics and intermediate reactions in situ and in time. This is done by detecting products in time, after controlled injection of isotopically labelled reactants [228]. In TAP, on the other hand, the surface processes and kinetic behaviour are directly influenced by controlled reactant supply. Short pulses of reactants are let into a microreactor under vacuum, while products are analyzed. High resolution can be achieved since the residence time under vacuum is extremely small [229].

On the reactor scale, transient behaviour can be characterized with non-linear frequency response (NFR) analysis. This method is based on detection of non-linear resonances that occur in the reactor, initiated by periodic modulation of inlet variables in time. Complex system responses are thus revealed, which can be used for mechanistic studies or reactor performance improvements [230, 231].

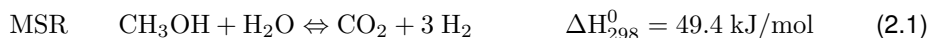
2.4.8. Direct integration with models

Besides their use for providing validation data, in-line sensors can be directly connected with models. Digital twin of the physical system can be used for real time monitoring and reactor control, while the sensor data can simultaneously update the model. Hybrid or data based models are a good candidate because of low calculation times required for real-time monitoring and control [232].

Flores-Tlacuahuac et al. [233] highlight several challenges with direct model integration with sensor data. First, sensor noise and outlier need to be filtered out efficiently and reliably. Second, the measured data does not include all parameters. The so-called difficult to measure variables are estimated with soft sensor methods. The method choice then depends on system characteristics, measured data, and method objectives. Finally, transfer learning is identified as highly beneficial, but under-defined topic with data driven models.

2.5. Case study: methanol steam reforming

Methanol steam reforming to hydrogen is recognized as one of the viable pathways for on-demand H_2 production on board of ships for fuel cell applications [167]. In these circumstances, high dynamic capabilities of the reactor are beneficial since they decrease the size and weight of peak shaving equipment on board of ships, such as intermediate H_2 tanks or batteries. This reaction is also typically done in packed bed reactor for such intermediate or larger scale, which makes it applicable to present article. The catalytic pellets of $CuO/ZnO/Al_2O_3$ composition are packed in a shell-and-tube heat exchanger, as shown in Figure 2.5, where three dominant reforming reactions are sustained: methanol steam reforming (MSR), methanol decomposition (MD), and water gas shift (WGS), shown in eq. 2.1-2.3.



This section shows the results of a numerical modelling case study on methanol steam reforming to hydrogen in a catalytic fixed bed reactor, heated by flue gas in a tube-in-shell heat exchanger arrangement. The developed in-house 1D and 2D models are used to simulate several transient scenarios, and the differences in performance and computational effort are reported.

2.5.1. Numerical models

The utilized unsteady 2D packed bed reactor model is explained in more detail in Chapters 3 and 4, and the code is available via Git repository [235]. The equations of mass and energy balance are:

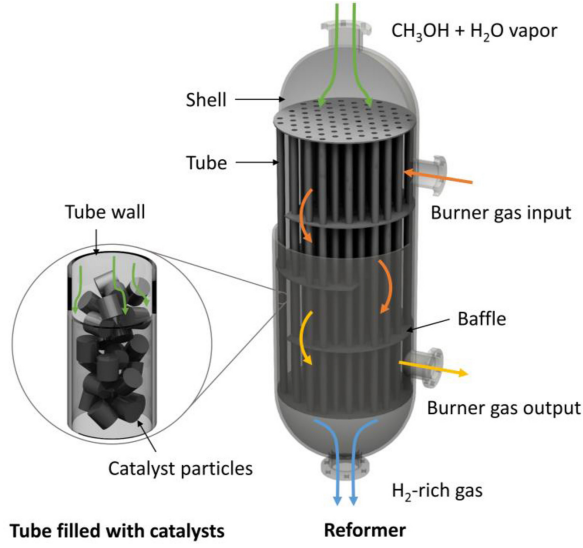


Figure 2.5.: Multi-tubular fixed bed methanol steam reforming reactor. Reprinted from [234] with permission of Elsevier, Copyright 2022.

$$\varepsilon \frac{\partial C_i}{\partial t} = -u_s \frac{\partial C_i}{\partial z} + D_{er} \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r} \frac{\partial C_i}{\partial r} \right) + \rho_c r_i, \quad (2.4)$$

$$\begin{aligned} & (\varepsilon \rho_f c_{p,f} + (1 - \varepsilon) \rho_s c_{p,s}) \frac{\partial T}{\partial t} = \\ & -u_s \rho_f c_{p,f} \frac{\partial T}{\partial z} + \lambda_{er} \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) + \sum \eta_j \rho_c (-\Delta H_j) r_j S_c, \end{aligned} \quad (2.5)$$

where ε is the catalyst bed porosity, C_i (mol m⁻³) are the specie concentrations, u_s (m s⁻¹) is the flow superficial velocity, D_{er} (m² s⁻¹) is the effective radial dispersion coefficient, ρ_c (kg m⁻³) is the catalyst bulk density, r_i (mol s⁻¹ m⁻²) is the formation/consumption rate of component i , T (K) is the temperature, λ_{er} (W m⁻¹ K⁻¹) is the effective radial thermal conductivity, ΔH_j (J mol⁻¹) is the reaction enthalpy of reaction j , r_j (mol s⁻¹ m⁻²) is the reaction rate of reaction j , S_c (m² kg⁻¹) is the catalyst surface area, and η are the effectiveness factors evaluated per reaction j . The highlighted radial terms are omitted in the 1D model, resulting in common 1D plug flow equations. The boundary conditions of the 2D simulation are presented in Table 2.3.

The model omits an axial dispersion term. Sahimi [236] distinguishes between several dispersion regimes dependent on the Peclet number. Thus, the *power-law* regime between $5 < Pe < 300$ is dominated by convective transport with some molecular diffusion, while the *purely convective* regime falls between $300 < Pe < 10^5$.

Table 2.3.: Simulation boundary conditions

	Coordinates	Boundary condition
Inlet	$z = 0$	$C_i = C_{in}$
	$0 \leq r \leq r_{max}$	$T = T_{in}$
Outlet	$z = z_{max}$	$\frac{\partial C_i}{\partial z} = 0$
	$0 \leq r \leq r_{max}$	$\frac{\partial T}{\partial z} = 0$
Wall	$0 \leq z \leq z_{max}$	$\frac{\partial C_i}{\partial r} = 0$
	$r = r_{max}$	$\frac{\partial T}{\partial r} = -\frac{h_t}{\lambda_{er}}(T_{wall} - T)$
Symmetry axis	$0 \leq z \leq z_{max}$	$\frac{\partial C_i}{\partial r} = 0$
	$r = 0$	$\frac{\partial T}{\partial r} = 0$

The characteristic flows for methanol steam reforming used in present simulations result in $Pe > 230$, which was deemed as sufficiently high to disregard the axial dispersion term.

The reaction kinetics are computed with a Langmuir-Hinshelwood model of Peppley et al. [237], and the pressure drop is calculated with the Ergun equation [238]. The flue gas energy equation was adapted from Varma et al. [239] for unsteady incompressible flow:

$$\rho_{fg} c_{p,fg} A_{pe} \frac{\partial T_{fg}}{\partial t} = -c_{p,fg} \dot{m} \frac{\partial T_{fg}}{\partial z} + d_{t,out} \pi N_t h_{s,fg} \Delta T_{fg}, \quad (2.6)$$

where ρ_{fg} (kg m^{-3}) is the flue gas density, $c_{p,fg}$ ($\text{J kg}^{-1} \text{K}^{-1}$) is the flue gas heat capacity, A_{pe} (m^2) is the interstitial area available for crossflow perpendicular to the bank of tubes at the widest point in the shell, $\dot{m}$ (kg s^{-1}) is the flue gas mass flow, $d_{t,out}$ (m) is the reactor tube outer diameter, N_t is the number of tubes in a reactor, and $h_{s,fg}$ ($\text{W m}^{-2} \text{K}^{-1}$) is the heat transfer coefficient from flue gas to the reactor tube outer wall.

Reactor tube wall temperature is computed according to:

$$\rho_w c_{p,w} \frac{\partial T_w}{\partial t} = k_w \frac{T_w}{\partial z} + U \Delta T_{fg,w} \frac{A_{t,out}}{V_t} - h_t \Delta T_{w,r} \frac{A_{t,in}}{V_t} \quad (2.7)$$

where ρ_w (kg m^{-3}) is the reactor tube density, $c_{p,w}$ ($\text{J kg}^{-1} \text{K}^{-1}$) is the reactor tube specific heat capacity, T_w (K) is the wall temperature, k_w ($\text{W m}^{-1} \text{K}^{-1}$) is the thermal conductivity of tube wall material, U ($\text{W m}^{-2} \text{K}^{-1}$) is the combined heat transfer coefficient, h_t ($\text{W m}^{-2} \text{K}^{-1}$) is the combined heat transfer coefficient of the tube side film, $\Delta T_{fg,w}$ (K) is the temperature difference between flue gas and tube wall, $\Delta T_{w,r}$ (K) is

the temperature difference between tube wall and reactants, $A_{t,out}$ (m^2) is the outer surface area of one reactor tube, $A_{t,in}$ (m^2) is the inner surface area of one reactor tube, and V_t (m^3) is the reactor tube volume. The combined heat transfer coefficient U is calculated according to:

$$U = \left(\frac{s_w}{k_w} \frac{d_{t,out}}{d_{lm}} + \frac{1}{h_s} \frac{d_{t,in}}{d_{t,out}} \right)^{-1}, \quad (2.8)$$

where s_w (m) is the tube wall thickness, $d_{t,out}$ (m) is the outer tube diameter, d_{lm} (m) is the log-mean reactor tube diameter, h_s ($W m^{-2} K^{-1}$) is the combined heat transfer coefficient of the shell side film, and $d_{t,in}$ (m) is the inner tube diameter.

The simulation domain is discretized with a uniform mesh. The adequate cell size for 2D simulation was obtained through a mesh independence study as shown in Figure 2.6. The outlet methanol conversion and CO content in the reformat are chosen as tracked variables. On a $d_{in} = 20$ mm reactor, it was shown that 100 axial and 20 radial cells are in the asymptotic range, which corresponds to the cell axial and radial dimension of 10mm x 0.5mm. This corresponds to 20 and 30 radial cells in reactor tubes with $d_{in} = 20$ mm and $d_{in} = 30$ mm, respectively; and 100 cells in the axial direction in both reactors.

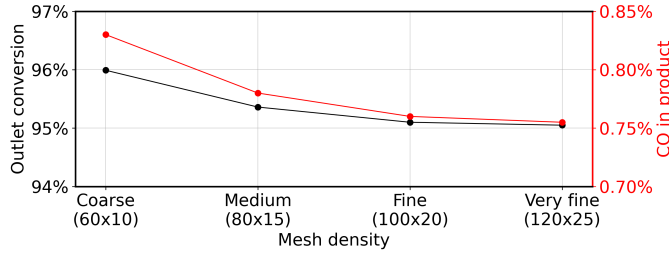


Figure 2.6.: Mesh independence study: effects of refining the mesh in axial and radial direction on the outlet methanol conversion and CO content in the product with the $d_{in} = 20$ mm reactor case.

Used numerical schemes include second order upwind for advection terms, and fourth order central differencing scheme for the radial terms. The convergence criteria for the steady state initialization was achieved by iterating until temperature and concentration residuals dropped below 10^{-8} . For dynamic simulations the time step size was kept constant at $4 \cdot 10^{-4}$ seconds. All cases were run simultaneously on a personal computer with Intel i7 processor. The resulting computational times for 20 minutes simulated time in unsteady cases were ≤ 30 hours with 2D model, and ≤ 14 hours with 1D model.

2.5.2. Model uncertainties

Three identified causes increase the degree of uncertainties in the present dynamic 2D model compared to the traditional steady plug flow approach. First, the dynamic

model uses correlations developed with steady state data. The Langmuir-Hinshelwood reaction rate expressions, such as the one used here, in general do not allow for inclusion of dynamic kinetic behaviour [240]. The reaction dynamics are not included in effectiveness factors either. In present study they are calculated with the Thiele modulus approach [241], which only considers internal diffusion limitations. The factors are evaluated at each timestep using local reaction rates, concentrations, catalyst size, and internal diffusivity. However, they do not include the intra-particle dynamics, which possibly dominate in transient regimes. In steady state, Zhu et al. [242] conclude the highest factor influence in the near-inlet zone, after which they quickly stabilize, as shown in Figure 2.7. The uncertainty at the near inlet region itself is low, due to heat transfer as main limitation for reaction rate. However, uncertainty remains because of error propagation and accumulation along the flow direction.

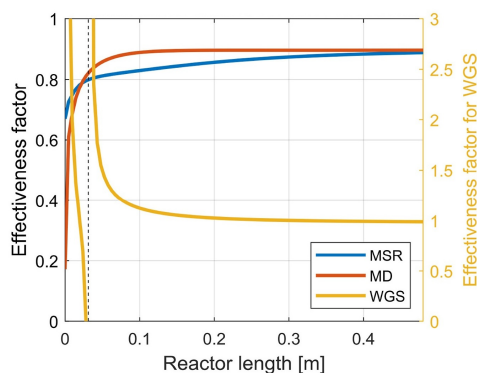


Figure 2.7.: Effectiveness factors for MSR, MD and WGS reactions along the methanol steam reforming reactor length. Reprinted from [242] with permission of Elsevier, Copyright 2022.

Second, at the time of writing the 2D model is only validated in steady state by Zhu et al. [234] as shown in Figure 2.8. In transient state, the accuracy also depends on interactions of process variables and model parameters in time. In other words, dynamic model inaccuracies are possible despite the simple addition of accumulation term to the left hand side of the validated steady state model.

The third component of uncertainty stems from the increased number of model parameters in a 2D model. Arguably the most significant added parameters are the effective dispersion coefficients because they regulate the radial transport. The coefficients are difficult to validate but detrimental to the model, which is why a sensitivity study was conducted. The formulas for mass (D_{er}) and thermal (λ_{er}) dispersion coefficients were modified with factors of 0.5 and 2, effectively halving and doubling them. The effects on CH_3OH conversion and CO content along the reactor length are shown in Figure 2.9. The D_{er} variation had little effect on both tracked parameters. The λ_{er} on the other hand had a slight effect on the conversion, and moderate effect on CO concentration. Since the effects are cumulative, the CO concentration differences were notable by the time products exit the reactor.

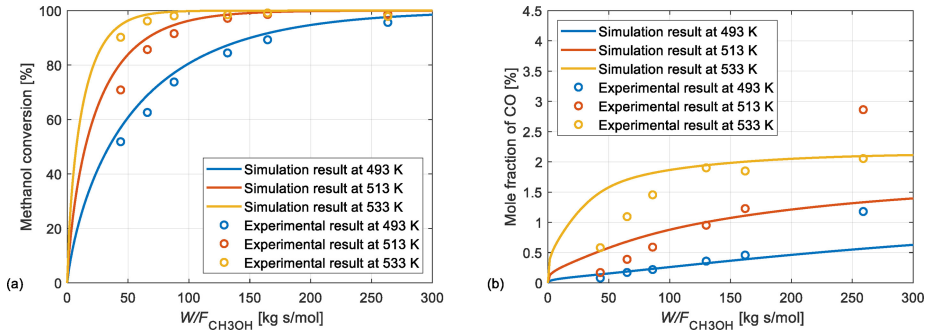


Figure 2.8.: Experimental validation of steady state methanol steam reforming model on a small packed bed experimental reactor (3.6 mL) with outlet methanol conversion and CO mole fraction. Reprinted from [234] with permission of Elsevier, Copyright 2022.

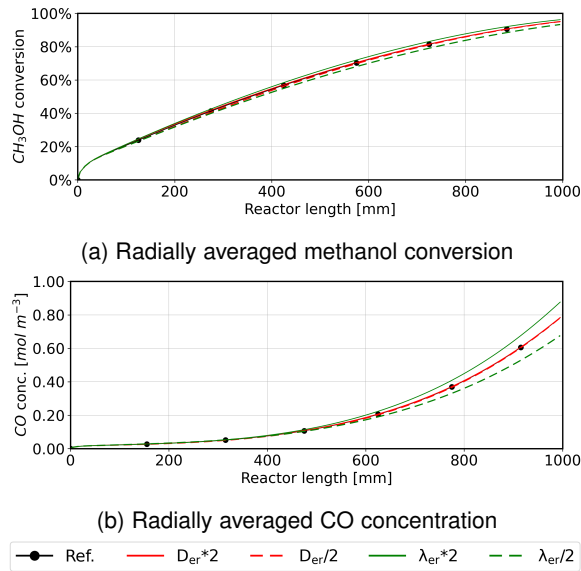


Figure 2.9.: Parameter sensitivity study: effects of doubling and halving the calculated radial mass (D_{er}) and heat (λ_{er}) effective dispersion coefficients on outlet methanol conversion and CO content along the reactor length.

The sensitivity analysis of Zhu shows that the radial reactant mixing is effective, and radial heat is the limiting factor, as expected. The effect of parameter variations on heat transfer limitations is further illustrated in Figure 2.10 which shows internal the temperature fields. In D_{er} variations the contours remain similar, which indicates approximately constant heat consumption due to reaction enthalpy. The λ_{er} variations notably affect the temperature field. The visible changes in relative sizes of hot and

cold spots are responsible for the resulting CO production variation.

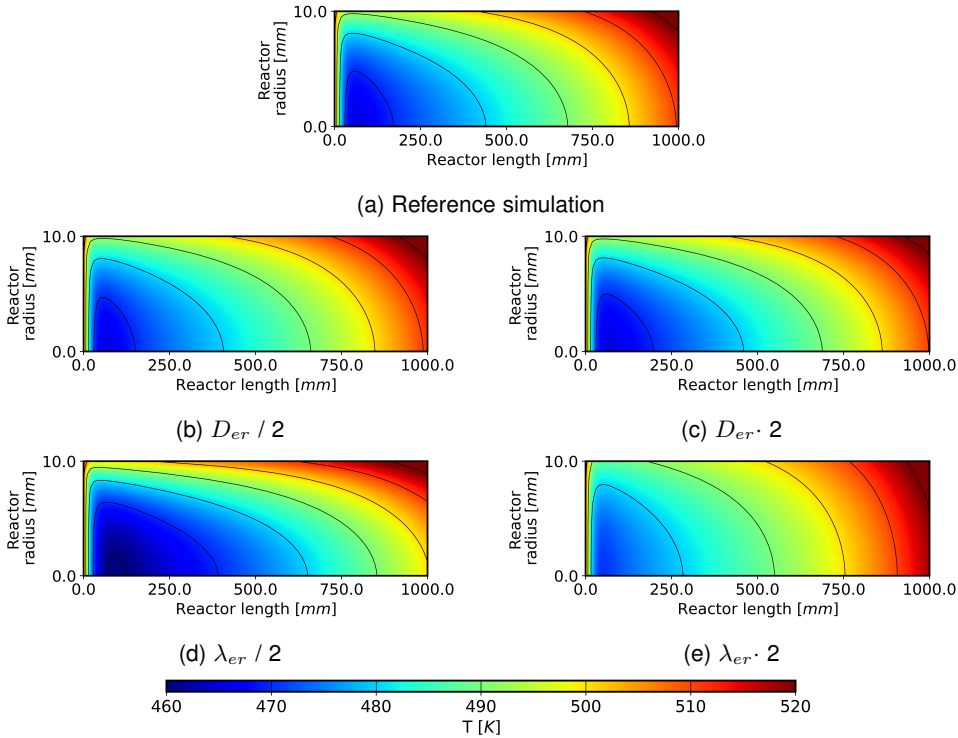


Figure 2.10.: Parameter sensitivity study: effects of doubling and halving the calculated radial mass (D_{er}) and heat (λ_{er}) effective dispersion coefficients on the internal temperature field.

2.5.3. Simulated cases

The case study simulates a small shell-and-tube reactor, in which 5 reactor tubes with catalyst pellets are heated with flue gas on the shell side. The complete list of reactor dimensions and constant process variables is provided in Table 2.4.

Table 2.5 shows the process variables defined for steady states between which simulated transients occurred. In total, 4 steady states are defined for each of the 1D and 2D models. First, the inner tube diameter is varied between $d_{in} = 20$ mm and $d_{in} = 30$ mm. Then, for each diameter specification two different reactant throughput rates $W_{cat.}/F_{CH_3OH}$ are specified. The temperature and mass flow of flue gas are determined by targeting 95% methanol conversion at the reactor outlet. A Conversion value below 100% is chosen for better control over selectivity and outlet composition, since the reverse water-gas shift becomes the dominant reaction after all methanol is converted. However, fixing the conversion produces slightly different predictions of flue

Table 2.4.: Reactor dimensions and input process variables

Reactor	Tube length [m]	1
	No. tubes [-]	5
	Tube wall thickness [m]	0.005
	Shell diameter [m]	0.24
	Tube pitch (triangular) [m]	0.1
	No. of baffle plates [-]	4
Flue gas	Inlet pressure [bar]	1.2
	Inlet temperature [K]	523
Reactant feed	Inlet pressure [bar]	3
	Steam to carbon ratio [-]	1.5

gas flow and inlet/outlet temperatures between 1D and 2D models. The differences are caused by lack of radial heat transfer in 1D model, which is shown in Figure 2.11 with characteristic steady state temperature fields produced by 1D and 2D models. The local differences in temperature fields affect the local reaction rates, and expectedly result in different product compositions at the outlet.

The case study simulates four dynamic events for each reactor diameter. The dynamic events are induced with step changes between boundary conditions for steady states, which are described in Table 2.6. The dynamic events represent extremes in throughput change during normal operation. These events were chosen because the internal reactor dynamics have most influence on the transient state and the product, and are the limiting factor on the duration of transient event. This is in contrast to events such as reactor startup and shut down, where external heat or reactant supply might be used to control the speed of transient event to prevent catalyst overheating.

Table 2.5.: Steady state input process variables resulting in 95% methanol conversion at the outlet for d_{in} 20 and 30 mm tubes, and throughputs of $W_{cat.}/F_{CH_3OH} = 150$ and $300 \text{ kg s mol}^{-1}$ in 1D and 2D simulations

	$W_{cat.}/F_{CH_3OH}$ [kg s mol ⁻¹]	Flue gas inlet T [K]	Flue gas flow [kg s ⁻¹]		Flue gas outlet T [K]	
			1D	2D	1D	2D
d20	300	673	2.62e-3	2.72e-3	564	569
	150	723	5.70e-3	6.10e-3	618	626
d30	300	673	3.85e-3	4.20e-3	509	520
	150	723	7.40e-3	8.40e-3	545	563

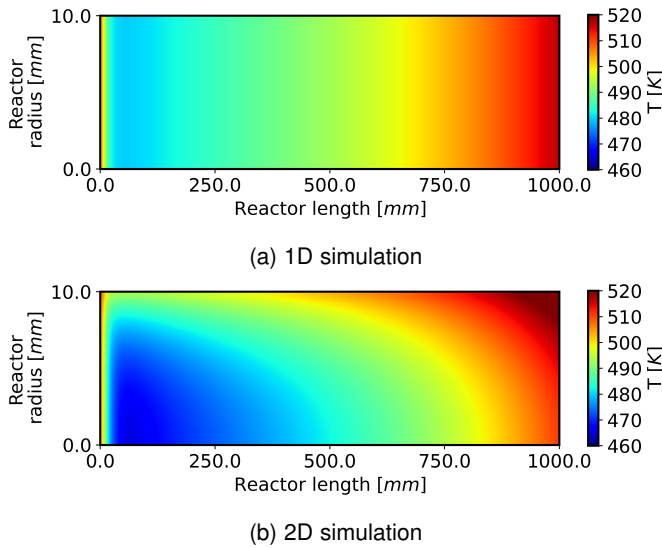


Figure 2.11.: The differences in temperature field plots between 1D and 2D simulations on a reactor with $d_{in} = 20$ mm at steady state with a throughput of $W_{cat}/F_{CH_3OH} = 150$ kg mol s⁻¹

Table 2.6.: Start and end steady states of four simulated unsteady cases

Case	Starting steady state W_{cat}/F_{CH_3OH} [kg s mol ⁻¹]	End steady state W_{cat}/F_{CH_3OH} [kg s mol ⁻¹]
1	300	150
2	150	300
3	Hot standby (no flow, reactor T = 473 K)	300
4	Hot standby (no flow, reactor T = 473 K)	150

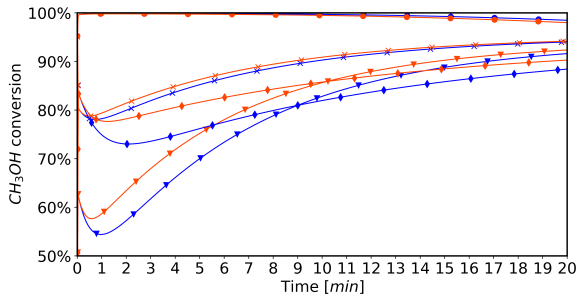
2.5.4. Results

Four unsteady cases were simulated with both models for each tube diameter: feed increase from $W_{cat}/F_{CH_3OH} = 300$ kg s mol⁻¹ to 150 kg s mol⁻¹, feed decrease from $W_{cat}/F_{CH_3OH} = 150$ kg s mol⁻¹ to 300 kg s mol⁻¹, feed increase to $W_{cat}/F_{CH_3OH} = 300$ kg s mol⁻¹ from reactor hot standby in non reactive conditions at 473 K, and feed increase to $W_{cat}/F_{CH_3OH} = 150$ kg s mol⁻¹ from hot standby.

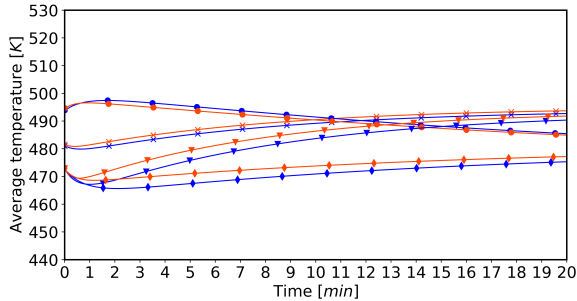
The direct plots of CH₃OH conversion and reactor temperatures for both models and all cases with $d_{in} = 20$ mm are shown in Figure 2.12. The plots for $d_{in} = 30$ cases in Figure 2.13 display the same trends but higher differences between the two models. This part of the results describes mainly $d_{in} = 20$ mm figures, but the claims are also valid for $d_{in} = 30$ mm figures. The difference between 1D and 2D model appears in quantity and temporal offset. The conversion dip visible in Figure 2.12a, most evident in the hot start cases, is caused by the difference in timescales of heat transfer to the reactor and reaction heat consumption. The exclusion of radial heat distribution in the 1D model artificially increases the time and intensity of radial heat penetration in the reactor. The conversion minimum in 1D is therefore higher, and is reached quicker than in 2D model.

The predictions of average reactor temperatures match closely in magnitude and trends between 1D and 2D models, as seen in Figure 2.12b. However, the minimum and maximum reactor temperatures visibly differ in magnitude, as shown in Figures 2.12c and 2.12d. Moreover, the minimum temperature is consistently lower in 2D than 1D, and the maximum temperature is higher in 2D than the 1D for all simulated cases. The minimum reactor temperature is higher by ~ 10 K in 1D model in all cases, while the 2D model predicts a higher maximum temperature between 1 and 10 K depending on the case. The lower difference in maximum temperatures indicate that there is a larger volume of zones close to maximum temperature in the 2D model than in the 1D model, since the average temperatures are balanced between the models.

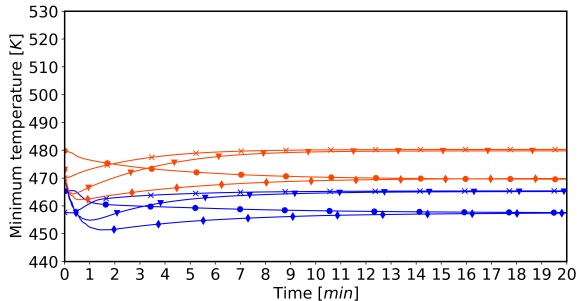
Figure 2.14 shows the relative differences between 1D and The 2D model predictions of methanol conversion and CO content at the outlet. The results show the slower radial heat transfer rate in 2D model. The near wall cells in the 2D model have higher temperature than the average of the entire radial section, which results in a lower temperature gradient between flue gas and reactor, and consequently lower heat transfer rate. During the feed increases, the 2D model therefore predicts lower conversion and CO content despite the higher temperatures and flue gas which were set to keep 95% conversion. During feed decrease case, the catalyst heat capacity provides more heat than necessary for the reaction, so conversion in both models stays around 100%. In this case, the difference is only in CO content. 2D model predicts more CO in the outlet due to hotspots near the reactor tube wall, which enable higher rates of the reverse water gas shift reaction. The largest difference in magnitude between the two models occurs in hot start cases, despite the similarity in average reactor temperature in active steady states and the hot standby condition. The uniform reactor temperature field during hot standby takes more time to develop a steady temperature profile, similar to the ones shown in Figure 2.11, than it takes for the temperature profile to adapt from one steady state to another. Furthermore, reactors with $d_{in} = 30$ mm have increased radial thermal resistance in the 2D model compared to $d_{in} = 20$ mm cases, which causes a larger difference between the two model predictions.



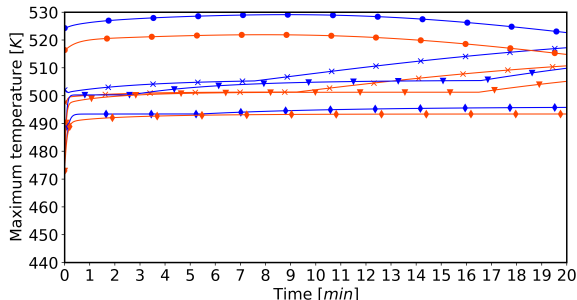
(a) CH₃OH conversion at outlet



(b) Average reactor temperature



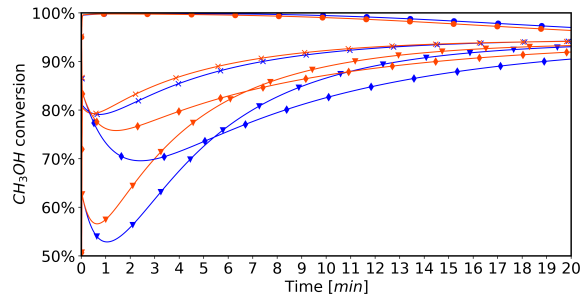
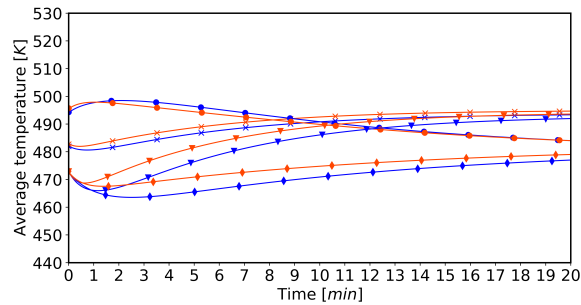
(c) Minimum temperature in the reactor



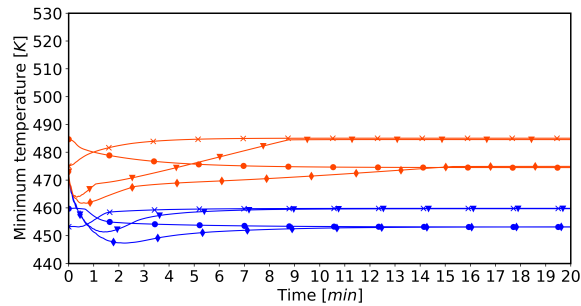
(d) Maximum temperature in the reactor



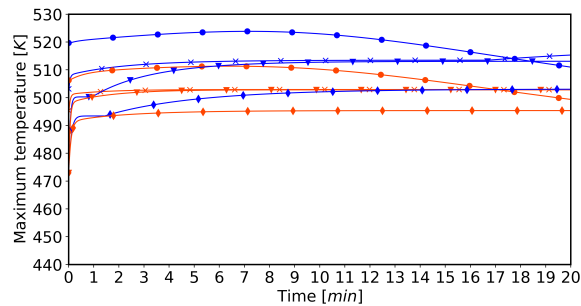
Figure 2.12.: Comparison of output process variables in time for 1D and 2D simulations on $d_{in} = 20\text{mm}$ reactor

(a) CH_3OH conversion at outlet

(b) Average reactor temperature



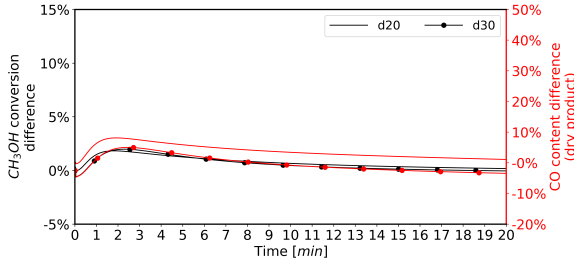
(c) Minimum temperature in the reactor



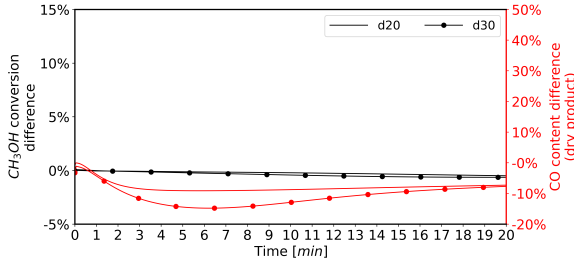
(d) Maximum temperature in the reactor

— 2D sim. — 1D sim. × Increase • Decrease ▼ Hotstart low ◆ Hotstart high

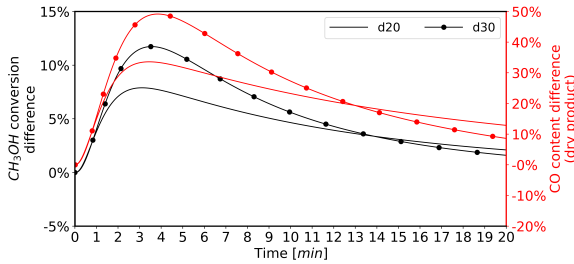
Figure 2.13.: Comparison of output process variables in time for 1D and 2D simulations on $d_{in} = 30\text{mm}$ reactor



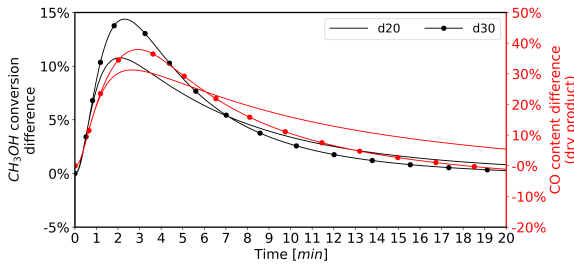
(a) Case 1: instantaneous feed increase from steady state $W_{cat}/F_{CH_3OH}=300$ to steady state $W_{cat}/F_{CH_3OH}=150 \text{ kg mol s}^{-1}$



(b) Case 2: instantaneous feed decrease from steady state $W_{cat}/F_{CH_3OH}=150$ to steady state $W_{cat}/F_{CH_3OH}=300 \text{ kg mol s}^{-1}$



(c) Case 3: instantaneous feed increase from hot standby at reactor temperature $T = 473 \text{ K}$ to steady state $W_{cat}/F_{CH_3OH}=300 \text{ kg mol s}^{-1}$



(d) Case 4: instantaneous feed increase from hot standby at reactor temperature $T = 473 \text{ K}$ to steady state $W_{cat}/F_{CH_3OH}=150 \text{ kg mol s}^{-1}$

Figure 2.14.: Difference plots of 1D model relative to the 2D model in predicting methanol conversion and CO content at the reactor outlet

2.6. Discussion

Dynamic reactor operation requires careful consideration to be addressed systematically across different types of analyses. Even the appropriateness of transient analyses is not clearly defined. The absence of such definitions limits the standardization of design and control approaches for dynamic chemical processing systems.

The common theme across the operation types is that the importance of dynamic analysis is higher when transients are often expected. With process flexibility as motivation, the dynamic analysis should be considered based on the frequency of interruptions to the design conditions. For example, consider an electrified plant that minimizes its environmental impact by increasing production when the renewable energy share is high in the connected grid. This plant potentially operates in dynamic conditions for a considerable amount of time, which reduces the accuracy of overall performance calculated with only steady analysis. In periodic processes, the dynamic analysis is recognized as necessary since these processes are defined with inherently time-dependent characteristics such as frequency and phase of process variables, and the analysis is mostly carried out on the reactor scale. Finally, the on-demand production should always include dynamic analysis on both the reactor and system scale. Combined transient capabilities of all system components determine the response to the expected product demand.

For the aforementioned general dynamic analysis in petrochemical industry, a sufficiency of a single technique is unlikely. Techniques with highest detectable species, such as Raman spectroscopy or TDLAS, tend to be expensive and expectedly less accessible in most laboratories and industrial settings. Instead, multi-technique approaches are more likely, for example an IR technique with a micro GC. The dynamic analyte monitoring can be further supplemented with specific sensors such as TDLAS, thin thermocouples, or fast pressure sensors. The combination may provide a better overview of the overall process in time. Moreover, this results in higher confidence for soft sensor methods, as well as data variety for integration with data-driven approaches.

The reviewed literature highlights the lack of experimental data as an obstacle for low adoption of mid-fidelity models, especially in unsteady modelling. Best data sources for mid-fidelity models are particle resolved CFD simulations, and specific cases where data gathering occurs regardless, such as pilot plant testing. Data driven approaches show high potential, especially in full scale plant for real-time monitoring, diagnostics, and control. However, these solutions remain inaccessible for many plant scale scientific studies due to required time investment, leaving them with 0D/1D models.

2.6.1. Case study

The case study of methanol steam reforming shows a considerable difference in conversion and selectivity during a transient state between 1D and 2D models. The difference between two models is high when ΔT between the outer shell flue gas and reactor is high, and long-lasting in time when the ΔT is low. The differences are

caused by internal process heat transfer limitations which are neglected without the radial model component. Local mispredictions of heat transfer in location and time cause a cumulative downstream error due to the convective heat transfer by the flow. The importance of radial model component is thus proportional to the magnitude of reactor heat transfer limitations.

In steady state, the models exhibit high similarity in outputs but require slightly different input process variables to account for heat transfer differences. There is little benefit in using 2D over 1D for predicting process conditions because the difference is comparatively small. Furthermore, in reality there are additional error sources such as heat transfer losses or measurement accuracy. The main added benefit of 2D in steady state is that this provides insight into internal temperature fields and their local extrema. The case study also shows that average reactor temperature alone, as used by Argyris et al. [192], is a poor metric for model comparison because it is very similar across the models.

The relatively long simulated timescales ran successfully with a 2D model on a personal computer with little code optimization in the present case study, which demonstrates hardware accessibility for the common user. The combined use of a 1D and 2D model is thus recommended for efficiency and accuracy in iterative reactor design tasks, especially for dynamic operation. Another added benefit of using any two models with various fidelity levels is the difference quantification between them. First, the difference is also the minimum possible error between model outputs and reality, which is also a measure of uncertainty in the simulation. The model difference has been shown to vary in time in unsteady cases, potentially hiding riskier operation. Second, the magnitude of model difference also indicates the minimum required accuracy of analytical techniques. If experimental data is available, the measurement uncertainty should be lower than model difference to correctly identify which model has better agreement with the data.

Higher amount of variables in 2D model introduces additional uncertainty in the model. The steady-state sensitivity study shows how effective radial thermal conductivity has a high effect on the process. Selectivity is most notably impacted. In transient state, the effects are likely higher. This part of the study highlights necessary confidence in the 2D model accuracy before it is used for design tasks.

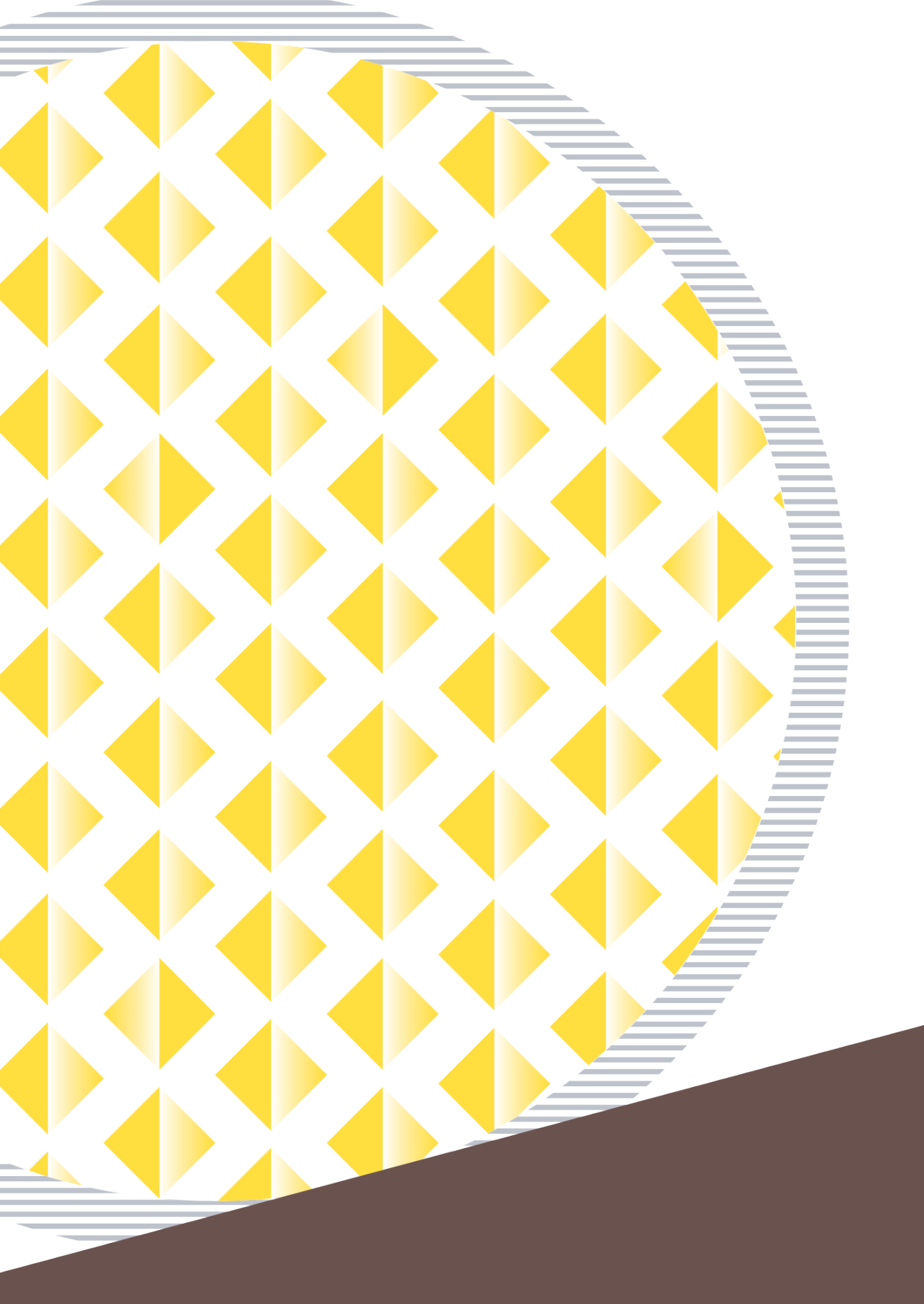
The transient state packed bed reactor analysis requires a metric for comparison across different geometries and operating regimes. The thermal storage application of packed beds relies on variables such as total stored energy and discharge rate [243], which on its own is insufficient under reactive conditions. Packed bed reactor metrics should reflect variation of conversion and product composition in time. Thus one could use known dimensionless numbers such as the Stanton or the Peclet number for comparing heat transfer to or within the reactor, and the Damköhler number for comparing reaction rate timescales. In heterogeneous models, the Biot number could be used to compare catalyst heat conduction resistance. Comprehensive comparisons of dynamic performance across different reactors and operating regimes most likely includes a combination of multiple dimensionless numbers.

2.7. Conclusions

This chapter analyses the unsteady operation of fixed bed reactor in the contexts of: unsteady operation type, applicable numerical modelling tools in the literature, unsteady analysis with instrumental techniques, and a modelling case study of methanol steam reforming. The key findings are:

- the unsteady analysis should be performed if the transient events in normal operation are often expected, and if the transient event causes or intensifies the heat transfer limitations;
- a combination of analytical techniques tailored to the process is most likely required and achieved for unsteady product analysis;
- 0D and 1D models are currently the most used in reactor design and evaluation, in both steady and unsteady cases, despite their known over simplifications, seemingly due to lack of experimental data and transferable empirical correlations for higher fidelity models, and high effort in custom model development;
- reviewed studies advise the use of unsteady models for reactor design tasks, but do not display a clear methodology to do so,
- hierarchical and hybrid modelling have high potential for future comprehensive development of methodologies in dynamic operation design and control,
- the methanol steam reforming case study shows a significant difference in transient selectivity predictions between 1D and 2D model, but negligible difference in steady state operation. Multiple models of various fidelity are best used in combination for unsteady process design;
- comprehensive metrics specifically for the transient regime are required for evaluation and comparison of unsteady fixed bed reactor operations.

The conclusions of this chapter represent key waypoints for achieving effective and systematic design, monitoring, and control in plants with unsteady-operated fixed bed reactors. The findings are especially important and applicable in renewable energy management, in which unsteady energy and reactant supply, or unsteady product demand, force the chemical plant to operate outside of its optimal steady state framework.



3

Internal heat transfer dynamics of a fixed bed reactor

Reactor internal heat and mass transfer limitations during changing hydrogen demand are investigated using the dynamic 2D model. The internal bed dynamics alone lead to relatively short stabilization times, often around 30 seconds and up to about 60 seconds for typical tube diameters. The results suggest that internal heat transfer is probably not the main cause of much slower reformer responses in practice.

Chapter published as: **Grenko, B.**, de Jong, W., van de Ketterij, R. and van Biert, L. *Dynamic modelling of methanol steam reforming to hydrogen in a packed bed reactor for shipboard fuel cells* (2025). *Chemical Engineering Journal*

3.1. Introduction

The dynamic power requirements in transport applications introduce added concerns to the methanol reforming system. Two significant and interconnected added considerations are: response time in forced operation, and reformer lifetime. The reactor transient response time is the period of time after a change in input process variables during which the reformer product composition deviate from the design values. Most apparent reformat composition aspect is the methanol conversion, whose decrease results in unfulfilled product demand and reprocessing of unreacted feedstock.

The dynamic reformer operation is expected to affect the lifetime of system components [245, 246]. The forced reactor operation causes fluctuations in internal temperature field. Local catalyst overheating can lead to permanent catalyst damage through sintering. Furthermore, the fluctuations in produced CO could damage the PEMFC anode catalyst. The manufacturers often specify CO limits at 0.2 ppm according to standard ISO 14687-2 [134, 135, 247], which commercial methanol reformers achieve with Palladium membranes for hydrogen separation [248, 249].

The expected CO levels are used to size the separator membrane, since Pd membranes are also poisoned by CO [250]. The magnitude of CO fluctuations is thus a critical input in dynamic system design. Alternatively, the high predicted CO levels could indicate bad transient performance of the reactor. In this case, the CO fluctuations could also be used as input in reactor sizing.

Evidently the impact of reactor dynamics should be included in the system design. However, unsteady process analyses are mostly left out of most research on methanol reforming, since the field predominantly focuses on novel conceptual systems and integration in steady state operation [251–254]. Stable composition and dynamic operation are conflicting objectives, and add a layer of complexity compared to steady operation. Investigation in reactor transient response is the first component of this addition.

This chapter investigates unsteady operation of tubular packed bed methanol steam reforming reactor by using a 2D model. The aim of this study is to indicate reformer transient time between two steady states through methanol conversion and CO fluctuation in the product. The simulated cases focus on the reformer transient response in the form of internal temperature field and reformat composition. These outcomes define additional operating constraints of methanol steam reformer and contribute to inputs for design of methanol reforming based maritime power system.

A 2D physics based model using finite difference approach was used to conduct simulation cases of four transient events on four reactor geometries. The effects of differences in forced operation inputs and reactor dimensions are shown, and analysed for their impact on transient time and produced CO fluctuations. Finally, the simulated reactor behaviour is contextualized against model simplifications, reformer integration with PEMFC, specific reactor heating methods.

3.2. Scope and assumptions

The transient time of methanol reformer, which is the time required for change between two steady operational states, is a significant characteristic since it propagates through the entire power production system. Transients dictate the size, weight, and overall necessity for hydrogen buffer tanks and/or batteries required for peak shaving. The PEM fuel cell has a transient response within seconds [136, 137, 255]. On the other hand, transient times in reforming systems are unknown, and commercial systems manufacturers only indicate startup from hot standby duration within the range of 5-45 minutes [62, 173, 256], depending on the unit size and requested H₂ flow rate. Reformer transient time could likely be a transient characteristic of the entire power system.

In the maritime sector, dynamic loads are specific to every ship so the transient requirements of a methanol reformer vary as well. Generally, the reformer does not necessarily need to be as fast as PEMFC in load changes, as long as the ship operation is not limited. A reference point for required transient capabilities is found in comparisons with marine internal combustion engines (ICE). Specifications of ICE manufacturers indicate 1-6 minutes for 100% load ramp up, mainly dependant on the engine temperature [257, 258]. If the reformer transient times are comparable to those of ICEs, similarity can also be expected in the total size and weight of peak shaving components.

This chapter aims to provide an indication of the characteristic transient time of a methanol steam reformer through numerical modelling. The influence of reactor size and input process variables is encompassed by the study. The scope is limited to the internal reformer transients, meaning that only the heat and mass transfer within the packed bed are observed. Heat transfer to the reactor is disregarded, and reactor wall temperature is directly controlled. This approach is intended to mimic the ideal reactor heating and show the transient limitations caused only by the packed bed. Consequently, simulations conclude a theoretical minimum of a reformer transient time. Finally, the chapter also demonstrates a new modelling framework for predicting forced operation of a methanol steam reformer.

Reactor model fidelity

Simulations are conducted on a single packed bed tube within a fixed multitube reactor. The focus of the present work is on the changing internal process variable fields, such as heat transfer and reaction rates, as well as the effects of unsteady developing interactions within the flow field. The differences between individual tubes are disregarded, assuming that provided heating is equal across the whole reactor.

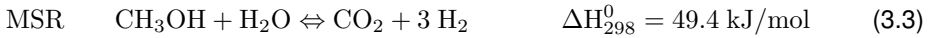
The reference model for present work is the 2D steady state model of Zhu et al. [234, 259], experimentally validated in a lab scale packed bed reactor filled with cylindrical catalyst particles, using gas analysers on the reformer outlet stream. This model is fitting for present investigations due to its fidelity level and low computational cost. The model is able to capture radial heat transfer and its interaction with internal 2D reformer fields. Simultaneously, the computational effort is not wasted on high fidelity level, as the simulations can run effectively on local machines. The alternative of fully comprehensive CFD models result in a highly detailed flow fields, but make

parametric studies impractical due to the necessity for high performance computing [260, 261]. The steady state model equations of Zhu et al. are:

$$u_s \frac{\partial C_i}{\partial z} = D_{er} \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r} \frac{\partial C_i}{\partial r} \right) + \eta_i \rho_c r_i, \quad (3.1)$$

$$u_s \rho_f c_{p,f} \frac{\partial T}{\partial z} = \lambda_{er} \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) + \sum \eta_j \rho_c (-\Delta H_j) r_j S_c, \quad (3.2)$$

where ε is the porosity, C_i (mol m⁻³) are the specie concentrations, u_s (m s⁻¹) is the flow superficial velocity, D_{er} (m² s⁻¹) is the effective radial dispersion coefficient, ρ_c is the catalyst bulk density, r_i is the production rate of component i , T (K) is the temperature, λ_{er} (W m⁻¹ K⁻¹) is the effective radial thermal conductivity, ΔH (J mol⁻¹) is the reaction heat, r_j is the reaction rate of reaction j , S_c (m² kg⁻¹) is the catalyst surface area, and η are the effectiveness factors. Additionally, the Ergun equation [238] is used to calculate pressure field in the bed. The kinetics model for CuO/ZnO/Al₂O₃ of Peppley et al. [237] is used, which is based on a Langmuir-Hinshelwood mechanism for surface reactions. This kinetic model includes all three reversible dominant reactions (eq.3.3-3.5). Detailed model description and formulae of all terms can be found in the comprehensive work of Zhu et al. [234, 259, 262].



Geometric parameter influence

Reactor tube dimensions influence the internal heat transfer, which affects reaction rates and consequently the composition of fuel cell feed. Heat transfer is identified as the dominant limiting mechanism of methanol steam reforming by Yoon et al. [263] in their experimental study. The two presently relevant ways of influencing the heat transfer are varying (i) the reactor tube diameter, and (ii) flow velocity. Reducing the internal diameter d_i decreases maximum radial heat penetration depth, and the increases ratio of heated area to internal volume.

The flow velocity affects heat transfer indirectly via radial mass transport. The internal radial mixing has a positive correlation with the superficial velocity u_s , which is reflected through the effective radial diffusion coefficient D_{er} and the effective radial thermal conductivity λ_{er} in model equations 3.1 - 3.2. Lengthening a reactor while keeping diameter d_i and residence time t_{res} constant therefore improves the internal heat transfer. Reactor diameter and length are therefore varied for capturing heat transfer differences in steady and dynamic operation.

Simulated reactor heating

A uniform axial wall temperature profile is used for all simulated cases in present work. In reality, the axial heat profile is specific to a heating method, which is defined during reactor design through parameters such as energy efficiency, complexity, control, reactor size, and other system objectives. Analysis of heating methods extends the study towards system differences, while the objective of current work is internal reactor dynamics. A theoretical uniform wall temperature profile is used to minimize differences in boundary conditions, and emphasize internal heat transfer effects.

Reactor wall temperature in dynamic simulations changes according to step functions. Despite not being realistic, a step function represents the most drastic change in wall temperature, and highlights reactor natural response. The realistic gradual changes impose their own transient time, obscuring the natural response of the reactor caused by its catalyst thermal capacity. Furthermore, a realistic wall heating transient time is caused by circumstances such as heating method and control strategy. A step function in this context is straightforward and the most meaningful comparison of different reformer tube geometries.

3.3. Methods

3.3.1. Dynamic model description

The used dynamic model is an extension of original Zhu's model with the temporal term and heat capacities. The new equations of mass and energy balances are:

$$\varepsilon \frac{\partial C_i}{\partial t} = -u_s \frac{\partial C_i}{\partial z} + D_{er} \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r} \frac{\partial C_i}{\partial r} \right) + \eta_i \rho_c r_i, \quad (3.6)$$

$$\begin{aligned} & (\varepsilon \rho_f c_{p,f} + (1 + \varepsilon) \rho_s c_{p,s}) \frac{\partial T}{\partial t} = \\ & -u_s \rho_f c_{p,f} \frac{\partial T}{\partial z} + \lambda_{er} \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) + \sum \eta_j \rho_c (-\Delta H_j) r_j S_c. \end{aligned} \quad (3.7)$$

The used in-house solver [264] is implemented in Python®. All unsteady cases are simulated on a local machine with Intel i7 processor within 30 minutes computation time. A finite difference approach is used on a uniform mesh with element size of 5e-3 m. The axial derivatives of species concentrations C_i and temperature T are evaluated with a 2nd order upwind scheme, while the radial derivatives are evaluated with a 4th order central difference scheme. Time is discretized with 4th order Runge-Kutta scheme, with time step size of 1e-4 s. The fitting time step and grid size is determined with sensitivity analyses to ensure that fast reaction rates are properly captured, which simultaneously resulted in a Courant number below 8.5e-3. The simulation boundary conditions are given in Table 3.1, and a graphical representation of the computational domain is shown in figure 3.1.

Table 3.1.: Simulation boundary conditions

	Coordinates	Boundary condition
Inlet	$z = 0$	$C_i = C_{in}$
	$0 \leq r \leq r_{max}$	$T = T_{in}$
Outlet	$z = z_{max}$	$\frac{\partial C_i}{\partial z} = 0$
	$0 \leq r \leq r_{max}$	$\frac{\partial T}{\partial z} = 0$
Wall	$0 \leq z \leq z_{max}$	$\frac{\partial C_i}{\partial r} = 0$
	$r = r_{max}$	$\frac{\partial T}{\partial r} = -\frac{h_t}{\lambda_{er}}(T_{wall} - T)$
Symmetry axis	$0 \leq z \leq z_{max}$	$\frac{\partial C_i}{\partial r} = 0$
	$r = 0$	$\frac{\partial T}{\partial r} = 0$

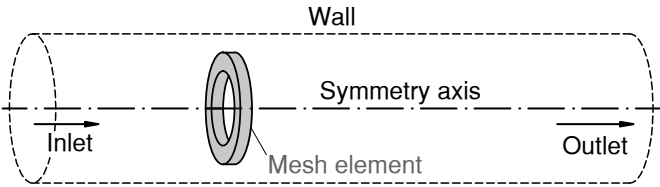


Figure 3.1.: Computational domain in a single reactor tube.

3.3.2. Simulation cases

Table 3.2.: Dimensions of four simulated reactor geometries

Reactor label	Internal diameter d_i [mm]	Reactor length l [mm]	Aspect ratio AR (l/d_i) [-]
d20 AR25	20	500	25
d20 AR100	20	2000	100
d30 AR25	30	750	25
d30 AR100	30	3000	100

Simulations are performed on four reactor geometries, whose dimensions are presented in Table 3.2. The tube diameters are chosen in accordance with experimental

Table 3.3.: Process variables of simulated steady states

Steady state	W_{cat}/F_{CH_3OH} [$kg\ s\ mol^{-1}$]	T_{wall} [K]	Feed increase in ref. to state 1
1	200	501	0%
2	150	508	50%
3	100	519	100%

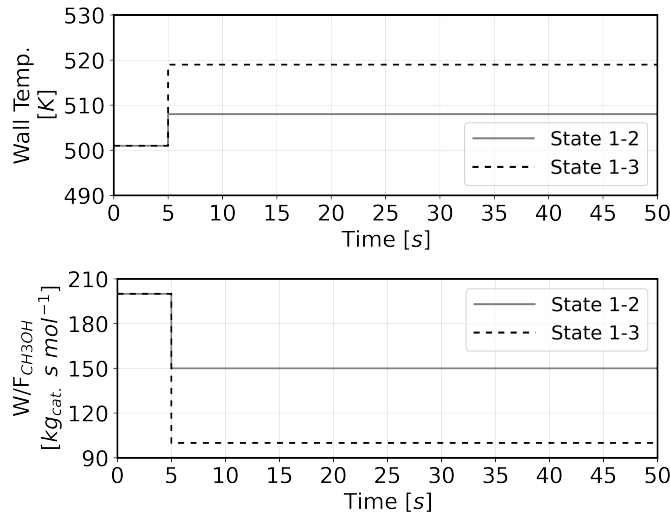


Figure 3.2.: Dynamic boundary conditions of T_{wall} (top) and W_{cat}/F_{CH_3OH} (bottom) for increasing H_2 production according to states presented in Table 3.3

work in the literature [263, 265–267], where 20 and 30 mm diameters are common for a MSR reactor. Diameters in this range are shown to effectively transfer heat radially in steady state, so their analysis during unsteady operation naturally follows. Reactor lengths in present study are defined through aspect ratios (AR), or length-to-width ratios. The superficial velocity, and effective radial mixing remain comparable across diameter changes. In experimental studies [263, 265–267] the reactors are often relatively small, with aspect ratios ranging between 20 and 50. On industrial scale, comparable reactors are found in methane steam reforming where aspect ratios range between 60 and 130 [268]. In present work, aspect ratios of 25 and 100 are chosen as representations of experimental and industrial reactor lengths. All simulations are performed assuming a commercial MSR catalyst with mass composition 40% CuO, 40% ZnO, and Al₂O₃ to balance. Catalyst pellets are spherical in shape with a diameter of 1.5 mm.

The transient reactor behaviour is observed by showcasing step changes between pre-defined steady states. The process variables of these steady states are chosen by

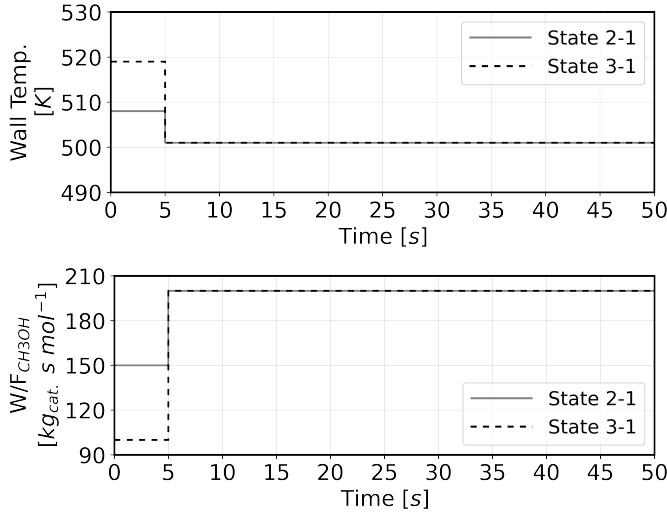


Figure 3.3.: Dynamic boundary conditions of T_{wall} (top) and W_{cat}/F_{CH_3OH} (bottom) for decreasing H_2 production according to states presented in Table 3.3

first picking the representative values of methanol feed, W_{cat}/F_{CH_3OH} ($kg s mol^{-1}$), with respect to literature [262, 263, 265–267]. The methanol feed is defined with respect to catalyst mass to make the performance comparisons valid across different scales. The wall temperature, T_{wall} , is then calculated with a simple 1D isothermal model. The calculations targeted a methanol conversion of $X_{CH_3OH} = 95\%$ at the reformer outlet, under 3 bar pressure and inlet feed temperature of 523 K. Conversion below 100% is intentionally targeted in the simulation steady states so that conversion increases in transient events may also be captured. The resulting feed and reactor wall temperatures of three steady states, named 1-3, correspond to the three reactor throughputs, and are given in Table 3.3.

Four dynamic events are simulated for each of the reactor geometries. Boundary condition step functions of T_{wall} and W_{cat}/F_{CH_3OH} are shown in Figures 3.2 and 3.3. The four events represent step changes between three steady states described in Table 3.3: small throughput increase (state 1-2), large throughput increase (state 1-3), small throughput decrease (state 2-1), and large throughput decrease (state 3-1). State 1 is the reference steady state in all simulations, where states 2 and 3 represent throughput changes by 50% and 100%, respectively. Step functions for input process variables are used to emphasize changes in reactor internal flow field variables, and to ensure the results are not influenced by realistic supporting equipment such as feed pump or reactor heating system.

3.4. Results

3.4.1. Steady state results and dimension effects

Conversion in 2D simulations is expected to deviate from the targeted 95%, due to different radial mixing and heat transfer rates specific for each geometry. These effects can be seen in Figure 3.4, which shows internal temperature field plots of all four geometries at steady state 1. The difference between all simulated geometries and steady states are shown in the appendix A.1 in Figures A.1-A.3. All cases display a cold spot near the inlet caused as the highest methanol concentration within the reactor, which is likely unavoidable. The relative size of the inlet cold spot grows with higher diameter and lower aspect ratio. These differences in the internal temperature distribution affect the conversion and product composition in both steady and transient operation, as shown in the next subsection.

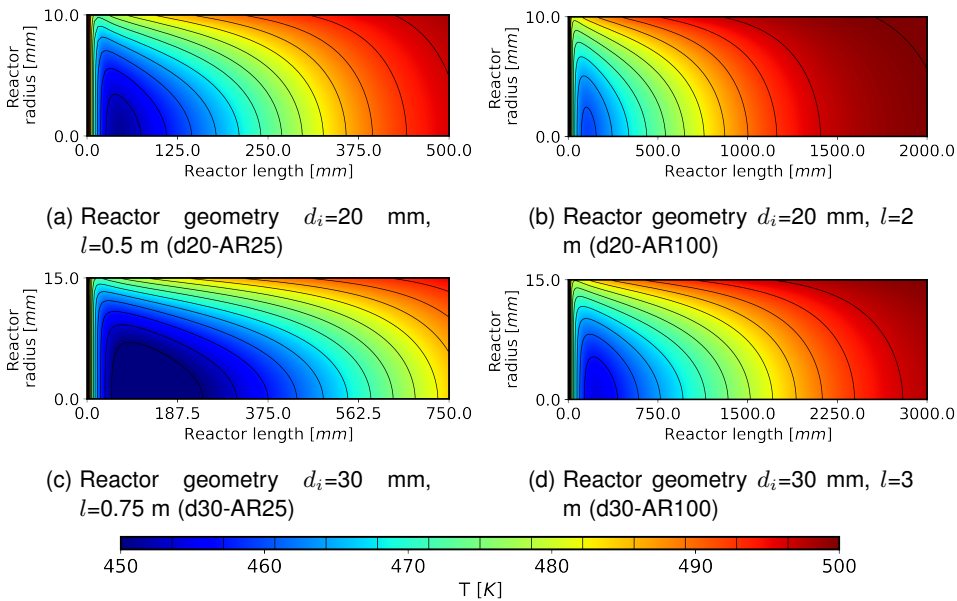


Figure 3.4.: Internal temperature fields of four reactor geometries with $W_{cat}F_{CH_3OH} = 200$, and $T_{wall}=501$ (steady state 1).

3.4.2. Dynamic simulation results

The results in this section predominantly show the reactor responses to large step function inputs, which shift between steady state 1-3, and state 3-1. The results presented in main text most clearly illustrate the performance trends, while full results are provided in the appendix A.2 in Figures A.4-A.7.

The results are shown with three plots: CH_3OH conversion, CO content in dry product gas, and relative H_2 rate. The CH_3OH conversion most evidently shows

the reactor transient time. It corresponds to stabilization of the disturbed internal temperature field. Tracking CO content in the dry product gas is directly linked to H_2 selectivity, due to the WGS reaction changing its direction after all methanol in the reactor has been consumed. Furthermore, this plot shows the amount of CO, and magnitude of its fluctuations in transients, indicating the varying amount of CO that must be separated before reaching the PEMFC. Finally, relative hydrogen production in time is shown. The H_2 rate at the outlet is shown relative to ideal steady state conversion of the reactant feed, previously defined as 95% conversion. This plot highlights the delay and deviation between required and produced H_2 rate. All plots are shown on a 50 second timeline. In this time, the plotted variables reach 97% of the values for new steady states, with the exception of d20-AR25 reactor whose variables react slowly and approach around 90% of the new steady state.

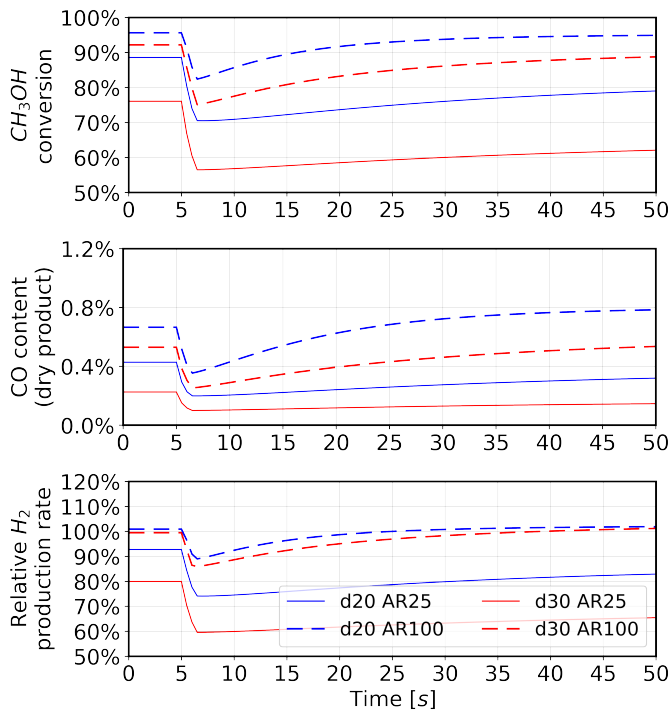


Figure 3.5.: Transient response of reactor outlet variables in four simulated reactor geometries to step H_2 production increase by 100% from steady state 1 to 3.

The CH_3OH conversion displays two distinct trends for ramp up, and ramp down events. In ramp up, as shown in Figure 3.5, the conversion in all cases drops for approximately two seconds before reaching the local minimum, indicating how the reaction draws heat from the catalyst. The time for conversion to increase again varies among reactors and depends on geometric factors since the added heat penetrates

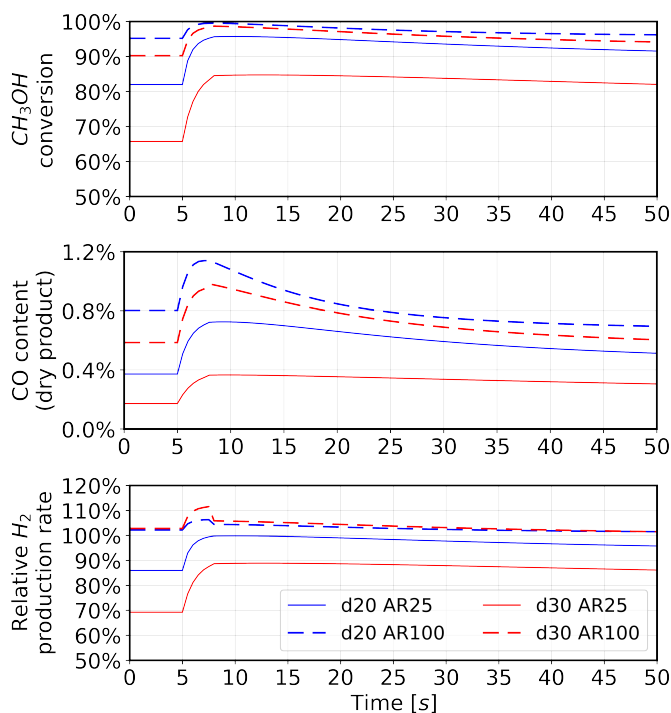


Figure 3.6.: Transient response of reactor outlet variables in four simulated reactor geometries to step H_2 production decrease by 50% from steady state 3 to 1.

the reactor radially, while the methanol feed $W_{cat}F_{CH_3OH}$ is in immediate flow contact with the entire catalyst mass. Larger diameters hence take longer to entirely heat up to new steady state. Longer reactors however have a quicker response, since the constant residence time causes higher velocity which promotes internal mixing and radial heat transfer. The positive geometric influences are seen on the AR100 reactors which reach new steady state the fastest, with the d20-AR100 showing the lowest relative drop in conversion. The opposite is seen on d30-AR25, which does not reach equilibrium within 50 seconds.

In the ramp down events, which are shown in Figure 3.6, the conversion temporarily spikes up, caused by thermal heat storage capacity of the catalyst, since it holds excessive heat for the new steady state. However, the magnitude of conversion disturbance is lower than in the ramp up event. The heat consumption by the reactants works in favour of achieving the equilibrium with lower average internal temperature, and the geometry has a lesser impact than in ramp ups. This is further supported by Figure 3.7, which shows CH_3OH conversion for all dynamic events on one reactor. Overall, the ramp down events show highly similar and uniform conversion trends, with low influence from the geometry.

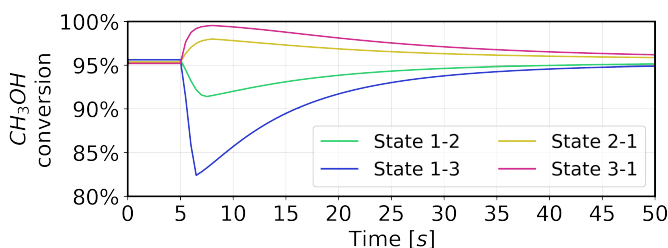


Figure 3.7.: Comparisons of CH_3OH conversions during step H_2 production increases by 50% and 100% (changing between states 1-2 and 1-3 respectively), and step returns to the original steady state 1 on reactor geometry $d_i=20$ mm and $l/d_i=100$ (d20-AR100).

The CO drop during ramp ups can be linked to the drop in conversion and overall lower reaction rates due to internal temperature decrease. In ramp downs, the spike up is caused by the reverse water gas shift reaction, which continues to produce CO at maximum conversions due to the thermal energy contained in the catalyst. The CO oscillation magnitude in simulated cases is linked to reactor volume and the amount of catalyst. The oscillation magnitude can be decreased with gradual temperature changes, allowing the catalyst temperature to progressively adapt. This signifies an additional check for reactors in transient operation, especially in large scale reactors operating at conversions close to 100%.

Finally, the achieved H_2 production rate plots show high correlation to CH_3OH conversion plots. The longer reactors show more pronounced production dips and spikes, but also stabilize quicker afterwards. Most notably, the d30-AR100 reactor produces similar relative H_2 rates as d20-AR100 despite having lower conversion, indicating higher selectivity towards hydrogen. Since these reactors have same AR, the selectivity increase is possibly caused by better radial mixing due to higher velocity. This is supported by temperature field plot in Fig. 3.4 which shows lower average temperature in d30-AR100, causing lower rate of reverse WGS reaction and better H_2 selectivity.

The influence of reactor geometry is quantified in Table 3.4 for H_2 ramp up from steady state 1 to state 3, and subsequent ramp down back to state 1. Comparisons in ramp ups are evaluated with time needed for the reactor to reach 95% conversion value of the new steady state, since this metric indicates the time spent in inefficient operation due to low internal reactor temperature. In both AR25 and AR100 cases, the diameter increase from 20 mm to 30 mm caused approximately 50% increase in conversion response. For AR increase to four times on a constant diameter, the results show a decrease of 36% and 41% increase in response time for d20 and d30 reactors respectively. The reactor diameter evidently had more influence in ramp up operation. In ramp downs, the reactors are compared with maximum increase of CO in the dry product, which is a consequence of temporary too high reactor temperature, and indicates a fluctuation of CO content that must be handled by the H_2 separation system. This comparison shows that diameter increase caused a relative maximum

Table 3.4.: Comparison of reactor geometry influence on performance characteristics during H₂ production 100% ramp up (state 1-3), and ramp down to the original state (state 3-1).

Reactor	Time for CH ₃ OH conv. to reach within 5% of new value during ramp up [s]	Max. increase of CO in dry product during ramp down
d20-AR25	30	95%
d30-AR25	57*	112%
d20-AR100	11	42%
d30-AR100	23	68%

*Outside of plotted range in Fig. 3.6

3

increase by 17% and 26% for AR25 and AR100 cases respectively. The reactor AR increase had a positive influence, since this metric decreased by 53% and 44% for d20 and d30 respectively. This comparison of geometric parameters on operation concludes different dominant influences for ramp up and ramp down procedures. Ultimately, the best performance is obtained by combining reactor length and small diameter, since the d20-AR100 reactor has the best performance by all metrics.

3.4.3. Discussion

The plotted performance metrics reveal a significant difference between increasing and decreasing the H₂ production. In ramp ups, the larger geometry and magnitude of H₂ demand change are correlated to disturbance size and transient time. Ramp up transients are sufficiently represented by the conversion plot. On the other hand, effects of ramp down events most negatively affect the CO production. Design of reactor and its inputs for forced operations should hence separately analyse production increasing and decreasing events for conversion drop and CO content increase respectively.

Maintaining CO levels of 0.2 ppm for low temperature PEMFC systems can be achieved in multiple ways. First, lower process temperature and pressure decrease CO selectivity. Second, the CO spike magnitude is proportional to throughput decrease. Decreasing the ramping rate reduces spikes in CO production. Third, the H₂ separation step can be designed for higher CO rates without drops in throughput and effectiveness [269, 270]. For high temperature PEMFC, same strategies apply, except the CO tolerance is around 3-5%, so the separator step can often be omitted [271, 272]. The chosen combination of strategies may depend on the sought system design characteristics.

All simulated hydrogen production rates asymptotically approach the new value within one minute. This is comparable to the transient time of marine internal combustion engines [257, 258], meaning catalyst thermal lag itself is not overly limiting. However, slower transients could be caused by the heat supply system. The

reactor heating method, its control, and characteristic heat transfer resistance are thus highly influential to overall power system transient time. The system designer therefore must consider response time of heating system itself and decide on the best situation specific solution.

In commercial methanol reforming units, the stated hot stand by start up times in 5-45 minutes range [62, 173, 256] are presumably caused by the heating system transient time. Present off-the-shelf units heat the reactor by combustion of unpermeated gas from the membrane separation of H_2 [173, 256], creating a complex system where the heating is dependant on reactor throughput and membrane permeation rate. This solutions prioritizes high autonomy and simple on-site installation, and thus opts for self-sustenance. If the heat is readily available from other sources, the reformer response could be improved most notably in start up operations.

Geometry and process variable limitations

Diameter choice influences the ratio between heated reactor wall area and internal catalyst volume. The ratio depends on the diameter according to:

$$\frac{A_{tube}}{V_{tube}} = \frac{C_{CS} l_{tube}}{A_{CS} l_{tube}} = \frac{\pi d_{tube}}{\pi (d_{tube}/2)^2} = \frac{4}{d_{tube}}, \quad (3.8)$$

where A_{tube} is the reactor tube area, V_{tube} is its volume, C_{CS} is the circumference of the tube cross section, A_{CS} is the area of the reactor tube cross section, l_{tube} is the reactor tube length, and d_{tube} is the reactor tube internal diameter. Increasing the diameter reduces available heating surface for the same volume of catalyst. The cases with d30 have generally lower conversion than d20, since using the same wall temperature across all cases means that d30 reactors received less heat per unit volume.

Equating the heat transfer rate in reactors with higher diameters could be realized by adjusting the wall temperature. However, different local maximum temperatures then influence process selectivity. Moreover, a higher wall temperature increases the cross section temperature gradient, causing differences in internal heat transfer rate. Every change in reactor geometry apparently influences process variables, so parametric studies of reactor dimensions are inherently not completely objective.

The uniform wall temperature simplification disregards the reactor tube heat capacity, and heat transfer from reactor filling to the tube. In reality, the tube also needs time to heat up, slowing down the ramp up operations. In ramp downs, the residual heat in the tube could potentially cause higher or longer CO spikes since it keeps heating the reactor for longer. However, in reality the tube heat can also be transferred back to the heating fluid so the extent of this issue in ramp down is hard to assume. This problem requires more detailed modelling with defined and simulated heating method.

The simulations show that flow velocity affects the radial heat distribution, but it is not the most determining factor. Higher superficial fluid velocities are observed in d30 reactors than the d20 counterparts, summarized in Table 3.5, but the heat distribution is worse according to the steady state temperature plots. A larger reactor diameter counteracts the benefits from higher fluid velocity for multiple reasons. First, the heat has to penetrate deeper into the reactor. Second, there is less heating area at larger

Table 3.5.: Superficial fluid velocity and volumetric flow of reactants at the reactor inlet at steady state 1.

	d20 AR25	d20 AR100	d30 AR25	d30 AR100
$u_s [m s^{-1}]$	7.08e-2	28.35e-2	10.71e-2	42.84e-2
$Q [m^3 s^{-1}]$	2.22e-5	8.9e-5	7.57e-5	30.28e-5

diameters, as discussed previously. Similarly, larger diameters have higher volumetric flow Q , as seen in Table 3.5, further implying a larger heating requirement. Overall the results indicate that increased reactor diameters require higher flow velocities and aspect ratios to maintain selectivity and transient response time.

3.5. Conclusions

This chapter offers insight into transient states of methanol steam reformers caused by the catalytic packing. Effects on internal flow fields, heat transfer, and overall performance during H_2 demand changes are shown. The influences of reactor tube geometry and process variables in unsteady state are assessed with numerical modelling. Key points for methanol steam reformers in the analysed range of dimensions from the current study are:

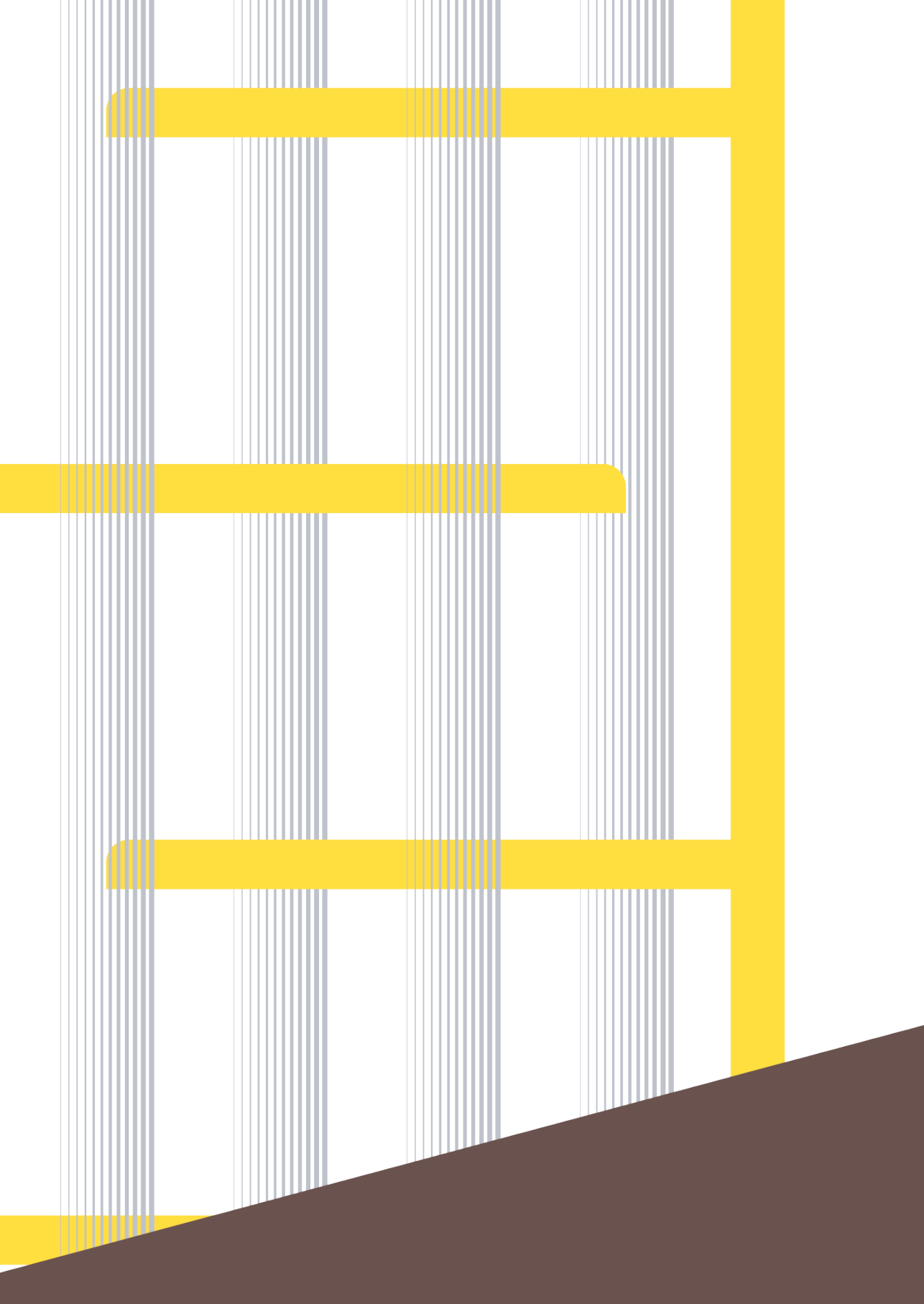
1. The shortest transient time for H_2 production stabilization is around 30 seconds in most cases,
2. Good selectivity and temperature distribution from small diameters and high aspect ratios also provide faster response and lower conversion drop in transients,
3. Transient time in ramp ups is influenced by reactor geometry and change magnitude much more than in ramp downs,
4. CH_3OH conversion is the most limiting performance metric in ramp up operations, while CO content in the product is the most limiting in ramp downs,
5. Aspect ratio is a more objective metric than length, but not completely independent from diameter,
6. Duration of transients in practice is likely dependant on reactor heat supply.

Following the present work, experimental validation of the dynamic part of the model is required. In addition, further dynamic simulations including specific heating method effects are required. The present study is limited with uniform wall temperature assumption, so inclusion of realistic heating systems is required for capturing their effects on the internal heat transfer and reaction rates, which are difficult to study experimentally. Simulations with broader geometry and process variable parameter space are also recommended for better generalization of the results. Furthermore, the

choice of a heating method is a closely related subject of interest. The choice may be influenced by performances of each method, but also depends on the technical and economical constraints of the heating system in an environment such as maritime. The heating system might also have to integrate with other on board systems and processes, steering the analysis towards an entire system design.

The study is performed in the interest of better understanding of reformer operation, which leads to better integration of methanol steam reformers into maritime setting. At present, the only option for on-board H_2 production from methanol is via autonomous commercial reforming systems. Despite their convenience, integrating the reformer with other on-board waste heat systems could increase efficiency, compactness, and affect transient response time. Furthermore, potential carbon capturing is also possible and integrating it directly into the methanol conversion process allows capturing a relatively pure stream of CO_2 .

This study suggests that dynamic operation of methanol reformers, as well as the entire methanol based fuel cell system, is not highly dependant on stabilization of reformer H_2 production, but rather mostly depends on heat integration and control strategy of the system. If slower unsteady operation is compulsory due to the heating system, quickly filling the H_2 demand becomes a larger issue than spikes in CO production. Transient modelling studies for system design should hence be addressed by including the reactor heating and its transient limitations.



4

Model validation and external heat transfer dynamics of a fixed bed reactor

The dynamic 2D model is experimentally validated against temperature and CO concentration data, demonstrating its suitability for capturing transient reactor behaviour in the design of dynamically operated fixed bed reactors. External heat-transfer effects, sensor interference, heat losses, and reactor heat capacity are shown to strongly influence measured and simulated performance.

Chapter published as: **Grenko, B.**, van Biert, L., van de Ketterij, R. and de Jong, W. *Experimental validation of a dynamic 2D model for catalytic methanol steam reforming in a fixed bed reactor* (2026). *Chemical Engineering Journal*

4.1. Introduction

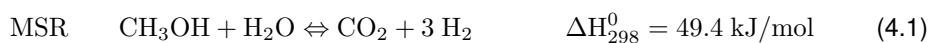
The variable power demand in particularly maritime transport requires design of components for the unsteady regime. The common 1D models used for steady state design generate conversion and selectivity errors in transient regimes, as already concluded by a previous analysis [138]. The analysis shows that the traditional design approach for a transport setting consequently mispredicts system performance characteristics during each power demand adjustment. Moreover, the selectivity misprediction in transients could significantly affect the lifetime of processing components in PEMFC-based systems, which have strict requirements of H₂ purity and allowed CO content. The analysis also concludes an expectedly increased necessity for dynamic models and procedures.

The 3D fixed bed reactor models are also unfit for design for the unsteady regime, due to the required computational effort [274–276]. Such 3D models tend to prioritize accuracy and resolve many of the flow characteristics. Overly high fidelity is limiting to the reactor design tasks due to the iterative nature, which is especially problematic in dynamic simulations. Designing a reactor for dynamic operation requires a model balanced for accuracy and computation time, which is a relatively new objective in the chemical process engineering literature.

This chapter validates a dynamic 2D pseudo-homogeneous model for methanol reforming in a fixed bed reactor. The presented mid-fidelity model is proposed as a balance in computational effort and accuracy with characteristics in between a 1D and a 3D model. A newly designed experimental setup is used to produce reference validation data. The validation in steady and unsteady state is carried out through measurements of internal bed temperature and carbon monoxide content in the reformat. These measurements directly and indirectly validate reaction rates, heat and mass transfer, and heat consumption in time within the bed. Some model uncertainty stems from the used semi-empirical equations. Several heating non-uniformities present in the experiments are also identified and shown to have a large influence on the overall process. The transient performance is found mostly affected by parameters such as heat capacity. The simulations agree with measurements in time, and ultimately the model is concluded fit for reactor design tasks in the transient regime.

4.1.1. Methanol steam reforming

The dominant reactions in methanol steam reforming (MSR) are the methanol steam reforming reaction, the water-gas shift (WGS), and the methanol decomposition (MD):



In this overall endothermic process, methanol conversion can occur either directly through MSR, or indirectly through MD followed by the WGS reaction. Large reactors are often constructed as shell and tube heat exchangers [277, 278]. Flue gas or steam are generally used as shell side heat supply medium [278], but electrically heated

reactors are also emerging recently [279]. The most common commercial catalytic pellets for the process is $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$.

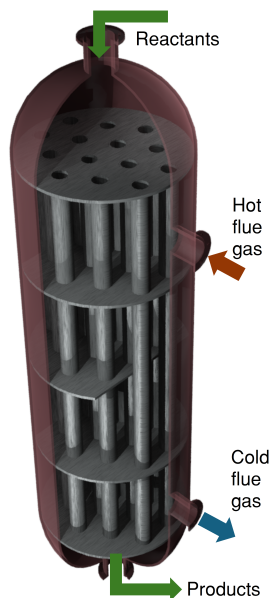


Figure 4.1.: Methanol steam reforming reactor as shell-and-tube heat exchanger heated with flue gas. Reprinted from [244] with permission of Elsevier, Copyright 2025.

4.2. Experimental methods

This section presents the designed experimental setup for unsteady methanol reforming validation. Material properties of the reactor and catalyst are reported, and experimental preparation procedures are explained. Then, the validation approach through performed measurements is described. Finally, the experimental uncertainties are identified and their assessment reported.

4.2.1. Experimental equipment and materials

An experimental setup is designed for dynamic operation and measurements in a packed bed methanol steam reformer. The setup schematic (Figure 4.2) shows an overview of the process, equipment, and their control integration. The inlet feed, which can be either methanol or a gas mixture, is pre-heated in the evaporator before entering the reactor. The process is monitored with temperature sensors inserted in the packed bed. The reactor back pressure is controlled with a diaphragm valve. The

outlet stream is condensed, sampled, and analysed using a gas chromatograph, and then vented.

The equipment is connected to a desktop PC either directly or via PLC, and it is controlled through LabView environment. A Gilson 305 high-performance liquid chromatography (HPLC) pump module precisely regulates the flow rate of liquid reactants. The reactants are then evaporated in a pipe section with a surrounding trace heating cable ($P_{\max}=1250$ W), and their temperature at the reactor inlet is controlled by a feedback loop using a thermocouple in the inert inlet zone of the reactor filled with alumina particles of 1.5 mm average diameter. Another trace heating wrapped around the reactor supplies the reaction heat ($P_{\max}=1600$ W), and the external wall temperature is regulated with a thermocouple positioned at the contact area of the trace heating and the reactor.

The pressure is controlled with a back pressure regulator placed directly after the reactor. A Pressure Control Solutions EQ-DA smart pilot pneumatic actuator controls the outlet pressure through an Equilibar dome loaded control valve, and is used as closed loop controller with the reference pressure reading from inlet or outlet pressure sensors.

In addition to temperature and pressure, the gas composition is analysed using an Agilent Micro gas chromatograph (GC). The GC uses Argon as a carrier gas, and has two columns heated at 373 K: 1 m column with Cox heated injector, and a 4 m column with 5CB heated injector.

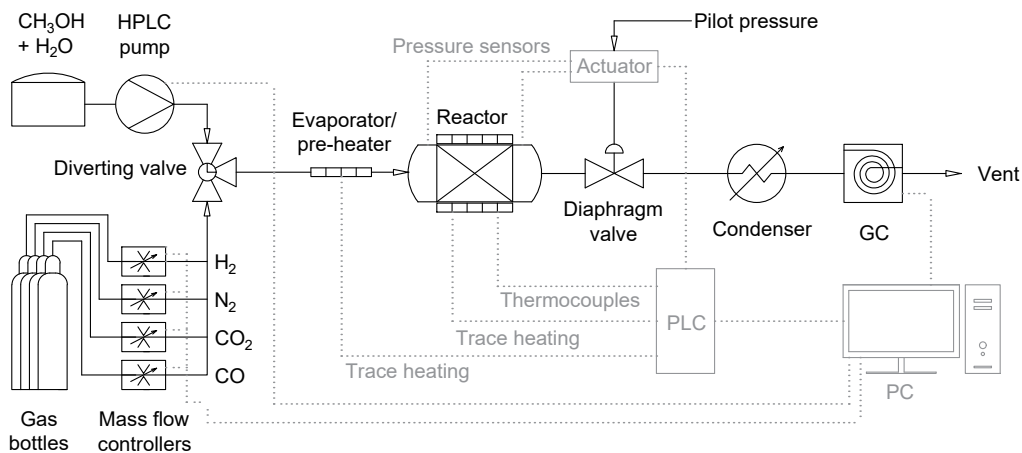


Figure 4.2.: Schematic of the experimental methanol steam reforming setup.

The reactor is made from Inconel 600 alloy material. Reactor material properties and dimensions are reported in Table 4.1. The internal surfaces in contact with hot reactants or products are coated with SilcoNert2000 inert coating to minimize side reactions. The coated surfaces include the reactor pipe, evaporator pipe, and all temperature and pressure sensors areas directly in contact with the flow. The reactor is vertically mounted to ensure downward reactant flow, as shown in the setup

photograph in Figure 4.3.

Table 4.1.: Properties of reactor tube made from Inconel 600

Parameter	Value	Description
d_{in} [mm]	30	Reactor internal diameter
s_w [mm]	5	Reactor wall thickness
l_r [mm]	300	Reactor length (active region)
$c_{p,w}$ (J kg ⁻¹ K ⁻¹)	444	Tube wall specific heat capacity
k_w [W m ⁻¹ K ⁻¹]	14.9	Thermal conductivity of reactor wall
ρ_w (kg m ⁻³)	8470	Density of the reactor wall

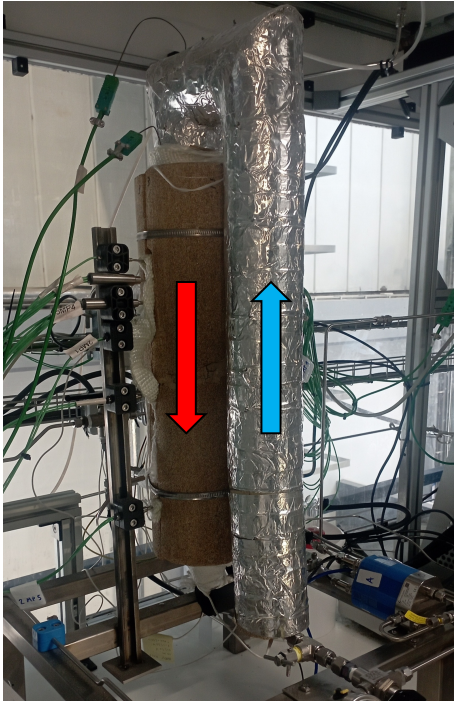


Figure 4.3.: Methanol steam reforming reactor vertically mounted for downward fluid flow (red arrow), and evaporator/pre-heater pipe leading up to the reactor top inlet with upward fluid flow (blue arrow).

The reactor contains 36 temperature sensors and 2 pressure sensors. The sensors are placed in the fixed bed according to Figure 4.4. The thermocouples (TCs) are distributed across 11 inserts consisting of single point, 5-point, and 2-point sensors. One single point sensor is inserted in the inert inlet zone to monitor and control the

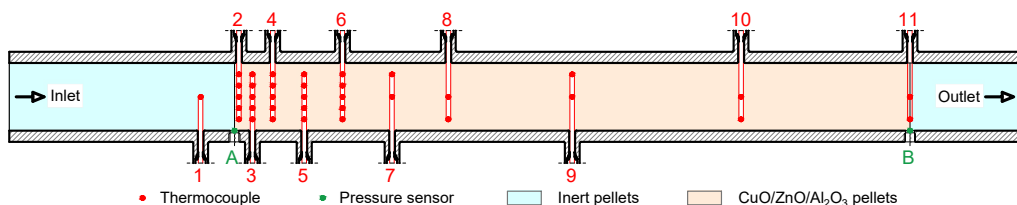


Figure 4.4.: Schematic of the cross section reactor tube showing flow direction, reactor packing zones, and thermocouple and pressure sensor placement within the reactor.

reactant inlet temperature. Five 5-point sensors are placed at the start of the active zone, where a high temperature gradient is expected. In 5-point sensors, the TCs are uniformly spaced 5 mm from each other and the reactor wall. In 2-point sensors, one TC is placed 5 mm away from the wall opposite to the insert point, and the other at the reactor centreline. The axial positions of all temperature sensor inserts are given in Table 4.2. The two pressure sensors are placed at the boundaries of the active catalyst zone, annotated with A and B in Figure 4.4.

Table 4.2.: Positions of temperature sensor inserts in the methanol steam reforming reactor

Insert number	1	2	3	4	6	5	7	8	9	10	11
Rel. distance from cat. zone start [mm]	- 15	2	8	17	48	31	70	95	150	225	300
No. of TC sensors in the insert	1	5	5	5	5	5	2	2	2	2	2

The designed reactor is filled with inert pellets and active catalyst pellets according to the schematic shown in figure 4.4. The reactor is divided into three zones in the axial direction: inert inlet, active middle, and inert outlet zone. The surrounding inert zones ensure that the gas flow in the active catalyst zone is not affected by pipe diameter variations at the inlet and outlet. The reactor total length is 450 mm, where the inert inlet zone is 100 mm, the active catalyst zone is 300 mm, and the inert outlet zone is 50 mm long. The packing zone interfaces are separated with quartz filters to prevent mixing.

The commercially available CuO/ZnO/Al₂O₃ cylindrical catalyst pellets supplied by Shandong Dengzhuo Chemical Co., Ltd with 40/40/20 wt% composition are used in the experiments. The pellets are crushed and sieved to $1\text{ mm} < d_p < 2\text{ mm}$ size fraction before loading them in the reactor. This way, approximately 20 pellets fit across the reactor diameter which minimizes the tube wall effects on the internal gas flow [280]. The reactor is filled with 0.296 kg of crushed catalyst. The resulting bulk density is $\rho_b = 1396\text{ kg m}^{-3}$, and bed porosity is $\varepsilon = 0.39$. The crushed catalyst surface area and average pore radius are obtained through measurements using an Anton Paar®

Autosorb 6100 high vacuum physisorption analyser. The complete list of catalyst properties is reported in Table 4.3.

Table 4.3.: Properties of the crushed commercial $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst pellets used in the experiments

Parameter	Value	Description
d_p [mm]	1.5	Catalyst pellet average diameter
ρ_c [kg m^{-3}]	1396	Catalyst bulk density
$\rho_{c,s}$ [kg m^{-3}]	2293	Catalyst material density
ε [-]	0.39	Bed porosity
$c_{p,s}$ [$\text{J kg}^{-1} \text{K}^{-1}$]	950	Catalyst specific heat capacity
S_c [$\text{m}^2 \text{kg}^{-1}$]	$118 \cdot 10^3$	Catalyst BET surface area
d_{pore} [$\text{\AA}$]	247	Catalyst average pore diameter

Prior to the experiments, the catalyst was activated with a hydrogen and nitrogen mixture in equal molar ratios through the reactor. The flow of 300 standard ml/min and reactor temperature of 500 K were maintained at ambient pressure during the activation. The flow was kept relatively low to regulate the exothermic activation reaction and keep the catalyst below the sintering temperature of ~ 570 K. The activation procedure was completed after the axial temperature profile was stable, which took about 10 hours.

4.2.2. Data gathering approach

Two experimental techniques are used for steady state validation: temperature measurements and gas analysis. The thermocouple inserts presented in Figure 4.4 relay axial and radial temperature gradients. The temperature profile is a result of external heat supply, axial and radial transport, and heat consumption by the reactions. A comparable temperature field from the model is achieved when all heat fluxes are correctly captured.

Outlet methanol conversion cannot be directly measured since the used gas chromatograph requires dry gas. Only the relative concentrations of H_2 , CO_2 , and CO can be measured.

The CO concentration measurement is used as conversion indicator since CO content is inversely proportional to the methanol conversion. As methanol is converted, the local bed temperatures rise due to lower reaction rates of MSR and MD (eqs. 4.1, 4.3). The equilibrium then shifts and the reverse WGS (eq. 4.2) produces CO. Thus CO concentration measurements are used in place of methanol conversion for validation.

For dynamic analysis, the gas chromatograph is run continuously and generates data points at ≈ 4 minute intervals. The gas residence time in the tubes leading to the GC has not been determined. However, the data points indicate a trend that can be captured by the model.

4.2.3. Experimental uncertainties and non-uniformities

Several uncertainties and non-uniformities are present in the experimental part of the study. Each uncertainty impacts the validation in a different way since they stem from various sources. The major concerns and their treatments are described here.

Crushed and sieved catalyst has irregular shapes and non-uniform pellet sizes. In the modelling equations, however, an average value of catalyst diameter ($d_p = 1.5$ mm) must be used. The pellet volume and macro surface area are calculated using equations for a spherical catalyst with equivalent diameter. These parameters are used in expressions for effective radial transport, heat transfer coefficient, and pressure drop. The isolated effects of the used catalyst shapes would have to be explored in a dedicated experimental study. In the present work, the affected expressions are observed within a sensitivity study shown in the *Numerical model* section.

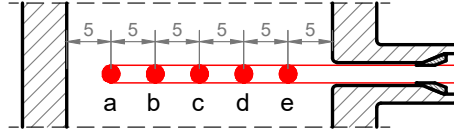
Deviations from ideal behaviour on the reactor bed scale are also observed. Over the course of the first $\simeq 50$ hours of operation the bed activity slowly decreased, after which it settled. The decrease was observed indirectly with temperature measurements. The inlet zone is found most affected by the decrease, for multiple likely reasons. First, possible bed settling shifts material away from the inlet in the vertically installed reactor. Second, the expected initial activity decreases due to sintering or pore clogging. Third, the inlet zone has less catalyst due to dense thermocouple placement. This can reinforce the activity decrease from settling.

The converged activity state is seen in Fig. 4.5 through a rapid decrease in temperature at the thermocouple insert at position 5. This decrease is generally expected at the initial contact of reactants with the catalyst. This effect is included in the model, and is explained in detail in the *Numerical model* section.

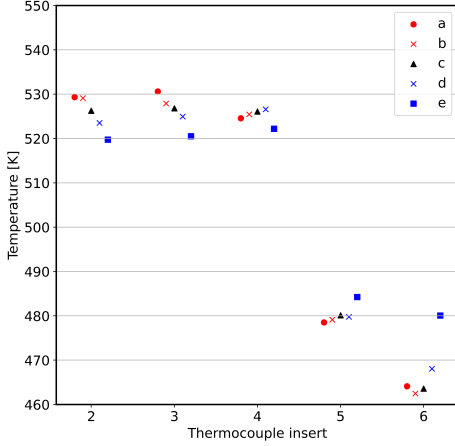
The effects of thermal conduction through the thermocouple inserts are investigated under steady state reforming conditions with 5-point inserts, as shown in Figure 4.5. The accuracy of the used K-type thermocouples is ± 2.5 K, so only higher gradients are used to draw conclusions. All steady states show similar behaviour like the process conditions reported in Figure 4.5.

The inserts numbered 2-4 in the low activity area indicate heat conduction away from the thermocouple with a gradient of up to 10 K across between sensors *a* and *e*. Inserts 5 and 6 are in an active heat transfer limited zone. The sensors *a-c* have a low gradient between them in all cases, which implies that conduction along the sensor is not dominant over heat exchange with the bed packing in this region. The conduction may still be present, but it is concluded tolerable. Therefore only sensors *a-c* are used for validation. The conduction is assumed to be the same for 2-point inserts, which have only *a* and *c* sensor positions, both of which are used in the validation.

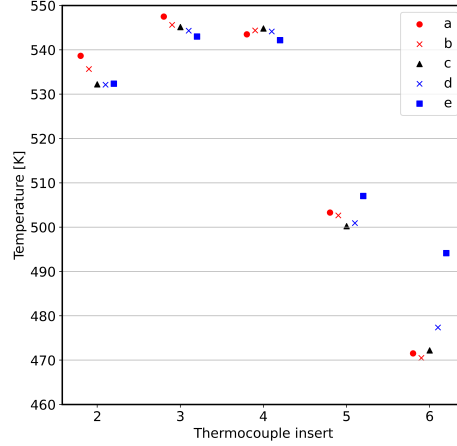
Finally, several imperfections are present in reactor heating, such as heat losses, trace heater wrapping non-uniformity, the inlet reactant temperature control, the reactor bed activity changes after stabilization, and variable heat capacity of the reactor due to its mounting. All these effects are quantified, and addressed a posteriori in the model, and are presented in detail in the *Numerical methods* section.



(a) Thermocouple sensor names in a 5-point insert relative to the point of insertion and gas-tight ferrule seal. Dimensions are drawn in mm.



(b) $P = 150 \text{ W}$; $W_{\text{cat.}}/F_{\text{CH}_3\text{OH}} = 200 \text{ kg mol s}^{-1}$



(c) $P = 224 \text{ W}$; $W_{\text{cat.}}/F_{\text{CH}_3\text{OH}} = 150 \text{ kg mol s}^{-1}$

Figure 4.5.: Temperature measurements from 5 point thermocouple inserts during two selected steady reforming operations with specified electric power input and methanol inlet flow at steam-to-carbon molar ratio of $S/C = 1.5$.

4.3. Numerical methods

The present model is created by extending the steady state 2D model of Zhu et al. [234, 259, 262], formulated in cylindrical coordinates. The newly developed model is open source and available from a git repository [235]. The formulae for terms not presented in the main text can be found in the Appendix B.1, and the original publications of Zhu et al. The mass and energy equations of an unsteady pseudo-heterogeneous model used in the present study are:

$$\varepsilon \frac{\partial C_i}{\partial t} = -u_s \frac{\partial C_i}{\partial z} + D_{er} \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r} \frac{\partial C_i}{\partial r} \right) + \rho_c r_i, \quad (4.4)$$

$$\begin{aligned} & (\varepsilon \rho_f c_{p,f} + (1 - \varepsilon) \rho_s c_{p,s}) \frac{\partial T}{\partial t} = \\ & -u_s \rho_f c_{p,f} \frac{\partial T}{\partial z} + \lambda_{er} \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) + \sum \eta_j \rho_c (-\Delta H_j) r_j S_c \end{aligned} \quad (4.5)$$

where ε (-) is the bed porosity, C_i (mol m⁻³) are the species concentrations, u_s (m s⁻¹) is the flow superficial velocity, D_{er} (m² s⁻¹) is the effective radial dispersion coefficient, ρ_c (kg m⁻³) is the catalyst bulk density, r_i (mol s⁻¹ m⁻²) is the formation/consumption rate of component i , $c_{p,f}$ (J kg⁻¹ K⁻¹) is the fluid (gas) phase specific heat capacity, $\rho_{c,f}$ (kg m⁻³) is the fluid (gas) phase density, $c_{p,s}$ (J kg⁻¹ K⁻¹) is the solid phase specific heat capacity, $\rho_{c,s}$ (kg m⁻³) is the solid phase (catalyst material) density, T (K) is the temperature, λ_{er} (W m⁻¹ K⁻¹) is the effective radial thermal conductivity, η_j are the effectiveness factors evaluated per reaction j , ΔH_j (J mol⁻¹) is the reaction enthalpy of reaction j , r_j (mol s⁻¹ m⁻²) is the reaction rate of reaction j , and S_c (m² kg⁻¹) is the catalyst BET surface area. The formulas for η_j calculated with Thiele modulus (approach validated by Zhu et al. [242]), D_{er} , and λ_{er} are shown in Appendix B.1.

Axial dispersion terms are not included in this model for computational efficiency. Axial effects are not dominant in flows with high Péclet numbers according to Sahimi et al. [236]. In the present work, Péclet numbers are always higher than 240, which falls under the regime as *dominated by convective transport* according to Sahimi. Above $Pe = 300$, the regime becomes *purely convective*.

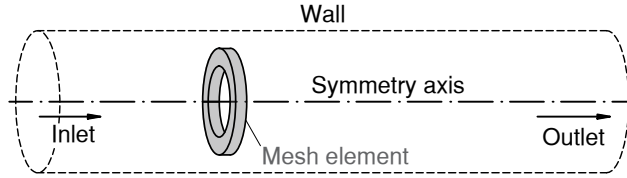


Figure 4.6.: Illustration of reactor tube domain boundaries and mesh element in cylindrical coordinates.

The simulation domain and representative mesh element shape for cylindrical coordinates are shown in Figure 4.6. The boundary condition equations are given in Table 4.4.

The energy conservation equation of the reactor tube wall is:

$$\rho_w c_{p,w} \frac{\partial T_w}{\partial t} = k_w \frac{\partial^2 T_w}{\partial z^2} + \frac{P_{el,in} * \eta_d}{V_t} - Q_{loss} \frac{A_{t,in}}{V_t} + U \Delta T_{w,r} \frac{A_{t,in}}{V_t}, \quad (4.6)$$

where ρ_w (kg m⁻³) is the reactor wall material, $c_{p,w}$ (J kg⁻¹ K⁻¹) is the reactor wall material specific heat capacity, T_w (K) is the wall temperature, k_w (W m⁻¹ K⁻¹) is the thermal conductivity of reactor wall material, $P_{el,in}$ (W) is the electric trace heater power, η_d (-) is the trace heater wrapping density (heat generation) factor, Q_{loss} (W m⁻²) is the area normalized heat loss, U (W m⁻² K⁻¹) is the overall (combined) heat transfer coefficient, $\Delta T_{w,r}$ (K) is the temperature difference between tube wall and reactants, $A_{t,in}$ (m²) is the inner surface area of one reactor tube, and V_t (m³) is the reactor tube wall volume. The external heating is thus applied to the reactor through the tube wall energy equation.

The overall heat transfer coefficient U (W m⁻² K⁻¹) includes resistances from the tube side gas film and within the reactor tube wall. It is calculated according to:

Table 4.4.: Simulation boundary conditions

Position	Coordinates	Boundary condition
Inlet	$z = 0$	$C_i = C_{in}$
	$0 \leq r \leq r_{max}$	$T = T_{in}$
Outlet	$z = z_{max}$	$\frac{\partial C_i}{\partial z} = 0$
	$0 \leq r \leq r_{max}$	$\frac{\partial T}{\partial z} = 0$
Wall	$0 \leq z \leq z_{max}$	$\frac{\partial C_i}{\partial r} = 0$
	$r = r_{max}$	$\frac{\partial T}{\partial r} = -\frac{\lambda_{er}}{U}(T_{wall} - T)$
Symmetry axis	$0 \leq z \leq z_{max}$	$\frac{\partial C_i}{\partial r} = 0$
	$r = 0$	$\frac{\partial T}{\partial r} = 0$

$$U = \left(\frac{1}{h_t} + \frac{s_w}{k_w} \frac{d_{t,out}}{d_{lm}} \right)^{-1}, \quad (4.7)$$

The used kinetics model (eqs. B.21-B.23 in Appendix B.1) has been developed by Peppley et al. [237] for a commercial CuO/ZnO/Al₂O₃ catalyst. The kinetic model is based on a Langmuir-Hinshelwood mechanism for surface reactions, and includes the three reversible dominant reactions of MSR described in eqs. 4.1-4.3. The pressure losses along the reactor bed are calculated with the semi-empirical model of Ergun [238].

4.3.1. Numerical schemes and discretization

A second order upwind scheme is used for advection terms, while a 4th order central differencing scheme is used for the radial terms. Before each unsteady simulation, a steady state is initialized until mass and energy balances converge to residuals below 10⁻⁵. A Runge-Kutta 4th order scheme is used for temporal evolution in the unsteady simulation. A constant unsteady timestep of 4·10⁻⁴ seconds was used based on the rates of reaction. The simulated domain is discretized with a uniform mesh with 45 axial and 30 radial cells. Figure 4.7 shows the results of a grid convergence study.

4.3.2. Parameter sensitivity study

Parameters with potentially high impact on the results are investigated in a sensitivity study. Effective radial coefficients for dispersion (D_{er}) and thermal conductivity (λ_{er}) are chosen due to their large role in radial transport terms. The tube side heat transfer coefficient (h_t) is included because of expected impact on radial heat transport. Finally, the pressure drop (Δ_p) is included due to its potential impact on reaction rates.

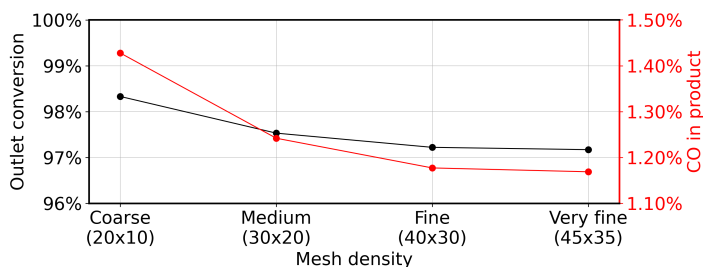


Figure 4.7.: Grid convergence study with outlet methanol conversion and CO content for $P=187$ W, $W_{cat.}/F_{CH_3OH}=200$ kg s mol⁻¹ case.

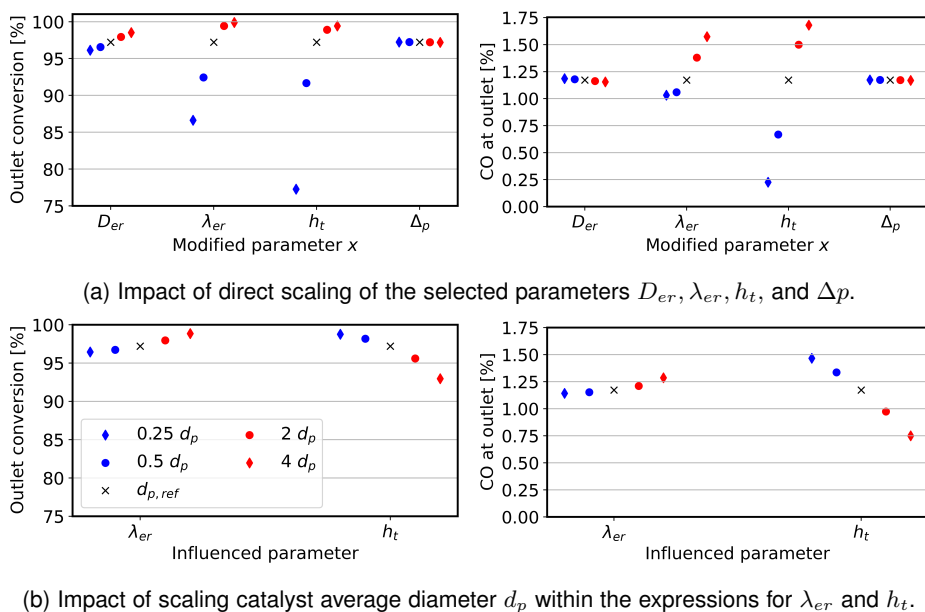


Figure 4.8.: Sensitivity analysis: impact of scaling selected parameters D_{er} , λ_{er} , h_t , and Δp ; and catalyst average diameter d_p within expressions for λ_{er} and h_t on the outlet conversion and CO concentration; simulation case $P=187$ W, $W_{cat.}/F_{CH_3OH}=200$ kg s mol⁻¹.

The sensitivity analysis of the described parameters was conducted by multiplying the result of their respective equations (presented in Appendix B.1) with factors of 0.25, 0.5, 2, and 4. The factor variation impact is characterized by methanol conversion, and CO concentration at the outlet. The sensitivity study in Figure 4.8a shows that scaling the radial heat transfer parameters, λ_{er} and h_t has the highest influence on conversion and selectivity.

As introduced in section 4.2.3, the crushed catalyst pellets are not uniform in size

in the present experiments. An averaged value of catalytic pellet diameter d_p is used in the model, namely in the formulas for D_{er} , λ_{er} , h_t , and Δ_p . Further analysis is conducted on the impact of d_p variations within the selected parameters.

The average value of d_p was also scaled by the factors of 0.25, 0.5, 2, and 4 within the expressions for the two most sensitive parameters λ_{er} and h_t . Results of this analysis in Figure 4.8b show a mild effect through λ_{er} , while h_t is sensitive to pellet size changes.

The size range of experimental catalyst pellets is relatively small compared to the investigated range. The sieved catalyst sizes range between 1 and 2 mm, which is 33% and 175% respectively of the average 1.5 mm value. The d_p variation has a negligible influence through λ_{er} in the present study. A larger effect is seen in h_t manipulation. Based on the results depicted in Figure 4.8b, the resulting uncertainty range within the experimental pellet size is around $\pm 1\%$ error for methanol conversion, and $\pm 5\%$ error for CO content at the outlet.

4.3.3. Modelling of experimental non-uniformities

Several experimental non-uniformities, first introduced in section 4.2.3, could not be resolved or predicted before conducting the experiments. Instead, they are assessed *a posteriori* and included in the model. This subsection describes the modelling additions of all experimental non-idealities.

Heat losses to the environment

Reactor heat losses were experimentally measured in stagnant, non-reactive conditions. Trace heating power was varied between 30W and 150W in 18 intervals, and thermocouple data was collected after a stable heat profile was established. Figure 4.9 shows experimental measurements with a heat loss map created from interpolating and extrapolating the measurements.

The resulting interpolation function is used to calculate local heat losses at the wall. The thermocouple measurements taken from within the reactor packing are used as wall temperatures, because no radial gradients were detected in stagnant steady state. Thus, function inputs from the simulation are local wall temperature and axial reactor distance, while the local heat loss is the output. The total heat losses in the interpolation function are normalized with total reactor area so in the code they could be multiplied by tube mesh cell area. The function is validated with simulations in stagnant non-reactive conditions. The results in Figure 4.10 show excellent agreement between simulated and experimental data.

Heating cable wrapping density

The second non-ideality emerges in wrapping of the trace heating cable. The mounts for thermocouples and pressure sensors protrude from the reactor, and prevent uniform wrapping of the heating cable. Consequently, the trace heater wrapping density varies along the reactor. The wrapping density is lowest near the reactor inlet, where thermocouple inserts are the most densely placed. The pressure sensors also have a relatively high impact on the wrapping since their mounting protrusions are larger, around 18 mm in diameter.

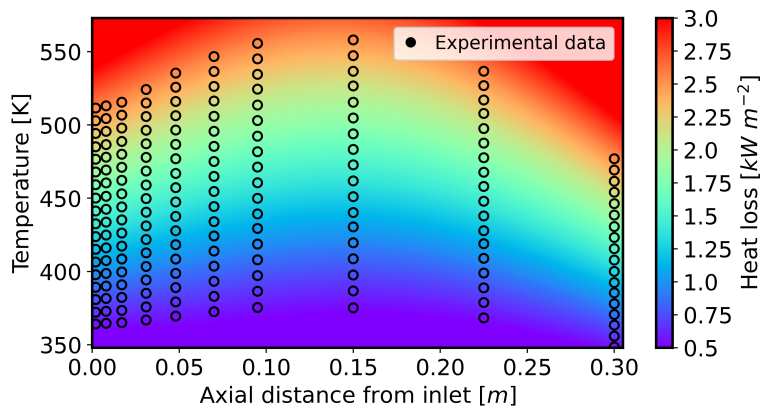


Figure 4.9.: Experimental heat loss measurements (circles coloured with heat loss value) at 18 temperature setpoints between heat input 30-150 W in non-reactive stagnant conditions plotted over a heat map of extrapolated heat loss values.

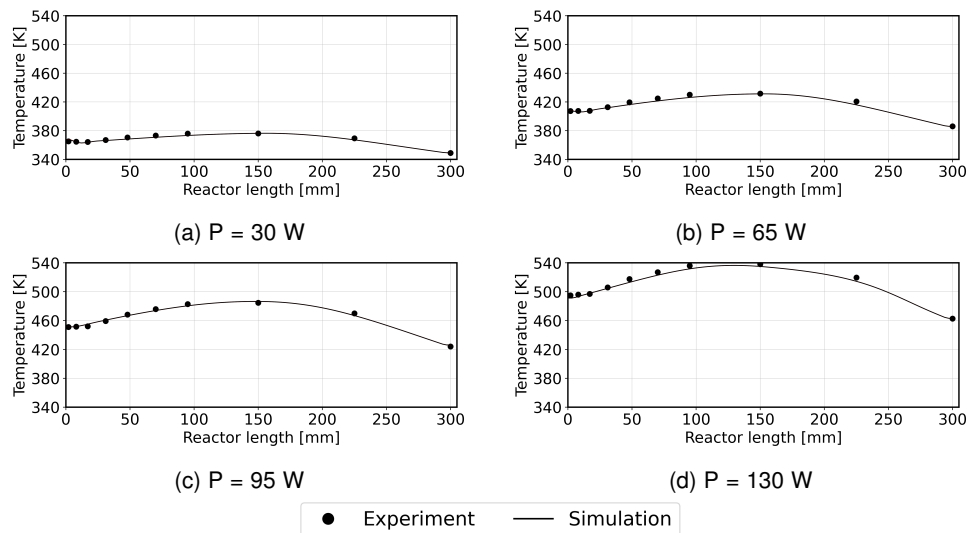


Figure 4.10.: Comparison of experimental and simulated data of reactor tube wall temperature at four different heating power inputs as validation of the heat loss function.

The effects of variable cable wrapping density are not seen in stagnant heating experiments because of heat conduction along the tube wall, and low heat input required to maintain the temperature. The effects instead manifest during reforming operations when heat is consumed by the reactions.

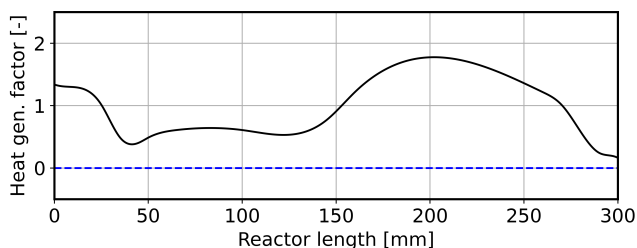


Figure 4.11.: Heat generation factor curve that accounts for variations in trace heating cable wrapping density along the reactor axis.

The axial variations in generated heat $P_{el,in}$ are corrected in the simulation by multiplication with dimensionless local heat generation factor. In this way, the heat generation factors account for varying axial heat input caused by differences in cable wrapping density. The applied heat generation factor profile is shown in Figure 4.11. The initial shape guess was made from visual approximation of wrapping density. Then, the profile shape was adjusted iteratively through comparisons with steady state experiments.

The heat generation factor curve must not change the total heat input to the reactor. The created curve is thus normalized by scaling its y values. The final curve encloses an area equal to the area under a horizontal line $y = 1$ between $0 < l < 300$ mm. In this way, the total heating power in simulations is the same as in experiments.

Reactor bed catalytic activity

Upon the initial operation stabilization after the first ~ 50 active hours, the average bed catalytic activity reduced in the near-inlet region. This is likely due to the combined effects of bed settling, catalyst sintering, and pore clogging, as suggested in Section 4.2.3. The activity decrease was observed as gradual advancement of the initial temperature drop in the direction of reactant flow, as shown in Figure 4.12. Although the temperature change is subtle, the measured CO concentration reduced significantly from the initial range of 1.08-1.17, to 0.53-0.72 mol m⁻³ in the stabilized bed.

The stabilized bed activity was translated to the model by applying reduction factors to the catalyst BET area value. In this way, bed porosity and heat capacity are unaffected, and only the reaction rates are reduced. The used reduction factor profile is shown in Figure 4.13.

Inlet temperature variations

The efficiency of reactant evaporator and pre-heater pipe at the inlet depends predominantly on reactant pressure, flow, and heat transfer efficiency. Consequently, the inlet temperature in the reactor is difficult to precisely control in practice. The approach in validation is therefore matching the simulation inlet temperature to the experimental measurements.

In steady state experiments, measurements are time averaged. Simulation inputs

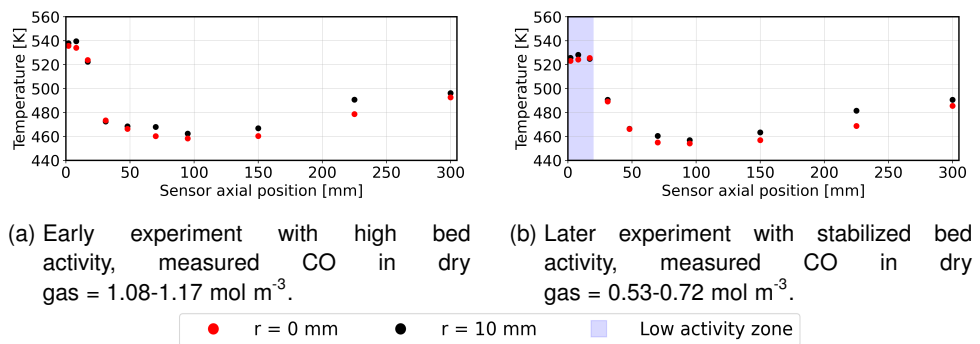


Figure 4.12.: Experimental temperature measurements showing a local drop in activity for case: $W_{cat.}/F_{CH_3OH} = 200 \text{ kg s mol}^{-1}$; $P_{el,in} = 150 \text{ W}$.

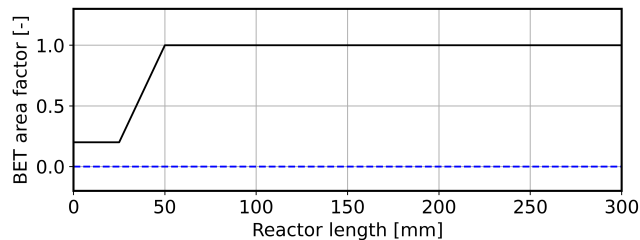


Figure 4.13.: Modification factor for catalyst BET area along the reactor axis.

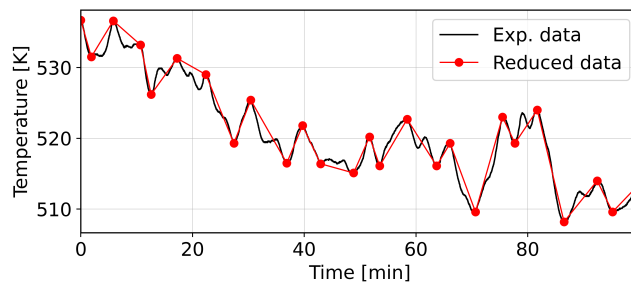


Figure 4.14.: Experimental measurement of inlet reactant temperature in time from sensor position T4, and reduced data set used as input for the unsteady simulation.

are then set as the time averaged values. In dynamic operation, the inlet temperature is matched in time with the measurements. The raw measured data is first reduced with the Ramer-Douglas-Peucker algorithm, as shown in Figure 4.14. The reduced points are then used in the simulations.

Thermal capacity of reactor support fixture

The support fixture clamps the reactor at its outlet. The support slows the temperature change in the dynamic experiments due to increased thermal capacitance. This is included in the model by scaling the heat capacity of reactor wall, as depicted in Figure 4.15.

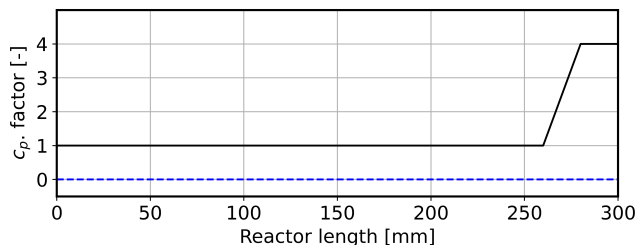


Figure 4.15.: Modification factor of react tube wall specific heat capacity along the reactor length.

4.3.4. Impact of heat transfer imperfections

Each addition of experimental non-idealities to the model has a different effect on the process. The additions are explored individually for their effects on the steady state temperature profile, as shown in Figure 4.16, and conversion and selectivity, shown in Figure 4.17.

The temperature field is most impacted by trace heater wrapping density and bed activity modifications. In terms of conversion and selectivity, the heat losses and bed activity factors have the most influence. In all cases the impact on conversion is small, around 1%, while the CO concentration changes up to 18%. Despite the fact that reaction rates couple the temperature field with conversion and selectivity, their interaction is not entirely obvious to the eye. For example, heat losses addition marginally alter the temperature field but have a high impact on conversion and selectivity. For this reason, all imperfections must apparently be included for accurate predictions of both the temperature field and outlet composition.

The inlet reactant temperature has an evident impact on conversion and selectivity, which is shown in Figure 4.18. The outlet CO concentration is directly proportional to the inlet temperature, with each 50 K increment causing $\simeq 0.35\%$ change in CO. The conversion response appears linear up to $\simeq 99\%$, while its sensitivity decreases as conversion approaches 100%. The inlet temperature in the experiments varies up to 40 K, so its matching further increases simulation accuracy.

Finally, the effects of reactor wall heat capacity factors are only present in transient state. Figure 4.19 shows its impact on outlet conversion, produced CO, and internal temperature change in time tracked at reactor outlet. The monitored values move slower towards the new steady state. The wall c_p modification in this case affects the reactor response by increasing its duration to a change in process variable.

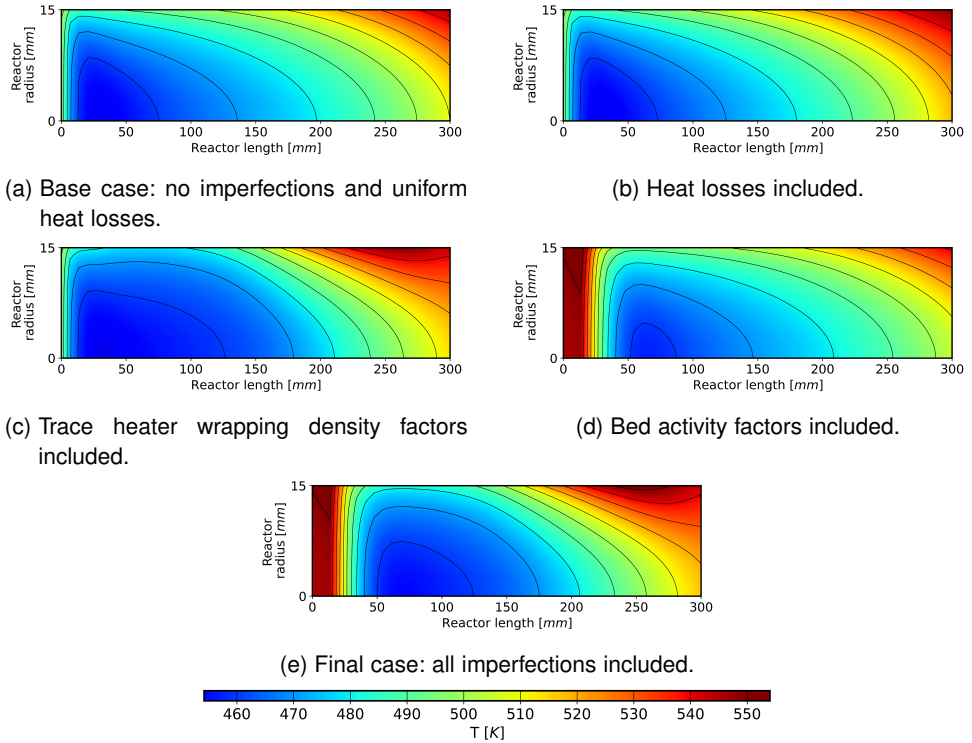


Figure 4.16.: Isolated effects of each heat non-uniformity inclusion in the simulation on internal reactor temperature field. Simulation case: $W_{cat.}/F_{CH_3OH} = 200 \text{ kg s mol}^{-1}$; $P_{el,in} = 150 \text{ W}$.

4.4. Experimental validation

All experiments are conducted at outlet pressure $p_{out} = 3 \text{ bar}$. Three flows are chosen for the experimental campaign: $W_{cat.}/F_{CH_3OH} = 120, 150, 200 \text{ kg s mol}^{-1}$, where $W_{cat.}/F_{CH_3OH}$ is the ratio of catalyst mass to methanol feed rate. The flow specifications are expressed in Table 4.5. Zhu et al. [234] note that flows lower than $W_{cat.}/F_{CH_3OH} = 200 \text{ kg s mol}^{-1}$ cause inconsistent experimental CO measurements, possibly due to non-uniform distributions of temperature and species concentration. $W_{cat.}/F_{CH_3OH} = 200 \text{ kg s mol}^{-1}$ is thus taken as the lower flow boundary in present study. The higher flow boundary of $W_{cat.}/F_{CH_3OH} = 120 \text{ kg s mol}^{-1}$ is set by the efficiency of evaporator/pre-heater pipe in the experiments. In other words, the inlet reactant temperature is too low at flows higher than $W_{cat.}/F_{CH_3OH} = 120 \text{ kg s mol}^{-1}$.

Three electrical power heating settings for the reactor are chosen: $P_{el,in} = 150, 187$, and 224 W . With these heating inputs the internal reactor temperature is kept below 573 K which minimizes catalyst sintering. The methanol conversion in all cases is in the 50% - 95% range.

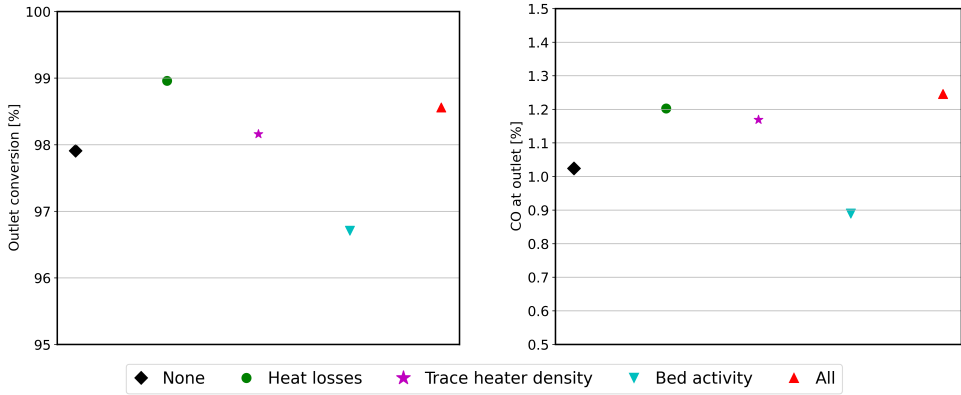


Figure 4.17.: Isolated effects of heat imperfection modifications in the simulation on outlet conversion and CO content. Simulation case: $W_{cat.}/F_{CH_3OH} = 200 \text{ kg s mol}^{-1}$; $P_{el,in} = 150 \text{ W}$.

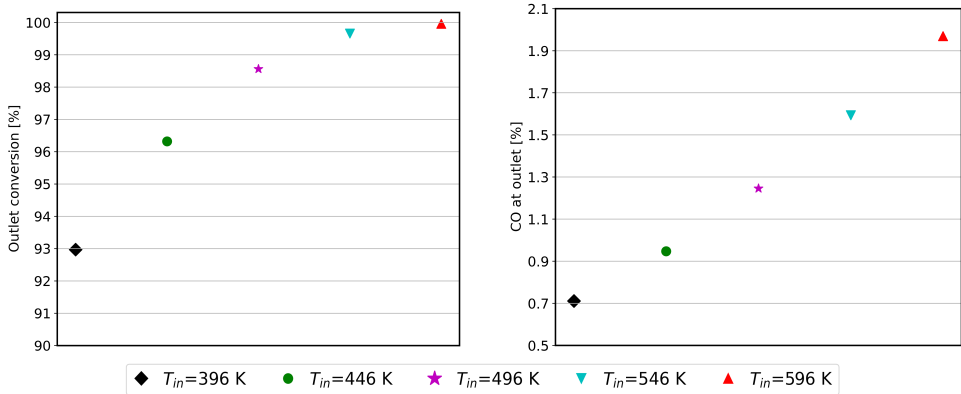


Figure 4.18.: Effects of inlet reactant temperature varied in 50 K increments in the simulation on outlet conversion and CO content. Simulation case: $W_{cat.}/F_{CH_3OH} = 200 \text{ kg s mol}^{-1}$; $P_{el,in} = 150 \text{ W}$.

Table 4.5.: Three reactant throughputs used in the experimental campaign, expressed in different flow units.

$W_{cat.}/F_{CH_3OH} [\text{kg s mol}^{-1}]$	120	150	200
Molar CH_3OH flow $[\text{mol min}^{-1}]$	0.37	0.296	0.222
Liquid mixture flow at pump $[\text{ml min}^{-1}]$	9.64	7.712	5.785

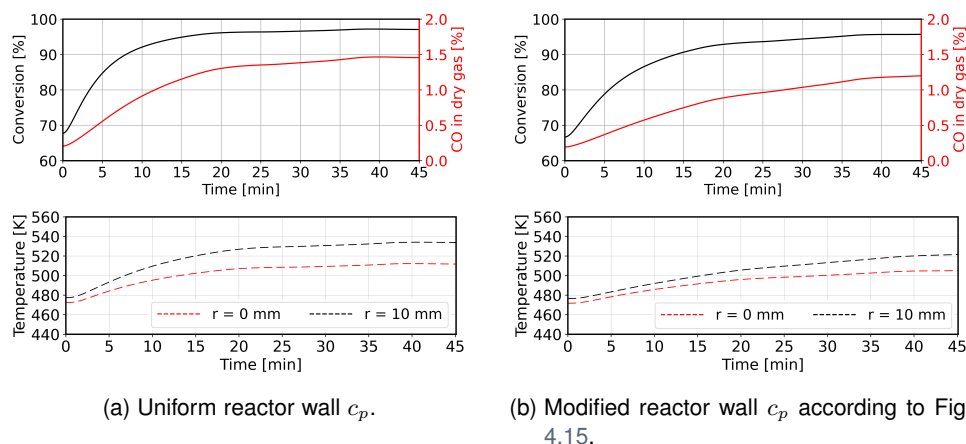


Figure 4.19.: Effects of reactor wall c_p modification on simulated conversion, CO production, and temperature in time shown at reactor outlet ($z = 300$ mm). Simulation case: heating power increase of $\Delta P_{el,in} = 150$ -224 W at reactant flow $W_{cat.}/F_{CH_3OH} = 150$ kg s mol⁻¹.

4.4.1. Steady state validation

The measured and simulated CO concentration in dry reformat gas is reported in Table 4.6, together with corresponding selected setpoints of heating power and reactant flow. The visualization of CO concentration in Figure 4.20 shows that the selectivity trend is matched very well by the simulations. In most cases, the predicted CO concentration is around the lower boundary of measured range.

The pressure sensor precision (± 0.1 bar) is too low for conclusive comparison of pressures. The simulated pressure drop values are around $\Delta p = 0.003$ bar, while the measurements indicate an average of $\Delta p = 0.05$ bar. The consistent low measured Δp values indicate a degree of accuracy. However, due to low precision, pressure values are not used in further validation.

The steady state validation through temperature sensor measurements is shown in Figure 4.21. Based on the bed activity, the reactor can be divided into three zones—excluding the low activity zone. The first two zones are heat transfer limited. In the first zone, $z < 50$ mm the endothermic reactions dominate the heat balance which is seen by rapid decrease of temperature. In the second zone, $50 \leq z \leq 150$ mm, the heat supply to the reactor is equal to the reaction heat consumption, indicated by the flat temperature profile. This limitation is partly caused by the lower trace heater wrapping density, which is supported by Figure 4.16c. In the third zone, $z > 150$ mm, the reaction rates slow down due to lower reactant concentrations, causing a temperature increase.

The three distinct reactor zones and their lengths are well captured by the simulations. The simulation is the most accurate in the first two zones, which are highly similar across all cases. In the third zone, the temperature predictions have the highest deviations from experiments, up to 15 K in some cases. The heat balance complexity increases in this zone, since there is not a single dominant heat flux component. The

Table 4.6.: Steady state validation: measured and simulated values of CO in dry reformat gas at different throughput and reactor heating power ($p = 3$ bar).

El. heating power [W]	$W_{cat.}/F_{CH_3OH}$ [kg s mol ⁻¹]	Measured CO in dry gas [mol m ⁻³]	Simulated CO in dry gas [mol m ⁻³]	Simulated CH ₃ OH conversion [%]
150	120	0.11 - 0.14	0.118	52.83
	150	0.25 - 0.28	0.199	65.53
	200	0.46 - 0.64	0.412	82.33
187	120	0.32 - 0.36	0.315	70.46
	150	0.62 - 0.69	0.615	84.95
	200	1.18 - 1.55	1.356	97.24
224	150	1.26 - 1.45	1.3797	95.28

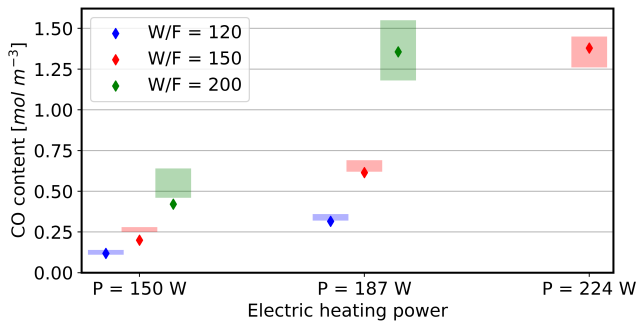


Figure 4.20.: Steady state validation: graphed measured range of CO in dry reformat gas (transparent rectangles) and simulated values (diamonds) at various inputs of reactor heating and reactant throughput.

individual terms in the energy equation (eq. 4.5) then have a larger influence over the end result.

The temperature trends are well captured by the simulations and overall accurate, same as with CO content predictions. The simulation precision, namely of the temperature prediction, is likely constrained by uncertainty from heat transfer parameters. For example, the tube side heat transfer coefficient h_t alone is sensitive to catalyst pellet size, and has an evident influence in the overall prediction, as illustrated by the sensitivity study. The validation precision is also expectedly affected by effective radial transport coefficients D_{er} and λ_{er} , omitted axial transport, precision of added heat irregularity factors, measurement accuracy, or other assumptions. The numerical parameters could be fine tuned, if more precision is needed.

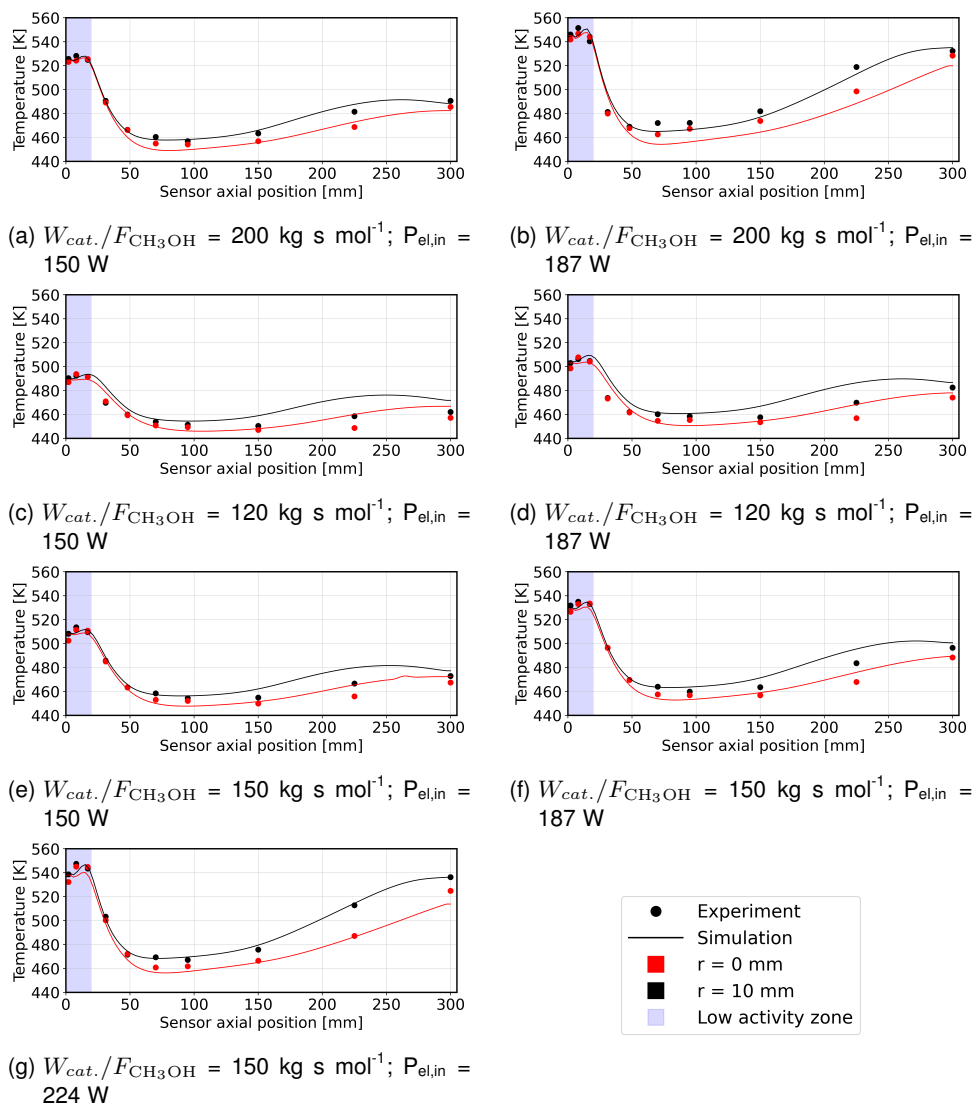


Figure 4.21.: Steady state validation: comparison of experimental and simulated temperature profiles, sampled at different radial and axial positions in the reactor.

4.4.2. Dynamic validation

The dynamic experiments are performed by observing the reactor response to step changes in input process variables. Reactant flow and reactor heating power are individually controlled in the experiments, and recorded temperatures are used for model validation. Table 4.7 shows the changes in reactor inputs used for validation

cases.

Table 4.7.: Variations of flow and heating power in dynamic experiments

Flow variation experiments		
Set heating power	Flow increase	Flow decrease
$P_{el,in}$ [W]	$W_{cat.}/F_{CH_3OH}$ [kg s mol ⁻¹]	$W_{cat.}/F_{CH_3OH}$ [kg s mol ⁻¹]
150	200 - 120	120 - 200
187	200 - 120	120 - 200

Heat variation experiments		
Set flow	Heating power increase	Heating power decrease
$W_{cat.}/F_{CH_3OH}$ [kg s mol ⁻¹]	$P_{el,in}$ [W]	$P_{el,in}$ [W]
150	150 - 187	187 - 150
150	150 - 224	224 - 150
200	150 - 187	187 - 150

The results in the main text show selected four cases: one increase and one decrease of flow and heating power each are presented in Figures 4.22-4.25. The focused cases are representative of all explored dynamic cases. The main text figures also put more focus on the comparisons in the second half of the reactor (inserts 9-11), where temperature variations are higher. The first half of the reactor is heat transfer limited, and the temperature variations are generally small. Validation for all sensors in the reactor for a full set of dynamic cases is given in the Appendix B.2.

In flow increase cases, as illustrated by Figure 4.22, the reactor response is characterized by fast initial temperature drop lasting about 5 minutes. The abruptly higher reaction rates immediately cause a temperature drop within the reactor. This is followed by a slow convergence towards the new value. Flow decrease in Figure 4.22 shows that the change is limited at reactor outlet due to the locally higher wall heat capacity, which is explained in section 4.3.3. A longer stabilization time is expected in downstream positions. However, the local wall thermal capacity likely has a high influence due to observed differences between flow increase and decrease.

The simulations match the experiments well in regions where the reaction rate is heat transfer limited in flow variation cases. The simulated temperature change is faster than measured near the outlet region. The simulated response is instantaneous, and majority of the change happens within the first two minutes. The following stabilization time is therefore shorter, particularly in the flow increase cases. The simulated temperature change rate then decreases to match more closely with the experiments.

The culprit of simulated fast temperature response is likely in the numerical approach. The pressure and velocity are coupled by the Ergun equation, and the changes are not gradual as in reality, but instantaneous. In the experiments, the flow velocity is affected the back pressure regulator, which in turn is influenced by

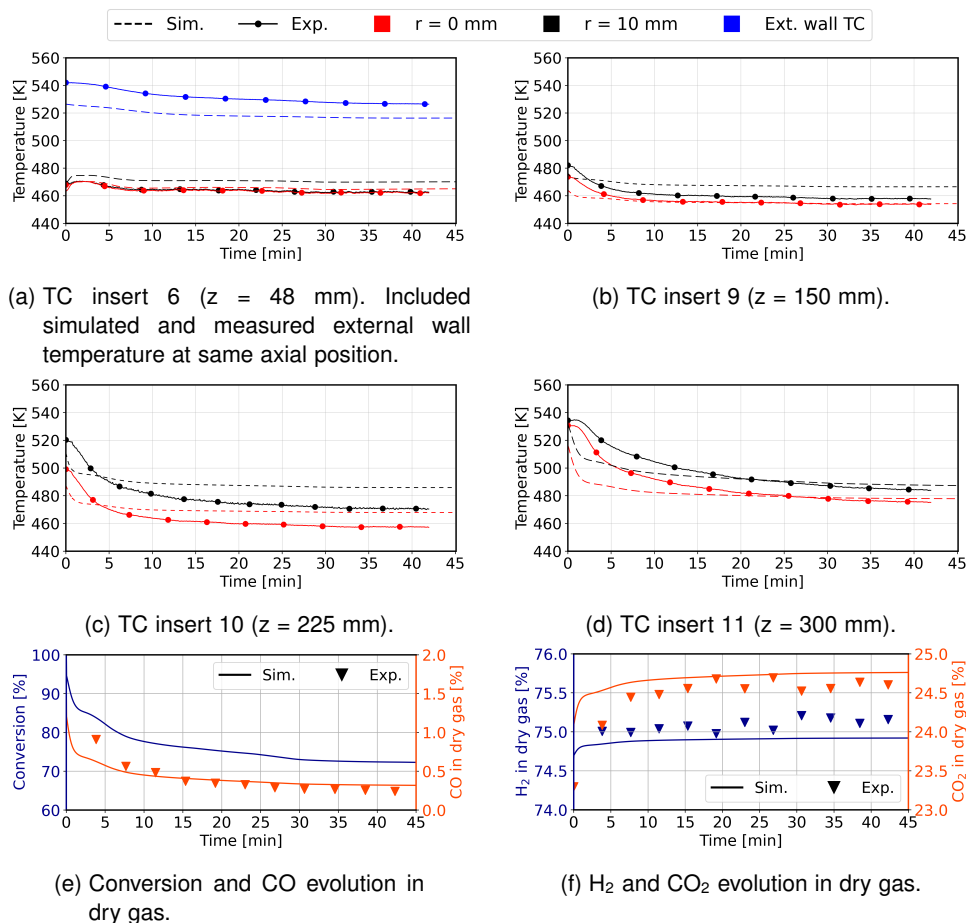


Figure 4.22.: Measured and simulated transient response in temperature and dry gas composition evolution for validation case: reactant flow increase $W_{cat.}/F_{CH_3OH}$ 200-120 kg s mol⁻¹ at $P_{el,in} = 187$ W.

expanding gas as reactions proceed. This interaction cannot be correctly represented by the Ergun equation.

The validations of dry gas composition also show that the experimental selectivity trends are well matched by the simulations. The simulated methanol conversion was calculated by dividing the reacted methanol molar flow by its inlet molar flow: $X_{CH_3OH} = (\dot{n}_{CH_3OH,in} - \dot{n}_{CH_3OH,out})/\dot{n}_{CH_3OH,in}$. The overly fast initial response seen in the temperature comparisons during the first minute is also visible here, particularly in the flow increase case. The trends for H_2 , CO_2 , and CO concentrations are also predicted well in time.

The variations of reactor heating power produce great matches between simulations and experiments. The trends in Figures 4.24 and 4.25 and their durations are captured

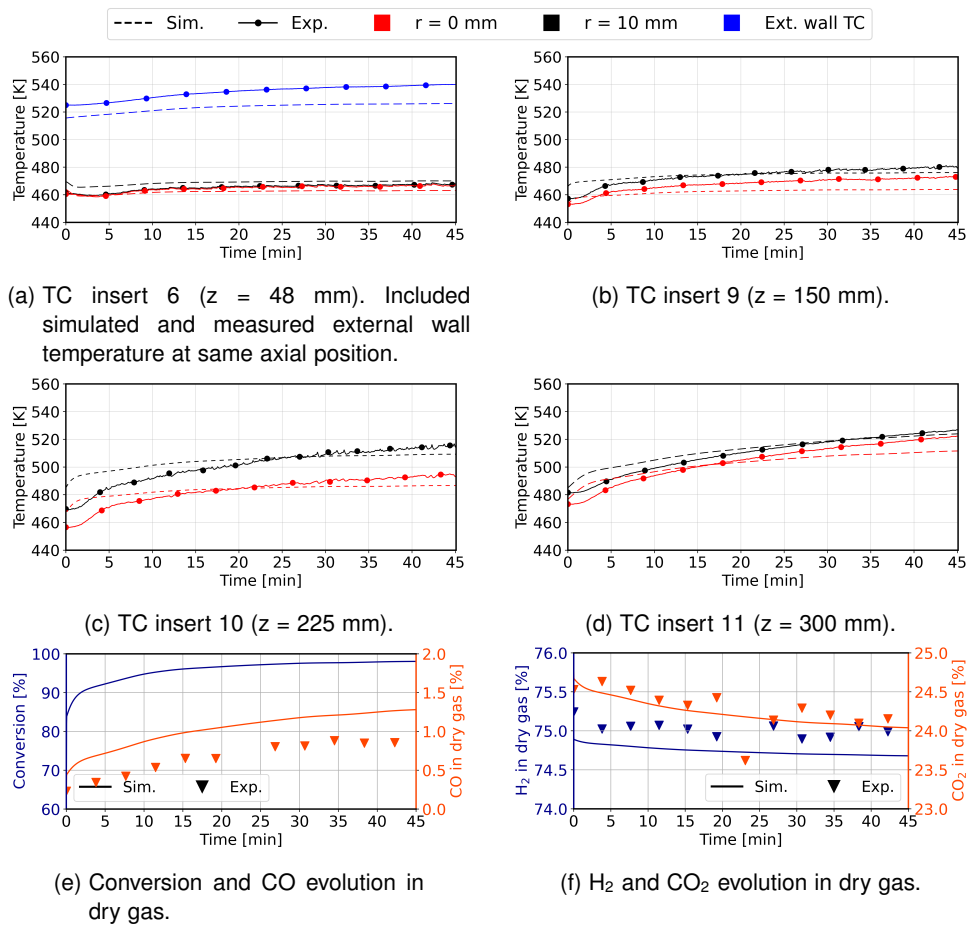


Figure 4.23.: Measured and simulated transient response in temperature and dry gas composition evolution for validation case: reactant flow decrease $W_{cat.}/F_{CH_3OH}$ 120-200 kg s mol⁻¹ at $P_{el,in} = 187$ W.

by the model in all reactor zones. The simulations shows a more moderate response to heat variations than to flow changes, which also corresponds with the measurements.

The temperature difference between inner ($r = 0$ mm) and outer ($r = 10$ mm) thermocouple generally stays similar during transients. In few instances, the difference noticeably varies and the simulation is able to capture it. Figures 4.22d, 4.24c, and 4.25c show this agreement. This also suggests the ability for accurate adaptation of effective radial thermal conductivity λ_{er} parameter in time.

The outlet CO concentration closely matches the experimental data in heat variation cases. Figures 4.24 and 4.25 show excellent agreement in both trends and predicted values.

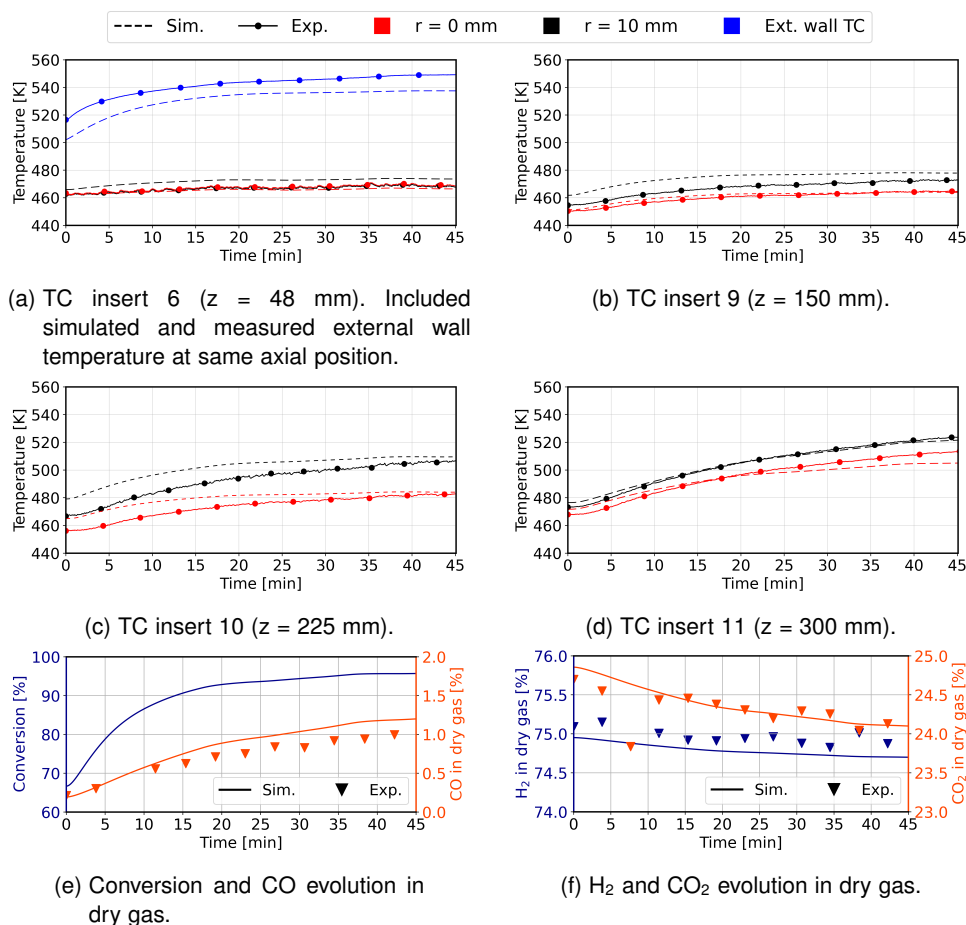


Figure 4.24.: Measured and simulated transient response in temperature and dry gas composition evolution for validation case: heating increase $P_{el,in}$ 150-224 W at $W_{cat.}/F_{CH_3OH} = 150 \text{ kg s mol}^{-1}$.

4.5. Discussion

The dynamic 2D model is successfully validated. The results show the model's ability to reasonably well predict internal temperature in time, and very well predict the CO selectivity in time. The selectivity in time is the most critical parameter for reformer combination with PEM fuel cells. The model is therefore applicable for unsteady reactor design tasks.

The present study foremost exposes the high influence of external heat transfer non-uniformities on reactor performance in both steady and transient regimes. The experimental measurements can be significantly clouded by various practical elements, which could be present on larger scales as well. The reactor-specific heat transfer

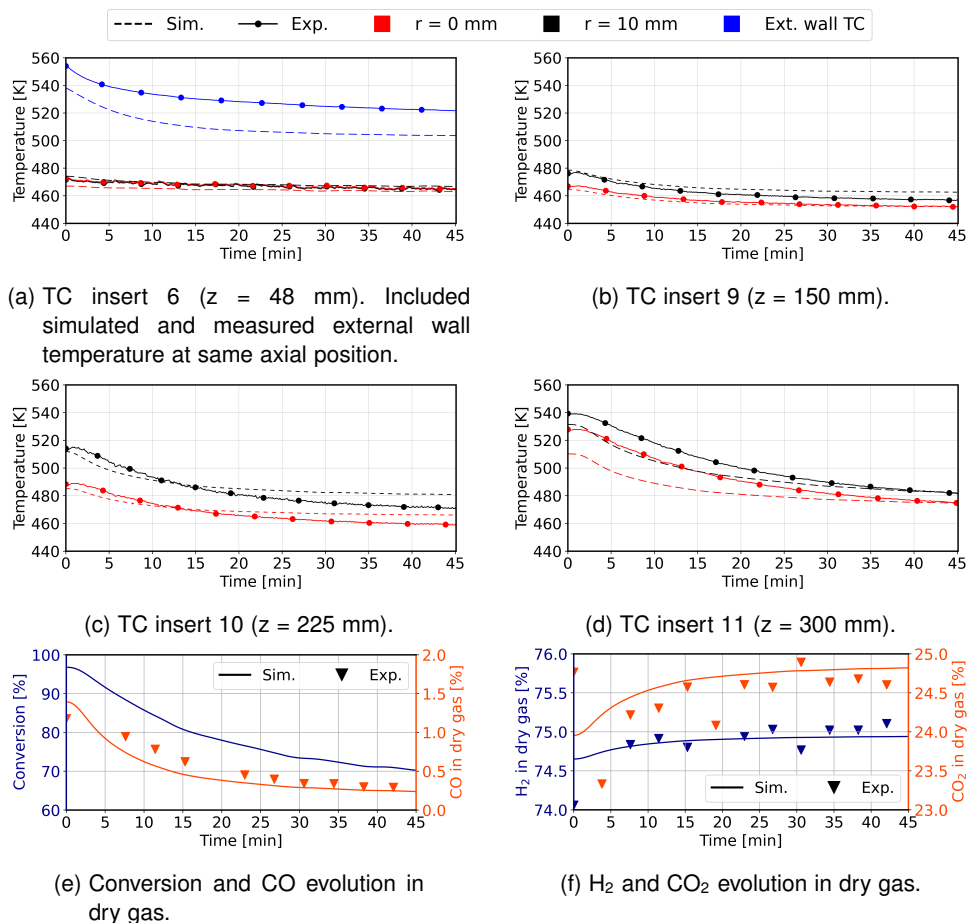


Figure 4.25.: Measured and simulated transient response in temperature and dry gas composition evolution for validation case: heating decrease $P_{el,in}$ 224-150 W at $W_{cat.}/F_{CH_3OH} = 150 \text{ kg s mol}^{-1}$.

characteristics can also affect the model precision. These characteristics in their effect proved to be as important as the choice of numerical correlations. The resulting implication is that the reactor design procedures should account for external heat transfer features.

Traditional shell-and-tube heat exchangers have multiple potential sources of heat supply non-uniformities. In steady state operation heat losses alter the flue gas temperature, which affects the heat supply for the reactions. Maintaining a steady inlet feed temperature can be challenging in practice, which affects both steady and dynamic reactor operation. The transient predictions may be affected by local variations of wall c_p caused by the baffle plates that support the tube bundles. These non-uniformities warrant further investigation into gravity of their effect in practice.

A key element in the presently used numerical model are the numerous sources of uncertainty. First are the multiple added modification factors for validation. They often cannot be directly measured, and in this study many are produced iteratively. The second source are a number of used semi-empirical correlations. This is amplified by the 2D pseudo-homogeneous nature of the model which introduces effective parameters such as D_{er} and λ_{er} . Third are the assumed uniformities in the model that are not necessarily true in reality. These are catalyst pellet size, ideal interfaces between active and passive zones, and uniform bed packing density which in reality is locally altered by the thermocouple inserts. The model agrees with measurements despite all assumptions. It is also likely that the assumptions are valid outside of the investigated parameter range, but the range of its validity is uncertain.

The present validity range is determined by process variables and reactor geometry. Since process variables were determined by the equipment capabilities, both aspects require a different experimental setup(s) to quantify the validity range. With respect to geometry, the uncertainty is situated in the effective radial transport parameters. Moghaddam et al. [195] show a dependency of λ_{er} on the reactor length. Moreover, the present study readily assumes that expressions for D_{er} , λ_{er} , h_t are valid in the transient regime. The assumption holds true in the present case, but it should ideally be explored individually in a separate study.

The invasive measurement technique with sensor inserts was expectedly shown influential on the experiment in practice. Radial insertion of multiple inserts at the zone of interest alters the zone activity and its heating. Alternatively, the sensors can be inserted in the axial direction. The bed packing is then uniform in axial direction, outer reactor surface is smooth, and heat conduction along the insert is decreased. However, axial inserts are significantly longer and likely thicker. They can bend more easily, or if they are thicker, displace enough catalyst to locally decrease the activity. Experimentally it is also difficult to precisely control individual parameters. For these reasons, suggested alternative approach is validation via high fidelity CFD models.

The follow-up to this work would be reactor scale-up, with the experimental part as the main hurdle. Experimental validation at larger scale should employ steam or flue-gas heating in a tube-and-shell heat exchanger. This would enable the study of industrially relevant thermal non-uniformities. On the modelling side, scale-up remains computationally efficient under the common assumption of identical tube behaviour. This is done by again simulating a single representative tube and preserves the existing model structure. The approach is demonstrated in the original steady state model [262]. The validity of identical tube behaviour could be further investigated, but requires a dedicated experimental study.

Finally, the present study occupies a distinct position within the fixed bed reactor literature. Some conclusions are shared with previous laboratory-scale experimental studies such as the importance of heat losses in experiments and modelling [281, 282], and noted influence of invasive measurement techniques [283]. The difference from previous studies stems from the primary objectives which is typically centred on process intensification [282, 284], scale-up [282, 283, 285], or the effects of reactor geometry and operating conditions [281, 283, 286]. In contrast, the present work is explicitly aimed at demonstrating that a practical level of model fidelity can reliably

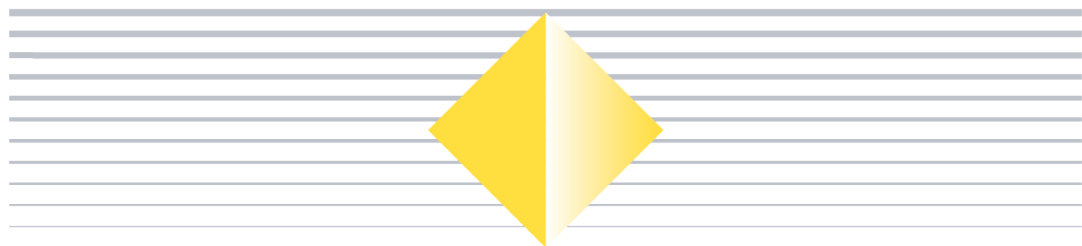
support unsteady reactor design. This contribution extends beyond the validation of a particular model. The study establishes and validates a general methodology for developing predictive reactor models, providing a framework that can be transferred to a wide range of fixed-bed reactor systems and reaction chemistries.

4.6. Conclusions and outlook

A dynamic 2D pseudo-homogeneous model for methanol steam reforming in a fixed bed reactor was presented and experimentally validated against temperature and CO concentration data. The developed model is an efficient contribution to the design toolkit of reactor designers for fixed bed reactors in transient regimes. The study shows that capturing external heat transfer effects is critical in validation studies. Their inclusion in reactor design tasks is also recommended, if known to the designer. The presented model has a relatively large number of parameters with uncertainty. The 2D model was shown valid for transient predictions. The temperatures sensor data was predicted within 15 K. The simulated flow variation events predict the temperature change around 4 minutes earlier than in reality. The simulated heat variation events follow the experimental trends closely. The CO concentration in the product is predicted exceptionally well in all cases, with the difference being up to 0.4% of CO in the reformat dry gas. The predicted CO trends very closely follow the experimental values. The validity outside of the explored geometry and process variable space may be strengthened with further experiments.

The used invasive experimental techniques proved effective, but have shortcomings. Sensor inserts interfered with the packed bed and reactor heating, and their presence influenced the measured data. The interferences were individually identified, presented, and then addressed a posteriori in the model. The invasive approach is thus not recommended for future studies, unless no other approach is possible. Alternatively, CFD based approach is possible for validations using detailed transient internal flow field variables.

The transient characteristics were adequately captured by the model, most accurately in cases with reactor heating manipulation. The model is therefore fit for transient reactor design tasks in methanol steam reforming. By modifying reaction kinetics the study also becomes relevant to other on-demand chemical conversion processes in packed bed reactors, positively helping usher in a hydrogen based future.



5

Conclusions and future outlook

In the long run we are all dead.

John Maynard Keynes

The key findings highlight that dynamic reactor design requires case-specific objectives, suitable models, sufficiently fast analytical instruments, and careful consideration of external heat supply to address the research questions. External heating effects, especially reactor/support heat capacity and heating system response, are likely more limiting than internal packed-bed heat transfer. The conclusions also point to future work toward novel reactor/catalyst arrangements, catalyst lifetime under dynamic operation, and broader maritime chemical reactor integration.

5.1. Conclusions

The main conclusions of this dissertation are laid out in the answers to posed research questions:

RQ.1 What are the emerging considerations in analysis and prediction of dynamically operated fixed bed methanol reforming reactors, compared to steady state operation?

The analysis of general fixed bed reactor dynamics in Chapter 2 reveals a need for several added considerations in reactor design, operation, and monitoring. First are the causes of dynamics since they determine the analysis objectives. They also influence the expected frequency of transient operation, and thus establish the importance and the required level of detail for such analysis. The analysis procedure with its objectives and performance metrics must be defined, likely for each specific case.

Numerical tools are an important part of reactor analysis and design. Chapter 2 finds that suitable dynamic models are not widely available. Prior to the analysis and design, one must consider which tools to use for the task. Ideally, a suitable and specific model is developed or adjusted by the user. Alternatively one may choose an available model (package) and compromise on either model fidelity or computational time.

The analytical instrumentation for transient state is also more complex than in steady state. The sampling rate becomes a decisive criterion and narrows down suitable techniques. Chapter 2 finds that a combination of techniques is more likely than relying on a single technique. The analytical approach is crucial for process monitoring, but also validation of physics-based dynamic models or training data input for data-based models. All of this adds to required scrutiny in technique selection.

RQ.2 What is the theoretical minimum for transient time of a fixed bed methanol reforming reactor?

The numerical analysis of internal reactor dynamics in Chapter 3 produced transient times up to ≈ 60 seconds for typical tube diameters (2-3 cm). These transient times are caused solely by radial heat and mass transfer within the packed bed. Such transient duration should not be overly limiting in a reformed methanol fuel cell system.

The analysis suggests that the speed of internal heat transfer is not the cause of slow transient times stated by methanol reformer manufacturers (5-45 min). Instead, external heat supply is likely the cause of slow load changes. The internal limitations contribute by amplifying the slow rate of external heat supply change, but are not the sole cause.

RQ.3 What are the limiting external factors to the transient time of a fixed bed methanol reforming reactor?

The experimental and modelling work in Chapter 4 uncovers several external heating influences on the transient regime. These are the heat capacity of

reactor and its support structure, axial heat loss profile, axial variations in heat supply, and stability of inlet reactant temperature. These factors are all present in practice, and their extent is seemingly specific to the reactor and heat supply system.

The highest influence in conducted experiments is attributed to the reactor structure heat capacity. This significantly prolonged the duration of transient events even in single, well-insulated laboratory scale reactor tube. The effects can be expected in practice, perhaps even to a higher extent due to the shell structure of shell-and-tube heat exchangers.

The reactor heating type also expectedly influences the transient times. The experiments included only electric heating. Heating arrangements with a medium such as steam or flue gas must also account for the transient response of the heating system itself. Moreover, each heating type produces a characteristic axial heat profile, resulting in different transient characteristics.

In addition to answering the research question, additional conclusions are drawn through this dissertation. Namely, conclusions around the developed dynamic model. The modelling aspect on its own is sufficiently complex, especially given the conclusions stemming from the model results.

First, the research demonstrates a working example of a fixed bed reactor dynamic model balanced for accuracy and computational efficiency. These features are essential in numerical tools meant for iterative use in design tasks. The inclusion of dynamic analyses is therefore brought closer to fixed bed reactor design.

A step further in dynamic modelling fidelity would be the pressure-velocity coupling. In the current formulation, the model accuracy in time is the lowest when feed changes. This is attributed to the pressure drop from the Ergun equation and consequent exclusion of gas expansion with conversion to hydrogen. However, this addition is likely situational since the model predicts transient event durations well enough as is. The added computational effort is worth only if higher accuracy is needed.

Despite a successful demonstration of the model in this dissertation, the difficulty in dynamic model development is expected to vary by case. The design targets and intended use is the motivator for custom dynamic models, which makes their development more diverse and difficult. Furthermore, it increases the difficulty in experimental data gathering for validation. The wider adoption of dynamic models also depends on the practicality of their development.

5.2. Outlook

Future work

Many recent advances in catalytic continuous-flow reactors are oriented towards creating uniform and ideal conditions. Research in monolith reactors, microreactors, or catalytic foam structures aim towards an isothermal reactor with minimal pressure drop. The same problems are also the core of classic methanol steam reforming. A logical continuation of present work would be in the direction of novel reactor

catalyst arrangements. Dynamic MSR in such reactors opens questions on product composition, modelling, control, and system integration.

The catalyst lifetime under dynamic conditions is another topic relevant for wider technology adoption. The load cycles might trigger different catalyst deactivation mechanisms also at different rates than in steady state. Understanding those relationships is especially important in transport applications for maintenance intervals or lifecycle assessments. The best results for catalyst degradation studies are expected through joint efforts of numerical and experimental approaches.

Maritime applications of chemical reactors

As the maritime sector continues to defossilize, chemical engineering is likely to become increasingly embedded in ship design and operation. Technologies such as ammonia cracking, LNG pre-reforming, carbon capture, and exhaust aftertreatment all rely on chemical reactor systems that must operate reliably in demanding onboard environments. Unlike conventional mass-produced industrial equipment, the components in maritime systems are often highly customized, creating opportunities for innovation, design iteration, and integration with other onboard processes in terms of heat or electrical energy.

The shift towards chemical engineering introduces significant technical and organizational challenges. The industry will need specialists capable of designing maritime-specific reactor technologies, developing suitable catalysts and control systems, and working closely with naval architects to integrate these processes into ship design. Whether regarded as an opportunity or an added layer of complexity, the trend makes it clear that chemical engineering will become an increasingly central element of future maritime systems.

Maritime transport can serve as an important stepping stone toward decarbonization in other sectors, particularly road transport, which accounts for roughly 70% of transport-related greenhouse gas emissions. The maritime industry provides a valuable testing ground for new fuel systems and chemical process technologies since ships are often custom-built and allow for greater design flexibility and experimentation. In contrast, road transport relies heavily on large-scale mass production. This technology must be highly optimized and reliable before the widespread deployment. Maritime applications could offer an intermediate scale for developing and validating smaller-scale chemical engineering systems, especially as transport sectors move away from conventional internal combustion engines toward alternative fuel and reactor-based solutions.

Bibliography

- [1] *Paris Agreement*. UN Treaty. United Nations, Dec. 2015. URL: https://treaties.un.org/pages/ViewDetails.aspx?src=TREATY&mtdsg_no=XXVII-7-d&chapter=27&clang=_en (visited on 04/11/2022).
- [2] European Commission. *The European Green Deal (Communication)*. COM (2019) 640 final. 2019. URL: <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex:52019DC0640>.
- [3] Copernicus Climate Change Service. *2025 Global Climate Highlights*. ECMWF Communication Section, 2026. DOI: <https://doi.org/10.24381/b3nm-p354>.
- [4] Climate Analytics and NewClimate Institute. *Warming Projections Global Update*. Climate Action Tracker, 2025. URL: <https://climateactiontracker.org/publications/warming-projections-global-update-2025/>.
- [5] Rhode, R. *Global Temperature Report for 2025*. Berkeley Earth, 2026. URL: <https://berkeleyearth.org/global-temperature-report-for-2025/>.
- [6] Meinshausen, M., Lewis, J., McGlade, C., Gutschow, J., Nicholls, Z., Burdon, R., Cozzi, L. and Hackmann, B. 'Realization of Paris Agreement pledges may limit warming just below 2 °C'. In: *Nature* 604.7905 (Apr. 2022), pp. 304–309. ISSN: 1476-4687. DOI: 10.1038/s41586-022-04553-z.
- [7] Jiang, J., Shi, S. and Raftery, A. E. 'Mitigation efforts to reduce carbon dioxide emissions and meet the Paris Agreement have been offset by economic growth'. In: *Communications Earth & Environment* 6.1 (Oct. 2025). ISSN: 2662-4435. DOI: 10.1038/s43247-025-02743-x.
- [8] Climate Watch. *Historical GHG Emissions*. Accessed: 2026-03-26. 2026. URL: https://www.climatewatchdata.org/ghg-emissions?breakBy=sector&chartType=percentage&end_year=2023&start_year=1990.
- [9] Mertens, J., Breyer, C., Belmans, R., Gendron, C., Geoffron, P., Fischer, C., Du Fornel, E., Ledent, O., Lester, R., Nicholas, K. A., Megrelis, L., de Miranda, P. E. V., Paton, C., Prudhomme, A., Verwee, P., Sala, O., Webber, M. and Debackere, K. 'How energy and chemistry converge for a fossil-free future'. In: *iScience* 28.11 (Nov. 2025), p. 113787. ISSN: 2589-0042. DOI: 10.1016/j.isci.2025.113787.
- [10] Tian, X., An, C. and Chen, Z. 'The role of clean energy in achieving decarbonization of electricity generation, transportation, and heating sectors by 2050: A meta-analysis review'. In: *Renewable and Sustainable Energy Reviews* 182 (Aug. 2023), p. 113404. ISSN: 1364-0321. DOI: 10.1016/j.rser.2023.113404.
- [11] Gür, T. M. 'Review of electrical energy storage technologies, materials and systems: challenges and prospects for large-scale grid storage'. In: *Energy & Environmental Science* 11.10 (2018), pp. 2696–2767. ISSN: 1754-5706. DOI: 10.1039/c8ee01419a.

- [12] Reddy, V. J., Hariram, N. P., Maity, R., Ghazali, M. F. and Kumarasamy, S. 'Sustainable E-Fuels: Green Hydrogen, Methanol and Ammonia for Carbon-Neutral Transportation'. In: *World Electric Vehicle Journal* 14.12 (Dec. 2023), p. 349. ISSN: 2032-6653. DOI: 10.3390/wevj14120349.
- [13] Franco, A. and Giovannini, C. 'Routes for Hydrogen Introduction in the Industrial Hard-to-Abate Sectors for Promoting Energy Transition'. In: *Energies* 16.16 (Aug. 2023), p. 6098. ISSN: 1996-1073. DOI: 10.3390/en16166098.
- [14] Martin, J., Dimanchev, E. and Neumann, A. 'Carbon abatement costs for renewable fuels in hard-to-abate transport sectors'. In: *Advances in Applied Energy* 12 (Dec. 2023), p. 100156. ISSN: 2666-7924. DOI: 10.1016/j.adapen.2023.100156.
- [15] Mekonnin, A. S., Wacawiak, K., Humayun, M., Zhang, S. and Ullah, H. 'Hydrogen Storage Technology, and Its Challenges: A Review'. In: *Catalysts* 15.3 (Mar. 2025), p. 260. ISSN: 2073-4344. DOI: 10.3390/catal15030260.
- [16] Langmi, H. W., Engelbrecht, N., Modisha, P. M. and Bessarabov, D. 'Hydrogen storage'. In: *Electrochemical Power Sources: Fundamentals, Systems, and Applications*. Elsevier, 2022, pp. 455–486. ISBN: 9780128194249. DOI: 10.1016/b978-0-12-819424-9.00006-9.
- [17] Ulucan, T. H., Akhade, S. A., Ambalakatte, A., Autrey, T., Cairns, A., Chen, P., Cho, Y. W., Gallucci, F., Gao, W., Grinderslev, J. B., Grubel, K., Jensen, T. R., de Jongh, P. E., Kothandaraman, J., Lamb, K. E., Lee, Y.-S., Makhoulfi, C., Ngene, P., Olivier, P., Webb, C. J., Wegman, B., Wood, B. C. and Weidenthaler, C. 'Hydrogen storage in liquid hydrogen carriers: recent activities and new trends'. In: *Progress in Energy* 5.1 (Jan. 2023), p. 012004. ISSN: 2516-1083. DOI: 10.1088/2516-1083/acac5c.
- [18] Van Rheenen, E. S., Padding, J. T., Kana, A. A. and Visser, K. 'Comparative energy analysis of hydrogen carriers as energy source on ships'. In: *Journal of Marine Engineering & Technology* (Jan. 2025), pp. 1–15. ISSN: 2056-8487. DOI: 10.1080/20464177.2024.2448057.
- [19] Tabibian, S. S. and Sharifzadeh, M. 'Statistical and analytical investigation of methanol applications, production technologies, value-chain and economy with a special focus on renewable methanol'. In: *Renewable and Sustainable Energy Reviews* 179 (June 2023), p. 113281. ISSN: 1364-0321. DOI: 10.1016/j.rser.2023.113281.
- [20] International Energy Agency. *Ammonia Technology Roadmap*. Accessed: 2026-03-27. 2021. URL: <https://www.iea.org/reports/ammonia-technology-roadmap>.
- [21] International Energy Agency. *Global Hydrogen Review 2025*. Accessed: 2026-03-27. 2021. URL: <https://www.iea.org/reports/global-hydrogen-review-2025>.
- [22] Jin, C., Choi, J., Lee, C. and Kim, M. 'Sustainable Maritime Decarbonization: A Review of Hydrogen and Ammonia as Future Clean Marine Energies'. In: *Sustainability* 17.24 (Dec. 2025), p. 11364. ISSN: 2071-1050. DOI: 10.3390/su172411364.
- [23] Hoang, A. T., Chen, W.-H., López-Escalante, M. C., Guerrero-Pérez, M. O., Rodríguez-Castellón, E., Kowalski, J., Le, T. T., Bui, V. G. and Nguyen, X. P. 'Methanol for decarbonization of the maritime sector: From ideological strategy to practical solutions'. In: *Renewable and Sustainable Energy Reviews* 229 (Apr. 2026), p. 116638. ISSN: 1364-0321. DOI: 10.1016/j.rser.2025.116638.
- [24] Pugazhendhi, A., Bharathi, D., Aljohani, B. S., Aljohani, K., Kamarudin, S., Sekar, M. and Shanmuganathan, R. 'Sustainable ammonia production, storage, and transport technologies for clean energy applications'. In: *International Journal of Hydrogen Energy* 194 (Dec. 2025), p. 152504. ISSN: 0360-3199. DOI: 10.1016/j.ijhydene.2025.152504.

- [25] Chen, W., Xu, X., Cheng, H., Feng, J. and Li, W.-Y. 'Sustainable methanol production processes from coal and biomass: Low CO₂ emissions and high efficiency'. In: *Energy* 330 (Sept. 2025), p. 136978. ISSN: 0360-5442. DOI: 10.1016/j.energy.2025.136978.
- [26] Moioli, E. 'Process intensification and energy transition: A necessary coupling?' In: *Chemical Engineering and Processing - Process Intensification* 179 (Sept. 2022), p. 109097. ISSN: 0255-2701. DOI: 10.1016/j.cep.2022.109097.
- [27] CO₂ Everything. *Carbon Footprint: Freight, Shipping*. Accessed: 2026-04-01. 2026. URL: <https://www.co2everything.com/co2e-of/freight-shipping>.
- [28] Golbazi, M. and Archer, C. 'Impacts of maritime shipping on air pollution along the US&East Coast'. In: *Atmospheric Chemistry and Physics* 23.23 (Dec. 2023), pp. 15057–15075. ISSN: 1680-7324. DOI: 10.5194/acp-23-15057-2023.
- [29] Toscano, D. 'The Impact of Shipping on Air Quality in the Port Cities of the Mediterranean Area: A Review'. In: *Atmosphere* 14.7 (July 2023), p. 1180. ISSN: 2073-4433. DOI: 10.3390/atmos14071180.
- [30] Viana, M., Rizza, V., Tobías, A., Carr, E., Corbett, J., Sofiev, M., Karanasiou, A., Buonanno, G. and Fann, N. 'Estimated health impacts from maritime transport in the Mediterranean region and benefits from the use of cleaner fuels'. In: *Environment International* 138 (May 2020), p. 105670. ISSN: 0160-4120. DOI: 10.1016/j.envint.2020.105670.
- [31] International Maritime Organisation. *MARPOL Consolidated edition 2017*. 6th ed. ISBN:9789280116571. International Maritime Organisation, 2017.
- [32] International Maritime Organization. *IMO 2020*. Accessed: 2026-04-01. 2020. URL: <https://www.imo.org/en/mediacentre/hottopics/pages/sulphur-2020.aspx>.
- [33] International Maritime Organization. *The IMO Net-Zero Framework*. Accessed: 2026-04-01. 2025. URL: <https://www.imo.org/en/mediacentre/hottopics/pages/faqs-the-imo-net-zero-framework.aspx>.
- [34] Harahap, F., Nurdawati, A., Conti, D., Leduc, S. and Urban, F. 'Renewable marine fuel production for decarbonised maritime shipping: Pathways, policy measures and transition dynamics'. In: *Journal of Cleaner Production* 415 (Aug. 2023), p. 137906. ISSN: 0959-6526. DOI: 10.1016/j.jclepro.2023.137906.
- [35] Issa, M., Ilinca, A. and Martini, F. 'Ship Energy Efficiency and Maritime Sector Initiatives to Reduce Carbon Emissions'. In: *Energies* 15.21 (Oct. 2022), p. 7910. ISSN: 1996-1073. DOI: 10.3390/en15217910.
- [36] Karvounis, P., Tsoumpris, C., Boulougouris, E. and Theotokatos, G. 'Recent advances in sustainable and safe marine engine operation with alternative fuels'. In: *Frontiers in Mechanical Engineering* 8 (Nov. 2022). ISSN: 2297-3079. DOI: 10.3389/fmech.2022.994942.
- [37] Van Biert, L. and Visser, K. 'Fuel cells systems for sustainable ships'. In: *Sustainable Energy Systems on Ships*. Elsevier, 2022, pp. 81–121. ISBN: 9780128244715. DOI: 10.1016/b978-0-12-824471-5.00010-4.
- [38] Xing, H., Stuart, C., Spence, S. and Chen, H. 'Fuel Cell Power Systems for Maritime Applications: Progress and Perspectives'. In: *Sustainability* 13.3 (Jan. 2021), p. 1213. ISSN: 2071-1050. DOI: 10.3390/su13031213.

- [39] Zwaginga, J., Lagemann, B., Erikstad, S. O. and Pruyn, J. 'Optimal Ship Fuel Selection under Life Cycle Uncertainty'. In: *Sustainability* 16.5 (Feb. 2024), p. 1947. ISSN: 2071-1050. DOI: [10.3390/su16051947](https://doi.org/10.3390/su16051947).
- [40] Zwaginga, J. J. and Pruyn, J. F. J. 'An Evaluation of Suitable Methods to Deal with Deep Uncertainty Caused by the Energy Transition in Ship Design'. In: *SNAME 14th International Marine Design Conference*. IMDC22. SNAME, June 2022. DOI: [10.5957/imdc-2022-252](https://doi.org/10.5957/imdc-2022-252).
- [41] Sagin, S., Haichenia, O., Karianskyi, S., Kuropyatnyk, O., Razinkin, R., Sagin, A. and Volkov, O. 'Improving Green Shipping by Using Alternative Fuels in Ship Diesel Engines'. In: *Journal of Marine Science and Engineering* 13.3 (Mar. 2025), p. 589. ISSN: 2077-1312. DOI: [10.3390/jmse13030589](https://doi.org/10.3390/jmse13030589).
- [42] La Colla, E., van Biert, L., **Grenko, B.** and Loeff, G. 'Experimental and modelling studies on HVO-methanol mixtures separation for superyachts applications'. In: *Conference Proceedings of INEC*. Institute of Marine Engineering, Science and Technology (IMarEST), Oct. 2024. DOI: <https://doi.org/10.24868/11193>.
- [43] Jacobs, I., de Vos, P., Seykens, X. L. J. and Negenborn, R. R. 'A Short Review of Ammonia Compression Ignition Engines for an SOFC-ICE Power Plant for Shipping'. In: *Transport Transitions: Advancing Sustainable and Inclusive Mobility*. Springer Nature Switzerland, 2025, pp. 465–471. ISBN: 9783031894442. DOI: [10.1007/978-3-031-89444-2_68](https://doi.org/10.1007/978-3-031-89444-2_68).
- [44] Kiouranakis, K. I., de Vos, P., Zoumpourlos, K., Coraddu, A. and Geertsma, R. 'Methanol for heavy-duty internal combustion engines: Review of experimental studies and combustion strategies'. In: *Renewable and Sustainable Energy Reviews* 214 (May 2025), p. 115529. ISSN: 1364-0321. DOI: [10.1016/j.rser.2025.115529](https://doi.org/10.1016/j.rser.2025.115529).
- [45] Zoumpourlos, K., Bekdemir, C., Geertsma, R., van de Ketterij, R. and Coraddu, A. 'Methanol sprays in marine engines: CFD modelling of port fuel injection systems'. In: *Journal of Marine Engineering & Technology* (Mar. 2025), pp. 1–17. ISSN: 2056-8487. DOI: [10.1080/20464177.2025.2473184](https://doi.org/10.1080/20464177.2025.2473184).
- [46] Vollbrandt, J., Coraddu, A. and Geertsma, R. 'Transient performance of alternatively fueled internal combustion engines for naval applications'. In: *Conference Proceedings of INEC*. Institute of Marine Engineering, Science and Technology (IMarEST), Nov. 2023. DOI: <https://doi.org/10.24868/11074>.
- [47] Vollbrandt, J., Merts, M., Geertsma, R. and Coraddu, A. 'Dynamic Performance and Control-Oriented Modeling of Marine Methanol Dual-Fuel Engines'. In: (2026). DOI: [10.2139/ssrn.6448302](https://doi.org/10.2139/ssrn.6448302).
- [48] Zwaginga, J., Stroo, K. and Kana, A. 'Exploring market uncertainty in early ship design'. In: *International Journal of Naval Architecture and Ocean Engineering* 13 (2021), pp. 352–366. ISSN: 2092-6782. DOI: [10.1016/j.ijnaoe.2021.04.003](https://doi.org/10.1016/j.ijnaoe.2021.04.003).
- [49] Souflis-Rigas, A., Pruyn, J. and Kana, A. A. 'Characterization of methanol power and energy systems uncertainties and evaluation of their impact on layout design'. In: *Journal of Marine Engineering & Technology* (Feb. 2025), pp. 1–13. ISSN: 2056-8487. DOI: [10.1080/20464177.2025.2462387](https://doi.org/10.1080/20464177.2025.2462387).
- [50] Souflis - Rigas, A., Pruyn, J. and Kana, A. 'A bi-objective Markov decision process approach to explore retrofit design pathways for maritime decarbonization'. In: (2025). DOI: [10.5281/ZENODO.17344816](https://doi.org/10.5281/ZENODO.17344816).

- [51] Van Rheenen, E., Scheffers, E., Zwaginga, J. and Visser, K. 'Hazard Identification of Hydrogen-Based Alternative Fuels Onboard Ships'. In: *Sustainability* 15.24 (Dec. 2023), p. 16818. ISSN: 2071-1050. DOI: 10.3390/su152416818.
- [52] Van Rheenen, E. S., Padding, J. T., Slootweg, J. C. and Visser, K. 'Hydrogen carriers for zero-emission ship propulsion using PEM fuel cells: an evaluation'. In: *Journal of Marine Engineering & Technology* 23.3 (Nov. 2023), pp. 166–183. ISSN: 2056-8487. DOI: 10.1080/20464177.2023.2282691.
- [53] Van Benten, M., Padding, J. and Schott, D. 'Experimental characterization of granular sodium borohydride under varying operational conditions across flow regimes'. In: *Powder Technology* 469 (Feb. 2026), p. 121739. ISSN: 0032-5910. DOI: 10.1016/j.powtec.2025.121739.
- [54] Van Benten, M., Padding, J. and Schott, D. 'Circular bunkering for maritime vessels using sodium borohydride'. In: *Renewable and Sustainable Energy Reviews* 223 (Nov. 2025), p. 116039. ISSN: 1364-0321. DOI: 10.1016/j.rser.2025.116039.
- [55] Postma, J. R. T., Habibi, P., Dey, P., Vlugt, T. J. H., Moulton, O. A. and Padding, J. T. 'Densities, Viscosities, and Self-Diffusion Coefficients of Aqueous Mixtures of NaBH₄, NaB(OH)₄, and NaOH Using the BH₄ Delft Force Field (DFF/BH₄)'. In: *Journal of Chemical & Engineering Data* 70.5 (Apr. 2025), pp. 1830–1842. ISSN: 1520-5134. DOI: 10.1021/acs.jced.4c00629.
- [56] Latorre, A., Soeiro, T. B., Geertsma, R., Coraddu, A. and Polinder, H. 'Shipboard DC Systems A Critical Overview: Challenges in Primary Distribution, Power-Electronics-Based Protection, and Power Scalability'. In: *IEEE Open Journal of the Industrial Electronics Society* 4 (2023), pp. 259–286. ISSN: 2644-1284. DOI: 10.1109/ojies.2023.3294999.
- [57] Mylonopoulos, F., Coraddu, A. and Polinder, H. 'A holistic framework for optimal ship energy system design, including operational requirements, lifetime cost, and vessel stability'. In: *Energy Conversion and Management: X* 30 (May 2026). ISSN: 2590-1745. DOI: 10.1016/j.ecmx.2026.101685.
- [58] Coraddu, A., Tamburello, S., Löffler, C., Ceyhan, H. E., van Biert, L. and Oneto, L. 'State-of-Art Energy Management Strategies for Hybrid Fuel Cell Applications for Ships'. In: *Fuel Cell and Hydrogen Technologies in Maritime Transportation*. Springer Nature Switzerland, 2025, pp. 121–178. ISBN: 9783031861109. DOI: 10.1007/978-3-031-86110-9_6.
- [59] Löffler, C., Geertsma, R., Polinder, H. and Coraddu, A. 'Energy management for hybrid and fully electric vessels via a multi-objective Equivalent Consumption Minimization Strategy'. In: *Energy Conversion and Management* 343 (Nov. 2025), p. 120150. ISSN: 0196-8904. DOI: 10.1016/j.enconman.2025.120150.
- [60] Kopka, T., Latorre, A., Coraddu, A. and Polinder, H. 'Energy-Based Voltage Stabilization in DC Shipboard Power Systems With Dual Loop Control'. In: *IEEE Access* 13 (2025), pp. 117105–117118. ISSN: 2169-3536. DOI: 10.1109/access.2025.3586382.
- [61] e1 Marine. *Marine Hydrogen Generators*. Accessed: 2026-04-17. URL: <https://www.e1marine.com/products>.
- [62] MMM Energy. *M Reformer Hydrogen Generator*. Accessed: 2025-07-25. URL: <https://www.methanolreformer.com/>.

- [63] Freudenberg. *Ship Lengths Ahead – Worlds first type-approved methanol-powered fuel cell system: RINA awards Freudenberg e-Power Systems*. Accessed: 2026-04-17. URL: <https://www.freudenberg.com/en/company/press-media/news-detail/2022-09-08-ship-lengths-ahead>.
- [64] PowerCell Group. *M2Power 250*. Accessed: 2026-04-17. URL: <https://powercellgroup.com/solutions/m2power-250/>.
- [65] Tamburello, S., van Biert, L. and Coraddu, A. 'Durability and prognostic modelling of low-temperature polymer electrolyte membrane fuel cells in maritime applications: A review'. In: *Energy Conversion and Management: X* 30 (May 2026), p. 101576. ISSN: 2590-1745. DOI: 10.1016/j.ecmx.2026.101576.
- [66] Broer, A., Polinder, H. and van Biert, L. 'Polymer electrolyte membrane fuel cell degradation in ships Review of degradation mechanisms and research gaps'. In: *Journal of Power Sources* 640 (June 2025), p. 236678. ISSN: 0378-7753. DOI: 10.1016/j.jpowsour.2025.236678.
- [67] Broer, A., Polinder, H. and van Biert, L. 'Salinity and volatile organic compounds in engine room air of a sea-going vessel'. In: *Journal of Marine Engineering & Technology* (Nov. 2025), pp. 1–9. ISSN: 2056-8487. DOI: 10.1080/20464177.2025.2578930.
- [68] Van Veldhuizen, B., Zera, E., van Biert, L., Modena, S., Visser, K. and Aravind, P. 'Experimental evaluation of a solid oxide fuel cell system exposed to inclinations and accelerations by ship motions'. In: *Journal of Power Sources* 585 (Nov. 2023), p. 233634. ISSN: 0378-7753. DOI: 10.1016/j.jpowsour.2023.233634.
- [69] Goselink, N., Boersma, B. and van Biert, L. 'Evaluating the thermodynamic performance of an SOFC and PEMFC combined system'. In: *Energy Conversion and Management* 354 (Apr. 2026), p. 121152. ISSN: 0196-8904. DOI: 10.1016/j.enconman.2026.121152.
- [70] Goselink, N., Boersma, B. and Van Biert, L. 'Thermodynamic Evaluation of a Combined SOFC-PEMFC Cycle System'. In: *Modelling and Optimisation of Ship Energy Systems 2023* (Dec. 2023). ISSN: 2950-4295. DOI: 10.59490/moses.2023.659.
- [71] Van Veldhuizen, B., van Biert, L., Ünlübayir, C., Visser, K., Hopman, J. and Aravind, P. 'Component sizing and dynamic simulation of a low-emission power plant for cruise ships with solid oxide fuel cells'. In: *Energy Conversion and Management* 326 (Feb. 2025), p. 119477. ISSN: 0196-8904. DOI: 10.1016/j.enconman.2024.119477.
- [72] Van Veldhuizen, B., van Biert, L., Amladi, A., Woudstra, T., Visser, K. and Aravind, P. 'The effects of fuel type and cathode off-gas recirculation on combined heat and power generation of marine SOFC systems'. In: *Energy Conversion and Management* 276 (Jan. 2023), p. 116498. ISSN: 0196-8904. DOI: 10.1016/j.enconman.2022.116498.
- [73] Nunes, L. J. R. 'Renewable Methanol as an Agent for the Decarbonization of Maritime Logistic Systems: A Review'. In: *Future Transportation* 5.2 (May 2025), p. 54. ISSN: 2673-7590. DOI: 10.3390/futuretransp5020054.
- [74] Macheli, L., Mukeru, B. M., Duma, Z., Patel, B. and Jewell, L. L. 'Not all CO₂ is equal: Source-specific constraints and viability trade-offs in methanol synthesis from industrial emissions'. In: *Renewable and Sustainable Energy Reviews* 232 (May 2026), p. 116808. ISSN: 1364-0321. DOI: 10.1016/j.rser.2026.116808.
- [75] RoodeGutzmer, Q. I., Kaiser, D. and Bertau, M. 'Renewable Methanol Synthesis'. In: *ChemBioEng Reviews* 6.6 (Dec. 2019), pp. 209–236. ISSN: 2196-9744. DOI: 10.1002/cben.201900012.

- [76] Worku, A. K., Ayele, D. W., Deepak, D. B., Gebreyohannes, A. Y., Agegnehu, S. D. and Kolhe, M. L. 'Recent Advances and Challenges of Hydrogen Production Technologies via Renewable Energy Sources'. In: *Advanced Energy and Sustainability Research* 5.5 (Feb. 2024). ISSN: 2699-9412. DOI: [10.1002/aesr.202300273](https://doi.org/10.1002/aesr.202300273).
- [77] Sun, J., Zhao, M., Huang, L., Zhang, T. and Wang, Q. 'Recent progress on direct air capture of carbon dioxide'. In: *Current Opinion in Green and Sustainable Chemistry* 40 (Apr. 2023), p. 100752. ISSN: 2452-2236. DOI: [10.1016/j.cogsc.2023.100752](https://doi.org/10.1016/j.cogsc.2023.100752).
- [78] Ma, J., Li, L., Wang, H., Du, Y., Ma, J., Zhang, X. and Wang, Z. 'Carbon Capture and Storage: History and the Road Ahead'. In: *Engineering* 14 (July 2022), pp. 33–43. ISSN: 2095-8099. DOI: [10.1016/j.eng.2021.11.024](https://doi.org/10.1016/j.eng.2021.11.024).
- [79] Buirma, M., Vleugel, J., Pruyn, J., Doedée, V. and Schott, D. 'Ship-Based Carbon Capture and Storage: A Supply Chain Feasibility Study'. In: *Energies* 15.3 (Jan. 2022), p. 813. ISSN: 1996-1073. DOI: [10.3390/en15030813](https://doi.org/10.3390/en15030813).
- [80] Ros, J. A., Skylogianni, E., Doedée, V., van den Akker, J. T., Vredeveltdt, A. W., Linders, M. J., Goetheer, E. L. and G M-S Monteiro, J. 'Advancements in ship-based carbon capture technology on board of LNG-fuelled ships'. In: *International Journal of Greenhouse Gas Control* 114 (Feb. 2022), p. 103575. ISSN: 1750-5836. DOI: [10.1016/j.ijggc.2021.103575](https://doi.org/10.1016/j.ijggc.2021.103575).
- [81] Thirumalesh, B. S. and Asapu, R. 'State of the Art of Methanol Reforming for Hydrogen Generation'. In: *ChemBioEng Reviews* 11.3 (Apr. 2024), pp. 543–554. ISSN: 2196-9744. DOI: [10.1002/cben.202300068](https://doi.org/10.1002/cben.202300068).
- [82] Agba, C., Gomez-Hernandez, A., Chou, Y.-C. and Erickson, P. 'Hydrogen production via methanol steam reforming: a review of H₂ production enhancement methods'. In: *Fuel* 421 (Oct. 2026), p. 139059. ISSN: 0016-2361. DOI: [10.1016/j.fuel.2026.139059](https://doi.org/10.1016/j.fuel.2026.139059).
- [83] Usman, M. and Yamada, T. 'Methanol Reforming for Hydrogen Production: Advances in Catalysts, Nanomaterials, Reactor Design, and Fuel Cell Integration'. In: *ACS Engineering Au* 5.4 (June 2025), pp. 314–346. ISSN: 2694-2488. DOI: [10.1021/acsengineeringau.5c00031](https://doi.org/10.1021/acsengineeringau.5c00031).
- [84] Todorovski, E., Todorovski, F., Sekavnik, M., Mori, M. and Lotri, A. 'Influence of simulated methanol reformat impurities (CO, CO₂, H₂O) on HT PEMFC performance'. In: *Electrochimica Acta* 562 (June 2026), p. 148676. ISSN: 0013-4686. DOI: [10.1016/j.electacta.2026.148676](https://doi.org/10.1016/j.electacta.2026.148676).
- [85] Chen, R., Luo, Q., Luo, X., Liang, Y., Chen, J., Yang, Z., Wang, C. and Chen, Y. 'Design and operation optimization of an on-site hydrogen production and purification integration system for PEMFC'. In: *Fuel* 370 (Aug. 2024), p. 131834. ISSN: 0016-2361. DOI: [10.1016/j.fuel.2024.131834](https://doi.org/10.1016/j.fuel.2024.131834).
- [86] Alentiev, D. A., Bermeshev, M. V., Volkov, A. V., Petrova, I. V. and Yaroslavl'tsev, A. B. 'Palladium Membrane Applications in Hydrogen Energy and Hydrogen-Related Processes'. In: *Polymers* 17.6 (Mar. 2025), p. 743. ISSN: 2073-4360. DOI: [10.3390/polym17060743](https://doi.org/10.3390/polym17060743).
- [87] Zhang, M., Liu, D., Wang, Y., Zhao, L., Xu, G., Yu, Y. and He, H. 'Recent Advances in Methanol Steam Reforming Catalysts for Hydrogen Production'. In: *Catalysts* 15.1 (Jan. 2025), p. 36. ISSN: 2073-4344. DOI: [10.3390/catal15010036](https://doi.org/10.3390/catal15010036).
- [88] Kappis, K., Papavasiliou, J. and Avgouropoulos, G. 'Methanol Reforming Processes for Fuel Cell Applications'. In: *Energies* 14.24 (Dec. 2021), p. 8442. ISSN: 1996-1073. DOI: [10.3390/en14248442](https://doi.org/10.3390/en14248442).

- [89] Taweekayujan, S., Prasertcharoensuk, P., Chen, Y.-S. and Arpornwichanop, A. 'Enhancing methanol-to-power: A comprehensive evaluation of an integrated methanol-reforming, high-temperature proton exchange membrane fuel cell, and organic Rankine cycle system'. In: *Energy* 321 (Apr. 2025), p. 135301. ISSN: 0360-5442. DOI: 10.1016/j.energy.2025.135301.
- [90] Kundu, A., Shul, Y. G. and Kim, D. H. 'Methanol Reforming Processes'. In: *Advances in Fuel Cell*. Elsevier, 2007, pp. 419–472. DOI: 10.1016/s1752-301x(07)80012-3.
- [91] Chih, Y.-K., Chen, W.-H. and Tran, K.-Q. 'Hydrogen production from methanol partial oxidation through the catalyst prepared using torrefaction liquid products'. In: *Fuel* 279 (Nov. 2020), p. 118419. ISSN: 0016-2361. DOI: 10.1016/j.fuel.2020.118419.
- [92] Guan, Y., Zheng, J., Rao, P., He, B. and Tu, Z. 'Operating regimes and performance reduction mechanisms of PEMFCs fueled by ammonia-decomposition-derived H₂/N₂ mixtures'. In: *Fuel* 421 (Oct. 2026), p. 138986. ISSN: 0016-2361. DOI: 10.1016/j.fuel.2026.138986.
- [93] Zhou, M., Feistner, J. C., Li, N., Araya, S. S., Cinti, G. and Liso, V. 'Experimental and numerical investigations of high-temperature PEM fuel cells under different anode dilution levels and varying temperatures'. In: *International Journal of Hydrogen Energy* 55 (Feb. 2024), pp. 1383–1392. ISSN: 0360-3199. DOI: 10.1016/j.ijhydene.2023.11.201.
- [94] Hos, T., Sror, G. and Herskowitz, M. 'Autothermal reforming of methanol for on-board hydrogen production in marine vehicles'. In: *International Journal of Hydrogen Energy* 49 (Jan. 2024), pp. 1121–1132. ISSN: 0360-3199. DOI: 10.1016/j.ijhydene.2023.08.315.
- [95] González-Arias, J., Zhang, Z., Reina, T. R. and Odriozola, J. A. 'Hydrogen production by catalytic aqueous-phase reforming of waste biomass: a review'. In: *Environmental Chemistry Letters* 21.6 (Aug. 2023), pp. 3089–3104. ISSN: 1610-3661. DOI: 10.1007/s10311-023-01643-w.
- [96] Lakhtaria, P., Ribeirinha, P., Huhtinen, W., Viik, S., Sousa, J. and Mendes, A. 'Hydrogen production via aqueous-phase reforming for high-temperature proton exchange membrane fuel cells - a review'. In: *Open Research Europe* 1 (Mar. 2022), p. 81. ISSN: 2732-5121. DOI: 10.12688/openreseurope.13812.3.
- [97] Gu, W., Chen, L., Li, Z., Xu, Z., Ge, Y., Mao, Y., Song, X., Li, J., Wu, P., Liao, J., Lu, M. and Wang, T. 'Efficient Hydrogen Production from Aqueous-Phase Methanol Reforming Enabled by Cu-Glu/AZ Catalysts'. In: *ACS Applied Energy Materials* (Apr. 2026). ISSN: 2574-0962. DOI: 10.1021/acsaem.5c04113.
- [98] Lu, Y., Wang, C., Luo, X., Shu, R., Lei, L., Liu, J., Tian, Z., Liao, Y. and Chen, Y. 'Aqueous phase reforming of methanol for hydrogen production over highly-dispersed PtLa/CeO₂ catalyst prepared by photochemical reduction method'. In: *International Journal of Hydrogen Energy* 62 (Apr. 2024), pp. 1054–1066. ISSN: 0360-3199. DOI: 10.1016/j.ijhydene.2024.03.164.
- [99] Neira D'Angelo, M. F., Ordonsky, V., van der Schaaf, J., Schouten, J. C. and Nijhuis, T. A. 'Aqueous phase reforming in a microchannel reactor: the effect of mass transfer on hydrogen selectivity'. In: *Catalysis Science & Technology* 3.10 (2013), p. 2834. ISSN: 2044-4761. DOI: 10.1039/c3cy00577a.
- [100] Sarbanha, A. A., Larachi, F. and Taghavi, S. M. 'Bubble and particle dynamics in a thin rectangular bubbling fluidized bed under emulated marine instabilities'. In: *Chemical Engineering Science* 280 (Oct. 2023), p. 119041. ISSN: 0009-2509. DOI: 10.1016/j.ces.2023.119041.

- [101] Heydari, N., Larachi, F., Kipping, R. and Schubert, M. 'Mass Transfer Performance and Hydrodynamics of a Bubble Column Reactor at Offshore Floating Conditions'. In: *Industrial & Engineering Chemistry Research* 62.31 (July 2023), pp. 12183–12190. ISSN: 1520-5045. DOI: 10.1021/acs.iecr.3c01600.
- [102] Wang, R., Ma, T., Ding, R., Liu, W. and Sun, D. 'Catalyst, Reactor, and Purification Technology in Methanol Steam Reforming for Hydrogen Production: A Review'. In: *Catalysts* 15.9 (Aug. 2025), p. 802. ISSN: 2073-4344. DOI: 10.3390/catal15090802.
- [103] Shen, Z., Nabavi, S. A. and Clough, P. T. 'Design and performance testing of a monolithic nickel-based SiC catalyst for steam methane reforming'. In: *Applied Catalysis A: General* 670 (Jan. 2024), p. 119529. ISSN: 0926-860X. DOI: 10.1016/j.apcata.2023.119529.
- [104] Wang, Q., Ren, Y., Kuang, X., Zhu, D., Wang, P. and Zhang, L. 'Electrically heated monolithic catalyst for in-situ hydrogen production by methanol steam reforming'. In: *International Journal of Hydrogen Energy* 48.2 (Jan. 2023), pp. 514–522. ISSN: 0360-3199. DOI: 10.1016/j.ijhydene.2022.10.005.
- [105] Zhou, S., Zhong, Y., Lin, W., You, H., Li, X., Wu, L. and Zhou, W. 'Design and performance evaluation of flexible tubular microreactor for methanol steam reforming reaction'. In: *International Journal of Hydrogen Energy* 47.85 (Oct. 2022), pp. 36022–36031. ISSN: 0360-3199. DOI: 10.1016/j.ijhydene.2022.08.194.
- [106] Xu, L., Cui, H., Bai, Z., Chen, H., Ding, B., Huang, X. and Zhu, C. 'Experimental investigation on hydrogen production by methanol steam reforming in a novel fractal microreactor'. In: *International Journal of Hydrogen Energy* 197 (Jan. 2026), p. 152707. ISSN: 0360-3199. DOI: 10.1016/j.ijhydene.2025.152707.
- [107] Muccioli, O., Ruocco, C., Meloni, E. and Palma, V. 'Effect of Pd salt precursor on the stability of structured foam catalysts for low-temperature methanol steam reforming'. In: *International Journal of Hydrogen Energy* 225 (Apr. 2026), p. 154529. ISSN: 0360-3199. DOI: 10.1016/j.ijhydene.2026.154529.
- [108] Gorji, S., Zarrinpashne, S., Zamaniyan, A., Mostoufi, N. and Kiarad, H. 'Synthesis and evaluation of bifunctional reforming-shift composite catalysts on metal foams for methanol steam reforming with reduced CO production'. In: *Journal of CO2 Utilization* 104 (Feb. 2026), p. 103323. ISSN: 2212-9820. DOI: 10.1016/j.jcou.2026.103323.
- [109] Zhang, H., Xu, C., Yu, H., Wu, H., Jin, F., Xiao, F. and Liao, Z. 'Enhancement of methanol steam reforming in a tubular fixed-bed reactor with simultaneous heating inside and outside'. In: *Energy* 254 (Sept. 2022), p. 124330. ISSN: 0360-5442. DOI: 10.1016/j.energy.2022.124330.
- [110] Kim, Y. T., Lee, J.-J. and Lee, J. 'Electricity-driven reactors that promote thermochemical catalytic reactions via joule and induction heating'. In: *Chemical Engineering Journal* 470 (Aug. 2023), p. 144333. ISSN: 1385-8947. DOI: 10.1016/j.cej.2023.144333.
- [111] Meloni, E., Iervolino, G. and Palma, V. 'Basics of Microwave Heating and Recent Advances'. In: *Advances in Microwave-assisted Heterogeneous Catalysis*. Royal Society of Chemistry, Nov. 2023, pp. 1–24. ISBN: 9781837670277. DOI: 10.1039/bk9781837670277-00001.
- [112] Blue World Technologies ApS. *HT PEM fuel cell system*. Accessed: 2026-04-17. URL: <https://www.blue.world/products/high-power-methanol-fuel-cell-platform/>.

- [113] Savva, C. 'Steam Methanol Reforming - SOFC - ORC System for a superyacht application: Simulation and Heat Management using Aspen Plus'. MA thesis. Delft University of Technology, 2025. URL: <https://resolver.tudelft.nl/uuid:bb44eaaf-9345-4366-ac9e-96bc8a728ac9>.
- [114] Schuller, G., Vázquez, F. V., Waiblinger, W., Auvinen, S. and Ribeirinha, P. 'Heat and fuel coupled operation of a high temperature polymer electrolyte fuel cell with a heat exchanger methanol steam reformer'. In: *Journal of Power Sources* 347 (Apr. 2017), pp. 47–56. ISSN: 0378-7753. DOI: [10.1016/j.jpowsour.2017.02.021](https://doi.org/10.1016/j.jpowsour.2017.02.021).
- [115] Li, N., Cui, X., Zhu, J., Zhou, M., Liso, V., Cinti, G., Sahlin, S. L. and Araya, S. S. 'A review of reformed methanol-high temperature proton exchange membrane fuel cell systems'. In: *Renewable and Sustainable Energy Reviews* 182 (2023), p. 113395. ISSN: 1364-0321. DOI: <https://doi.org/10.1016/j.rser.2023.113395>.
- [116] Yao, S., Yan, X., Xia, M., Wang, C. and Wang, S. 'Thermodynamic and economic analysis, optimization of SOFC/GT/SCO2/ORC hybrid power systems for methanol reforming-powered ships with carbon capture'. In: *Case Studies in Thermal Engineering* 67 (2025), p. 105840. ISSN: 2214-157X. DOI: <https://doi.org/10.1016/j.csite.2025.105840>.
- [117] Yang, P., Zhang, Y., Yang, C., Chen, J., Liu, Z., Deng, C. and Yang, S. 'Thermodynamic performance comparison of a SOFC system integrated with steam reforming and dry reforming by utilizing different fuels'. In: *Energy Conversion and Management* 300 (2024), p. 117981. ISSN: 0196-8904. DOI: <https://doi.org/10.1016/j.enconman.2023.117981>.
- [118] Hu, Y., Han, C., Li, W., Hu, Q., Wu, H. and Luo, Z. 'Experimental evaluation of methanol steam reforming reactor heated by catalyst combustion for kW-class SOFC'. In: *International Journal of Hydrogen Energy* 48.12 (2023), pp. 4649–4664. ISSN: 0360-3199. DOI: <https://doi.org/10.1016/j.ijhydene.2022.10.274>.
- [119] Demers, G. T. and Milcarek, R. J. 'Solid oxide fuel cell power generation from thermal partial oxidation of methanol reformat'. In: *Energy Conversion and Management* 354 (Apr. 2026), p. 121281. ISSN: 0196-8904. DOI: [10.1016/j.enconman.2026.121281](https://doi.org/10.1016/j.enconman.2026.121281).
- [120] Demers, G. and Milcarek, R. J. 'Methanol Partial Oxidation for Solid Oxide Fuel Cell Power Generation'. In: *Volume 9: Micro- and Nano-Systems Engineering and Packaging; Safety Engineering, Risk and Reliability Analysis; Special Symposium on Additive Manufacturing on Benchmark Test Series; Special Symposium on Power; Research Posters*. IMECE2025. American Society of Mechanical Engineers, Nov. 2025. DOI: [10.1115/imece2025-167125](https://doi.org/10.1115/imece2025-167125).
- [121] Chiu, W.-C., Hou, S.-S., Chen, C.-Y., Lai, W.-H. and Horng, R.-F. 'Hydrogen-rich gas with low-level CO produced with autothermal methanol reforming providing a real-time supply used to drive a kW-scale PEMFC system'. In: *Energy* 239 (Jan. 2022), p. 122267. ISSN: 0360-5442. DOI: [10.1016/j.energy.2021.122267](https://doi.org/10.1016/j.energy.2021.122267).
- [122] Li, Y., Fang, M., Zhang, Q., Wang, X. and Lei, X. 'Modeling of Methanol Steam Reforming in a Monolith Reactor: Effects of Internal Diffusion, Substrate Parameters, and Operating Conditions'. In: *ACS Omega* 11.10 (Mar. 2026), pp. 16043–16057. ISSN: 2470-1343. DOI: [10.1021/acsomega.5c10513](https://doi.org/10.1021/acsomega.5c10513).
- [123] Wang, F., Guan, D., Wu, C., Zhang, X. and Wang, G. 'Numerical study on induction heating enhanced methanol steam reforming for hydrogen production'. In: *DeCarbon* 6 (Dec. 2024), p. 100075. ISSN: 2949-8813. DOI: [10.1016/j.decarb.2024.100075](https://doi.org/10.1016/j.decarb.2024.100075).

- [124] Guan, D., Wang, F., Zhang, X., Dou, W. and Sun, Y. 'Comprehensive study on catalytic coating tubular reactor with electromagnetic induction heating for hydrogen production through methanol steam reforming'. In: *International Journal of Hydrogen Energy* 50 (Jan. 2024), pp. 1–17. ISSN: 0360-3199. DOI: 10.1016/j.ijhydene.2023.07.316.
- [125] Cheng, K., Wang, J., Shao, Y., Fu, L., Wu, Z., Zhang, Y., Yang, J., Wu, K., Zhang, Y., Chen, W., Huang, X., Ma, C. and Ran, J. 'Techno-economic assessment and multi-objective optimization of a hybrid methanol-reforming proton exchange membrane fuel cell system with cascading energy utilization'. In: *Energy* 313 (Dec. 2024), p. 133856. ISSN: 0360-5442. DOI: 10.1016/j.energy.2024.133856.
- [126] Zhao, H. and Hou, Q. 'Thermodynamic performance study of the MR SOFC-HAT-CCHP system'. In: *International Journal of Hydrogen Energy* 44.8 (Feb. 2019), pp. 4332–4349. ISSN: 0360-3199. DOI: 10.1016/j.ijhydene.2018.12.129.
- [127] Ma, Y., Wang, Z., Liu, H., Tang, H., Ji, Y. and Han, F. 'Efficient and sustainable power propulsion for all-electric ships: An integrated methanol-fueled SOFC-sCO₂ system'. In: *Renewable Energy* 230 (Sept. 2024), p. 120822. ISSN: 0960-1481. DOI: 10.1016/j.renene.2024.120822.
- [128] Bernardinelli, F. 'Comparative modelling of membrane and packed-bed methanol reformers integrated with low temperature PEMFC for on-board ship applications'. MA thesis. Delft University of Technology, 2025. URL: <https://resolver.tudelft.nl/uuid:b9bdd97-65f5-4dbf-81ca-95f7da9f0139>.
- [129] Zhu, Y., He, Z., Xuan, T., Huang, Y. and Zhong, W. 'Analysis and optimization of energy conversion for an on-board methanol reforming engine with thermochemical recuperation'. In: *Fuel* 378 (Dec. 2024), p. 132767. ISSN: 0016-2361. DOI: 10.1016/j.fuel.2024.132767.
- [130] Li, C., Wang, J., Liu, H., Guo, F., Xiu, X., Wang, C., Qin, J. and Wei, L. 'Thermodynamic performance analysis of direct methanol solid oxide fuel cell hybrid power system for ship application'. In: *Renewable Energy* 230 (Sept. 2024), p. 120809. ISSN: 0960-1481. DOI: 10.1016/j.renene.2024.120809.
- [131] Zhang, B., Maloney, D., Farida Harun, N., Zhou, N., Pezzini, P., Medam, A., Hovsopian, R., Bayham, S. and Tucker, D. 'Rapid load transition for integrated solid oxide fuel cell Gas turbine (SOFC-GT) energy systems: A demonstration of the potential for grid response'. In: *Energy Conversion and Management* 258 (Apr. 2022), p. 115544. ISSN: 0196-8904. DOI: 10.1016/j.enconman.2022.115544.
- [132] Mounica, V. and Obulesu, Y. P. 'Hybrid Power Management Strategy with Fuel Cell, Battery, and Supercapacitor for Fuel Economy in Hybrid Electric Vehicle Application'. In: *Energies* 15.12 (June 2022), p. 4185. ISSN: 1996-1073. DOI: 10.3390/en15124185.
- [133] Di Micco, S., Sztrinko, P., Cappiello, A., Cigolotti, V. and Minutillo, M. 'Multi-Fuel SOFC System Modeling for Ship Propulsion: Comparative Performance Analysis and Feasibility Assessment of Ammonia, Methanol and Hydrogen as Marine Fuels'. In: *Journal of Marine Science and Engineering* 13.10 (Oct. 2025), p. 1960. ISSN: 2077-1312. DOI: 10.3390/jmse13101960.
- [134] Ballard Power Systems. *FCgen-HPS*. Accessed: 2024-08-12. URL: https://www.ballard.com/about-ballard/publication_library/product-specification-sheets/fcgen-hps-spec-sheet.
- [135] Proton Motor Hydrogen Fuel Cells. *MyModule Fuel Cell*. Accessed: 2024-08-12. URL: <https://www.proton-motor.com/en/hymodule/>.

- [136] Huang, Z., Shen, J., Chan, S. H. and Tu, Z. 'Transient response of performance in a proton exchange membrane fuel cell under dynamic loading'. In: *Energy Conversion and Management* 226 (2020), p. 113492. ISSN: 0196-8904. DOI: <https://doi.org/10.1016/j.enconman.2020.113492>.
- [137] Yang, Q., Gao, B., Xiao, G. and Jin, D. 'Analysis of PEMFC undershoot behavior and performance stabilization under transient loading'. In: *International Journal of Hydrogen Energy* 50 (2024), pp. 1358–1372. ISSN: 0360-3199. DOI: <https://doi.org/10.1016/j.ijhydene.2023.07.013>.
- [138] **Grenko, B.**, de Jong, W., van de Ketterij, R. and van Biert, L. 'Analytical and numerical aspects of dynamic industrial chemical process analysis in fixed bed reactors'. In: *Chemical Engineering Science* 325 (2026), p. 123421. ISSN: 0009-2509. DOI: <https://doi.org/10.1016/j.ces.2026.123421>.
- [139] Bashmakov, I., Nilsson, L., Acquaye, A., Bataille, C., Cullen, J., de la Rue du Can, S., Fischedick, M., Geng, Y. and Tanaka, K. 'Industry'. In: *Climate Change 2022 - Mitigation of Climate Change*. Cambridge University Press, Aug. 2023, pp. 1161–1244. ISBN: 9781009157926. DOI: [10.1017/9781009157926.013](https://doi.org/10.1017/9781009157926.013).
- [140] Klüh, D., Anetjärvi, E., Melin, K. and Vakkilainen, E. 'Comparative techno-economic assessment of methanol production via directly and indirectly electrified biomass gasification routes'. In: *Energy Conversion and Management* 314 (2024), p. 118649. ISSN: 0196-8904. DOI: <https://doi.org/10.1016/j.enconman.2024.118649>.
- [141] Bielefeld, S., Cvetkovi, M. and Ramirez, A. R. 'Electrification in the Petrochemical Industry: Can Flexibility Enable Low-Carbon Utility Systems?' In: *34th European Symposium on Computer Aided Process Engineering / 15th International Symposium on Process Systems Engineering*. Ed. by F. Manenti and G. V. Reklaitis. Vol. 53. Computer Aided Chemical Engineering. Elsevier, 2024, pp. 2227–2232. DOI: <https://doi.org/10.1016/B978-0-443-28824-1.50372-0>.
- [142] Tiggeloven, J. L., Faaij, A. P. C., Kramer, G. J. and Gazzani, M. 'Optimizing Emissions Reduction in AmmoniaEthylene Chemical Clusters: Synergistic Integration of Electrification, Carbon Capture, and Hydrogen'. In: *Industrial & Engineering Chemistry Research* 64.8 (2025), pp. 4479–4497. DOI: [10.1021/acs.iecr.4c03817](https://doi.org/10.1021/acs.iecr.4c03817).
- [143] Chen, C. and Yang, A. 'Power-to-methanol: The role of process flexibility in the integration of variable renewable energy into chemical production'. In: *Energy Conversion and Management* 228 (2021), p. 113673. ISSN: 0196-8904. DOI: <https://doi.org/10.1016/j.enconman.2020.113673>.
- [144] Fischer, K. L. and Freund, H. 'On the optimal design of load flexible fixed bed reactors: Integration of dynamics into the design problem'. In: *Chemical Engineering Journal* 393 (2020), p. 124722. ISSN: 1385-8947. DOI: <https://doi.org/10.1016/j.cej.2020.124722>.
- [145] Zimmermann, R. T., Bremer, J. and Sundmacher, K. 'Load-flexible fixed-bed reactors by multi-period design optimization'. In: *Chemical Engineering Journal* 428 (2022), p. 130771. ISSN: 1385-8947. DOI: <https://doi.org/10.1016/j.cej.2021.130771>.
- [146] Mbatha, S., Cui, X., Debiagi, P., Panah, P. G., Everson, R. C. and Musyoka, N. M. 'Detailed assessment of dynamic startup, shutdown, and flexibility of the adiabatic, gas-and water-cooled methanol fixed bed reactor: Comparison for power to methanol application'. In: *Chemical Engineering Science* 319 (2026), p. 122280. ISSN: 0009-2509. DOI: <https://doi.org/10.1016/j.ces.2025.122280>.

- [147] Bielefeld, S., Cvetkovi, M. and Ramírez, A. 'Should we exploit flexibility of chemical processes for demand response? Differing perspectives on potential benefits and limitations'. In: *Frontiers in Energy Research* Volume 11 - 2023 (2023). DOI: [10.3389/fenrg.2023.1190174](https://doi.org/10.3389/fenrg.2023.1190174).
- [148] Cegla, M., Semrau, R., Tamagnini, F. and Engell, S. 'Flexible process operation for electrified chemical plants'. In: *Current Opinion in Chemical Engineering* 39 (2023), p. 100898. ISSN: 2211-3398. DOI: <https://doi.org/10.1016/j.coche.2023.100898>.
- [149] Stegehake, C., Riese, J. and Grünewald, M. 'Modeling and Validating Fixed-Bed Reactors: A State-of-the-Art Review'. In: *ChemBioEng Reviews* 6.2 (2019), pp. 28–44. DOI: <https://doi.org/10.1002/cben.201900002>.
- [150] Wentrup, J., Pesch, G. R. and Thöming, J. 'Dynamic operation of Fischer-Tropsch reactors for power-to-liquid concepts: A review'. In: *Renewable and Sustainable Energy Reviews* 162 (2022), p. 112454. ISSN: 1364-0321. DOI: <https://doi.org/10.1016/j.rser.2022.112454>.
- [151] Tiggeloven, J. L., Faaij, A. P. C., Kramer, G. J. and Gazzani, M. 'Optimization of Electric Ethylene Production: Exploring the Role of Cracker Flexibility, Batteries, and Renewable Energy Integration'. In: *Industrial & Engineering Chemistry Research* 62.40 (2023), pp. 16360–16382. DOI: [10.1021/acs.iecr.3c02226](https://doi.org/10.1021/acs.iecr.3c02226).
- [152] Giannikopoulos, I., Skouteris, A., Allen, D. T., Baldea, M. and Stadtherr, M. A. 'Network-Based Analysis of Electrified Chemical Processing with Renewable Energy Sources'. In: *32nd European Symposium on Computer Aided Process Engineering*. Ed. by L. Montastruc and S. Negny. Vol. 51. Computer Aided Chemical Engineering. Elsevier, 2022, pp. 937–942. DOI: <https://doi.org/10.1016/B978-0-323-95879-0.50157-0>.
- [153] Foslief, S. S., Knudsen, B. R., Bjarghov, S. and Korpås, M. 'Faster decarbonization of heavy industries in low-carbon power grids: using process flexibility for handling grid congestions'. In: *Energy & Environmental Science* 17.22 (2024), pp. 8838–8854. ISSN: 1754-5706. DOI: [10.1039/d4ee03888f](https://doi.org/10.1039/d4ee03888f).
- [154] Caspari, A., Offermanns, C., Schäfer, P., Mhamdi, A. and Mitsos, A. 'A flexible air separation process: 2. Optimal operation using economic model predictive control'. In: *AIChE Journal* 65.11 (2019), e16721. DOI: <https://doi.org/10.1002/aic.16721>.
- [155] Leipold, J., Nikolic, D., Seidel-Morgenstern, A. and Kienle, A. 'Optimization of methanol synthesis under forced periodic operation in a non-isothermal fixed-bed reactor'. In: *Computers & Chemical Engineering* 196 (2025), p. 109040. ISSN: 0098-1354. DOI: <https://doi.org/10.1016/j.compchemeng.2025.109040>.
- [156] Leipold, J., Nikolic, D., Seidel-Morgenstern, A. and Kienle, A. 'Multi-objective Optimization of Forced Periodic Operation of Methanol Synthesis in a Fixed-Bed Reactor'. In: *34th European Symposium on Computer Aided Process Engineering / 15th International Symposium on Process Systems Engineering*. Ed. by F. Manenti and G. V. Reklaitis. Vol. 53. Computer Aided Chemical Engineering. Elsevier, 2024, pp. 1603–1608. DOI: <https://doi.org/10.1016/B978-0-443-28824-1.50268-4>.
- [157] Nikoli, D., Felischak, M., Seidel-Morgenstern, A. and Petkovska, M. 'Periodic Operation with Modulation of Inlet Concentration and Flow Rate Part II: Adiabatic Continuous Stirred-Tank Reactor'. In: *Chemical Engineering & Technology* 39.11 (2016), pp. 2126–2134. DOI: <https://doi.org/10.1002/ceat.201600187>.

- [158] Hollmann, J. and Kabelac, S. 'Steady-State and Transient Operation of Solid Oxide Fuel Cell Systems with Anode Off-Gas Recirculation within a Highly Constrained Operating Range'. In: *Energies* 16.23 (2023). DOI: [10.3390/en16237827](https://doi.org/10.3390/en16237827).
- [159] van Biert, L., Godjevac, M., Visser, K. and Aravind, P. 'Dynamic modelling of a direct internal reforming solid oxide fuel cell stack based on single cell experiments'. In: *Applied Energy* 250 (2019), pp. 976–990. ISSN: 0306-2619. DOI: <https://doi.org/10.1016/j.apenergy.2019.05.053>.
- [160] Bruns, B., Herrmann, F., Polyakova, M., Grünewald, M. and Riese, J. 'A systematic approach to define flexibility in chemical engineering'. In: *Journal of Advanced Manufacturing and Processing* 2.4 (2020). DOI: <https://doi.org/10.1002/amp2.10063>.
- [161] Luo, J., Moncada, J. and Ramirez, A. 'Development of a Conceptual Framework for Evaluating the Flexibility of Future Chemical Processes'. In: *Industrial & Engineering Chemistry Research* 61.9 (2022), pp. 3219–3232. DOI: [10.1021/acs.iecr.1c03874](https://doi.org/10.1021/acs.iecr.1c03874).
- [162] Kiefer, F., Nikolic, M., Borgschulte, A. and Dimopoulos Eggenschwiler, P. 'Sorption-enhanced methane synthesis in fixed-bed reactors'. In: *Chemical Engineering Journal* 449 (2022), p. 137872. ISSN: 1385-8947. DOI: <https://doi.org/10.1016/j.cej.2022.137872>.
- [163] Li, H., Tian, H., Chen, S., Sun, Z., Liu, T., Liu, R., Assabumrungrat, S., Saupsor, J., Mu, R., Pei, C. and Gong, J. 'Sorption enhanced steam reforming of methanol for high-purity hydrogen production over Cu-MgO/Al₂O₃ bifunctional catalysts'. In: *Applied Catalysis B: Environmental* 276 (2020), p. 119052. ISSN: 0926-3373. DOI: <https://doi.org/10.1016/j.apcatb.2020.119052>.
- [164] Barresi, A. A., Baldi, G. and Fissore, D. 'Forced Unsteady-State Reactors as Efficient Devices for Integrated Processes: Case Histories and New Perspectives'. In: *Industrial & Engineering Chemistry Research* 46.25 (2007), pp. 8693–8700. DOI: [10.1021/ie070477k](https://doi.org/10.1021/ie070477k).
- [165] Marín, P., Díez, F. V. and Ordóñez, S. 'Reverse flow reactors as sustainable devices for performing exothermic reactions: Applications and engineering aspects'. In: *Chemical Engineering and Processing - Process Intensification* 135 (2019), pp. 175–189. ISSN: 0255-2701. DOI: <https://doi.org/10.1016/j.cep.2018.11.019>.
- [166] Sheintuch, Moshe and Nekhamkina, Olga. 'Dynamics and control of loop reactors: a review'. In: *Math. Model. Nat. Phenom.* 16 (2021), p. 43. DOI: [10.1051/mmnp/2021035](https://doi.org/10.1051/mmnp/2021035).
- [167] van Biert, L., Godjevac, M., Visser, K. and Aravind, P. 'A review of fuel cell systems for maritime applications'. In: *Journal of Power Sources* 327 (2016), pp. 345–364. ISSN: 0378-7753. DOI: <https://doi.org/10.1016/j.jpowsour.2016.07.007>.
- [168] Ketterij, R. G. v. d., Geertsma, R., Grasman, A., Pothaar, M. and Coraddu, A. 'Alternative Fuels, Propulsion and Power Systems for the Future Navy A Route Towards Reduced Emissions and Signatures, and Fossil Fuel Independence'. In: *Climate Security and the Military: Concepts, Strategies, and Partnerships*. Ed. by G. Frerks, R. Geertsma, J. Klomp and T. Middendorp. Vol. 2023. LUP NL ARMS. Leiden University Press, 2024. Chap. 14. DOI: [10.24415/9789400604780-019](https://doi.org/10.24415/9789400604780-019).
- [169] Rheenen, E. S. V., Padding, J. T., Slootweg, J. C. and Visser, K. 'Hydrogen carriers for zero-emission ship propulsion using PEM fuel cells: an evaluation'. In: *Journal of Marine Engineering & Technology* 23.3 (2024), pp. 166–183. DOI: [10.1080/20464177.2023.2282691](https://doi.org/10.1080/20464177.2023.2282691).

- [170] Van Veldhuizen, B., van Biert, L., Aravind, P. V. and Visser, K. 'Solid Oxide Fuel Cells for Marine Applications'. In: *International Journal of Energy Research* 2023.1 (2023), p. 5163448. DOI: <https://doi.org/10.1155/2023/5163448>.
- [171] Duong, P. A., Ryu, B. R., Nam, T. T., Lee, Y. H., Jung, J., Lee, J.-K. and Kang, H. 'Comparative Study of Thermodynamic Performances: Ammonia vs. Methanol SOFC for Marine Vessels'. In: *Chemical Engineering & Technology* 47.9 (2024), e202400118. DOI: <https://doi.org/10.1002/ceat.202400118>.
- [172] Shi, J., Wu, Q., Mei, D., Liu, H. and Wang, Y. 'Development of pure hydrogen generation system based on methanol steam reforming and Pd membrane'. In: *International Journal of Hydrogen Energy* 69 (2024), pp. 147–157. ISSN: 0360-3199. DOI: <https://doi.org/10.1016/j.ijhydene.2024.04.359>.
- [173] RIX Industries. *M2H2 Series Mobile Hydrogen Generator*. Accessed: 2025-07-25. URL: <https://www.rixindustries.com/hydrogen-generation-systems>.
- [174] Amogy Inc. *Ammonia-to-power*. Accessed: 2025-07-25. URL: <https://amogy.co/ammonia-to-power>.
- [175] gCapitan Maritime News. *Hydrogen-Powered Towboat Project Receives Key USCG Approval*. Accessed: 2025-07-25. URL: <https://tinyurl.com/49wwjdzw>.
- [176] PowerCell Sweden AB. *PowerCell receives first order for next-generation marine fuel cell system from OEM customer, valued at SEK 44 million*. Accessed: 2025-07-25. URL: <https://tinyurl.com/4p88kj6b>.
- [177] Seborg, D. E., Mellichamp, D. A. and Edgar, T. F. *Process Dynamics and Control*. Third. Wylie Series in Chemical Engineering. John Wiley & Sons, 2011. ISBN: 9780470646106.
- [178] Jakobsen, H. A. 'Chemical Reaction Engineering'. In: *Chemical Reactor Modeling: Multiphase Reactive Flows*. Springer International Publishing, 2014. Chap. 11, pp. 789–807. DOI: 10.1007/978-3-319-05092-8_6.
- [179] Conesa, J. 'Forced Unsteady State Operation of Chemical Reactors'. In: *Chemical Reactor Design*. John Wiley & Sons, Ltd, 2019. Chap. 7, pp. 157–171. ISBN: 9783527823376. DOI: <https://doi.org/10.1002/9783527823376.ch7>.
- [180] Bogatykh, I. and Osterland, T. 'Characterization of Residence Time Distribution in a Plug Flow Reactor'. In: *Chemie Ingenieur Technik* 91.5 (2019), pp. 668–672. DOI: <https://doi.org/10.1002/cite.201800170>.
- [181] Zagoruiko, A. N., Bobrova, L., Vernikovskaya, N. and Zazhigalov, S. 'Unsteady-state operation of reactors with fixed catalyst beds'. In: *Reviews in Chemical Engineering* 37.1 (2021), pp. 193–225. DOI: doi:10.1515/revce-2019-0017.
- [182] Tesser, R. and Santacesaria, E. 'Revisiting the Role of Mass and Heat Transfer in GasSolid Catalytic Reactions'. In: *Processes* 8.12 (2020). ISSN: 2227-9717. DOI: 10.3390/pr8121599.
- [183] Fabrik, M., Salama, A. and Ibrahim, H. 'State-of-the-art in methane-reforming reactor modeling: challenges and new insights'. In: *Reviews in Chemical Engineering* 38.8 (2022), pp. 991–1022. DOI: doi:10.1515/revce-2020-0038.
- [184] Harkou, E., Adamou, P., Al-Salem, S., Atanasova, N., Tang, J., Manos, G., Villa, A., Dimitratos, N. and Constantinou, A. 'Computational fluid dynamics (CFD) modelling as a power multiplier tool for the design improvement of gaseous and liquid fuels: current status, challenges and perspectives'. In: *Fuel* 404 (2026), p. 136401. ISSN: 0016-2361. DOI: <https://doi.org/10.1016/j.fuel.2025.136401>.

- [185] Micale, D., Ferroni, C., Uglietti, R., Bracconi, M. and Maestri, M. 'Computational Fluid Dynamics of Reacting Flows at Surfaces: Methodologies and Applications'. In: *Chimie Ingenieur Technik* 94.5 (2022), pp. 634–651. DOI: <https://doi.org/10.1002/cite.202100196>.
- [186] Fischer, K. L. and Freund, H. 'Intensification of load flexible fixed bed reactors by optimal design of staged reactor setups'. In: *Chemical Engineering and Processing - Process Intensification* 159 (2021), p. 108183. ISSN: 0255-2701. DOI: <https://doi.org/10.1016/j.cep.2020.108183>.
- [187] Gottheil, L. and Bremer, J. 'Enabling Load-Flexible Ammonia Synthesis via Polytrropic Fixed-Bed Reactors'. In: *34th European Symposium on Computer Aided Process Engineering / 15th International Symposium on Process Systems Engineering*. Ed. by F. Manenti and G. V. Reklaitis. Vol. 53. Computer Aided Chemical Engineering. Elsevier, 2024, pp. 1891–1896. DOI: <https://doi.org/10.1016/B978-0-443-28824-1.50316-1>.
- [188] Karpilov, I. and Pashchenko, D. 'Steam methane reforming over a preheated packed bed: Heat and mass transfer in a transient process'. In: *Thermal Science and Engineering Progress* 42 (2023), p. 101868. ISSN: 2451-9049. DOI: <https://doi.org/10.1016/j.tsep.2023.101868>.
- [189] Giglio, E., Pirone, R. and Bensaid, S. 'Dynamic modelling of methanation reactors during start-up and regulation in intermittent power-to-gas applications'. In: *Renewable Energy* 170 (2021), pp. 1040–1051. ISSN: 0960-1481. DOI: <https://doi.org/10.1016/j.renene.2021.01.153>.
- [190] Kataria, P., Yeo, W. S. and Nandong, J. 'Reviewing the dynamic modeling aspects of chemical looping hydrogen production'. In: *International Journal of Hydrogen Energy* 82 (2024), pp. 1282–1299. ISSN: 0360-3199. DOI: <https://doi.org/10.1016/j.ijhydene.2024.08.033>.
- [191] Peltola, P., Alobaid, F., Tynjälä, T. and Ritvanen, J. 'Overview of Fluidized Bed Reactor Modeling for Chemical Looping Combustion: Status and Research Needs'. In: *Energy & Fuels* 36.17 (2022), pp. 9385–9409. DOI: [10.1021/acs.energyfuels.2c01680](https://doi.org/10.1021/acs.energyfuels.2c01680).
- [192] Argyris, P. A., de Leeuwe, C., Abbas, S. Z. and Spallina, V. 'Mono-dimensional and two-dimensional models for chemical looping reforming with packed bed reactors and validation under real process conditions'. In: *Sustainable Energy and Fuels* 6.11 (2022), pp. 2755–2770. ISSN: 2398-4902. DOI: [10.1039/d2se00351a](https://doi.org/10.1039/d2se00351a).
- [193] Fischer, K. L., Langer, M. R. and Freund, H. 'Dynamic Carbon Dioxide Methanation in a Wall-Cooled Fixed Bed Reactor: Comparative Evaluation of Reactor Models'. In: *Industrial & Engineering Chemistry Research* 58.42 (2019), pp. 19406–19420. DOI: [10.1021/acs.iecr.9b02863](https://doi.org/10.1021/acs.iecr.9b02863).
- [194] Fatahillah, M. R., Monjezi, R., Ouyang, Y., Thybaut, J. W., Poelman, D. and Heynderickx, G. J. 'Computational Fluid Dynamics Simulation of a High-Throughput Catalytic Fixed-Bed Reactor for Total Oxidation of Methane'. In: *Industrial & Engineering Chemistry Research* 63.7 (2024), pp. 3290–3300. DOI: [10.1021/acs.iecr.3c03611](https://doi.org/10.1021/acs.iecr.3c03611).
- [195] Moghaddam, E., Foumeny, E., Stankiewicz, A. and Padding, J. 'Multiscale modelling of wall-to-bed heat transfer in fixed beds with non-spherical pellets: From particle-resolved CFD to pseudo-homogenous models'. In: *Chemical Engineering Science* 236 (2021), p. 116532. ISSN: 0009-2509. DOI: <https://doi.org/10.1016/j.ces.2021.116532>.
- [196] Weng, J., Wen, S., Shu, Z., Jiang, J., Ye, G. and Zhou, X. 'A 2D Continuum Model Based on Particle-Resolved CFD for Packed-Bed Reactors'. In: *Industrial & Engineering Chemistry Research* 64.16 (2025), pp. 8516–8530. DOI: [10.1021/acs.iecr.5c00351](https://doi.org/10.1021/acs.iecr.5c00351).

- [197] Dixon, A. G. 'Fixed bed heat transfer parameter estimation a new look at an old problem'. In: *Chemical Engineering Science* 302 (2025), p. 120874. ISSN: 0009-2509. DOI: <https://doi.org/10.1016/j.ces.2024.120874>.
- [198] Huerta-Rosas, B., Juarez-García, M., Núñez-López, J. M., Alcocer-García, H., Segovia-Hernández, J. G. and Sánchez-Ramírez, E. 'Power-to-X Technologies for Net-Zero: Bridging Process Innovation, System Integration, and Policy'. In: *Process Integration and Optimization for Sustainability* (Aug. 2025). ISSN: 2509-4246. DOI: 10.1007/s41660-025-00570-3.
- [199] Rentschler, P., Klahn, C. and Dittmeyer, R. 'The Need for Dynamic Process Simulation: A Review of Offshore Power-to-X Systems'. In: *Chemie Ingenieur Technik* 96.1-2 (2024), pp. 114–125. DOI: <https://doi.org/10.1002/cite.202300156>.
- [200] Bizon, K. and Continillo, G. 'Efficient optimization of a multifunctional catalytic fixed-bed reactor via reduced-order modeling approach'. In: *Chemical Engineering Research and Design* 165 (2021), pp. 214–229. ISSN: 0263-8762. DOI: <https://doi.org/10.1016/j.cherd.2020.11.007>.
- [201] Wang, M., Bu, S., Zhou, B., Gong, B., Li, Z. and Chen, D. 'Physics-informed neural networks for effective diffusion characteristics inversion in packed bed at low flow rates'. In: *International Journal of Heat and Mass Transfer* 244 (2025), p. 126970. ISSN: 0017-9310. DOI: <https://doi.org/10.1016/j.ijheatmasstransfer.2025.126970>.
- [202] Grimm, M., Paul, S. and Chainais, P. 'Process-constrained batch Bayesian approaches for yield optimization in multi-reactor systems'. In: *Computers & Chemical Engineering* 189 (2024), p. 108779. ISSN: 0098-1354. DOI: <https://doi.org/10.1016/j.compchemeng.2024.108779>.
- [203] Hu, T., Qin, L., Zhou, L., Zheng, X. and Zhu, L.-T. 'Analysis and optimization of methanol production and temperature gradient in CO₂ hydrogenation fixed bed reactors using CFD and Bayesian optimization'. In: *Chemical Engineering Science* 321 (2026), p. 123030. ISSN: 0009-2509. DOI: <https://doi.org/10.1016/j.ces.2025.123030>.
- [204] Han, J.-R. and Kim, Y.-H. 'CFD-based multi-objective Bayesian optimization approach for compact and efficient hydrogen production in steam reforming reactor'. In: *Journal of Industrial and Engineering Chemistry* 139 (2024), pp. 378–389. ISSN: 1226-086X. DOI: <https://doi.org/10.1016/j.jiec.2024.05.015>.
- [205] Fialkov, A. B., Lehotay, S. J. and Amirav, A. 'Less than one minute low-pressure gas chromatography - mass spectrometry'. In: *Journal of Chromatography A* 1612 (2020), p. 460691. ISSN: 0021-9673. DOI: <https://doi.org/10.1016/j.chroma.2019.460691>.
- [206] Harris, D. and Lucy, C. *Quantitative Chemical Analysis*. 9th ed. New York, NY: W.H. Freeman & Company, 2016.
- [207] Langford, V. 'Real-Time Monitoring of Volatile Organic Compounds in Ambient Air Using Direct-Injection Mass Spectrometry'. In: *LCGC North America* 40 (July 2022), pp. 174–179. DOI: <https://doi.org/10.56530/lcgc.na.nf7066t5>.
- [208] Pleil, J. D., Hansel, A. and Beauchamp, J. 'Advances in proton transfer reaction mass spectrometry (PTR-MS): applications in exhaled breath analysis, food science, and atmospheric chemistry'. In: *Journal of Breath Research* 13.3 (June 2019), p. 039002. DOI: 10.1088/1752-7163/ab21a7.
- [209] Ren, M., Wan, Y., Ji, Y. and Chen, J. 'Trace detection of natural gas leakage using novel hollow-electrode radiofrequency glow discharge ion-source mass spectrometry'. In: *Analytical Methods* 17 (21 2025), pp. 4403–4410. DOI: 10.1039/D5AY00302D.

- [210] Dryahina, K., Smith, D. and panl, P. 'Quantification of methane in humid air and exhaled breath using selected ion flow tube mass spectrometry'. In: *Rapid Communications in Mass Spectrometry* 24.9 (2010), pp. 1296–1304. DOI: <https://doi.org/10.1002/rcm.4513>.
- [211] Guerrero-Pérez, M. O. and Patience, G. S. 'Experimental methods in chemical engineering: Fourier transform infrared spectroscopyFTIR'. In: *The Canadian Journal of Chemical Engineering* 98.1 (2020), pp. 25–33. DOI: <https://doi.org/10.1002/cjce.23664>.
- [212] Giechaskiel, B. and Clairotte, M. 'Fourier Transform Infrared (FTIR) Spectroscopy for Measurements of Vehicle Exhaust Emissions: A Review'. In: *Applied Sciences* 11.16 (2021). ISSN: 2076-3417. DOI: [10.3390/app11167416](https://doi.org/10.3390/app11167416).
- [213] Jha, R. K. 'Non-Dispersive Infrared Gas Sensing Technology: A Review'. In: *IEEE Sensors Journal* 22.1 (2022), pp. 6–15. DOI: [10.1109/JSEN.2021.3130034](https://doi.org/10.1109/JSEN.2021.3130034).
- [214] Liang, J.-G., Jiang, Y., Wu, J.-K., Wang, C., von Gratowski, S., Gu, X. and Pan, L. 'Multiplex-gas detection based on non-dispersive infrared technique: A review'. In: *Sensors and Actuators A: Physical* 356 (2023), p. 114318. ISSN: 0924-4247. DOI: <https://doi.org/10.1016/j.sna.2023.114318>.
- [215] Tan, X., Zhang, H., Li, J., Wan, H., Guo, Q., Zhu, H., Liu, H. and Yi, F. 'Non-dispersive infrared multi-gas sensing via nanoantenna integrated narrowband detectors'. In: *Nature Communications* 11.1 (Oct. 2020). DOI: [10.1038/s41467-020-19085-1](https://doi.org/10.1038/s41467-020-19085-1).
- [216] Das, R. S. and Agrawal, Y. 'Raman spectroscopy: Recent advancements, techniques and applications'. In: *Vibrational Spectroscopy* 57.2 (2011), pp. 163–176. ISSN: 0924-2031. DOI: <https://doi.org/10.1016/j.vibspec.2011.08.003>.
- [217] Majumder, D., Janani, R., Scrimshire, A., Stone, A., Brooks, W., Holcroft, C., Werner, R., Green, S., Wheeler, N. and Bingham, P. A. 'Raman gas sensing technology: A new horizon?' In: *Sensors and Actuators Reports* 9 (2025), p. 100311. ISSN: 2666-0539. DOI: <https://doi.org/10.1016/j.snr.2025.100311>.
- [218] Petrov, D. V. and Matrosov, I. I. 'Raman Gas Analyzer (RGA): Natural Gas Measurements'. In: *Applied Spectroscopy* 70.10 (2016), pp. 1770–1776. DOI: [10.1177/0003702816644611](https://doi.org/10.1177/0003702816644611).
- [219] Gao, Y., Dai, L.-K., Zhu, H.-D., Chen, Y.-L. and Zhou, L. 'Quantitative Analysis of Main Components of Natural Gas Based on Raman Spectroscopy'. In: *Chinese Journal of Analytical Chemistry* 47.1 (2019), pp. 67–76. ISSN: 1872-2040. DOI: [https://doi.org/10.1016/S1872-2040\(18\)61135-1](https://doi.org/10.1016/S1872-2040(18)61135-1).
- [220] Avetisov, V., Bjoroey, O., Wang, J., Geiser, P. and Paulsen, K. G. 'Hydrogen Sensor Based on Tunable Diode Laser Absorption Spectroscopy'. In: *Sensors* 19.23 (2019). DOI: [10.3390/s19235313](https://doi.org/10.3390/s19235313).
- [221] Liang, T., Qiao, S., Liu, X. and Ma, Y. 'Highly Sensitive Hydrogen Sensing Based on Tunable Diode Laser Absorption Spectroscopy with a 2.1 micrometer Diode Laser'. In: *Chemosensors* 10.8 (2022). ISSN: 2227-9040. DOI: [10.3390/chemosensors10080321](https://doi.org/10.3390/chemosensors10080321).
- [222] Wang, Q., Sun, P., Zhang, Z., Zhang, L., Pang, T., Wu, B., Xia, H., Guo, Q., Sigrist, M. W. and Culshaw, B. 'Multi-component gas measurement aliasing spectral demodulation method for interference separation in laser absorption spectroscopy'. In: *Sensors and Actuators B: Chemical* 369 (2022), p. 132292. ISSN: 0925-4005. DOI: <https://doi.org/10.1016/j.snb.2022.132292>.
- [223] Sun, J., Chang, J., Wang, C. and Shao, J. 'Tunable diode laser absorption spectroscopy for detection of multi-component gas: a review'. In: *Applied Spectroscopy Reviews* 59.8 (2024), pp. 1086–1107. DOI: [10.1080/05704928.2024.2302608](https://doi.org/10.1080/05704928.2024.2302608).

- [224] Liu, Y., Shang, Q., Chen, L., Wang, E., Huang, X., Pang, X., Lu, Y., Zhou, L., Zhou, J., Wang, Z. and Lyu, Y. 'Application of Portable CH₄ Detector Based on TDLAS Technology in Natural Gas Purification Plant'. In: *Atmosphere* 14.12 (2023). DOI: 10.3390/atmos14121709.
- [225] Nwaboh, J. A., Pratzler, S., Werhahn, O. and Ebert, V. 'Tunable Diode Laser Absorption Spectroscopy Sensor for Calibration Free Humidity Measurements in Pure Methane and Low CO₂ Natural Gas'. In: *Applied Spectroscopy* 71.5 (2017), pp. 888–900. DOI: 10.1177/0003702816658672.
- [226] Sampaolo, A., Patimisco, P., Giglio, M., Zifarelli, A., Wu, H., Dong, L. and Spagnolo, V. 'Quartz-enhanced photoacoustic spectroscopy for multi-gas detection: A review'. In: *Analytica Chimica Acta* 1202 (2022), p. 338894. ISSN: 0003-2670. DOI: <https://doi.org/10.1016/j.aca.2021.338894>.
- [227] Abina, A., Puc, U., Jazbinek, M. and Zidanek, A. 'Analytical Gas Sensing in the Terahertz Spectral Range'. In: *Micromachines* 14.11 (2023). ISSN: 2072-666X. DOI: 10.3390/mi14111987.
- [228] Holmen, A., Yang, J. and Chen, D. 'Steady-State Isotopic Transient Kinetic Analysis (SSITKA)'. In: *Springer Handbook of Advanced Catalyst Characterization*. Springer International Publishing, 2023. Chap. 41, pp. 935–965. DOI: 10.1007/978-3-031-07125-6_41.
- [229] Morgan, K., Maguire, N., Fushimi, R., Gleaves, J. T., Goguet, A., Harold, M. P., Kondratenko, E. V., Menon, U., Schuurman, Y. and Yablonsky, G. S. 'Forty years of temporal analysis of products'. In: *Catalysis Science & Technology* 7.12 (2017), pp. 2416–2439. ISSN: 2044-4761. DOI: 10.1039/c7cy00678k.
- [230] Meyer, D., Schumacher, J., Friedland, J. and Güttel, R. 'Frequency Response Analysis of the Unsteady-State CO/CO₂ Methanation Reaction: An Experimental Study'. In: *Industrial & Engineering Chemistry Research* 61.5 (2022), pp. 2045–2054. DOI: 10.1021/acs.iecr.1c04547.
- [231] Mane, S., Dhote, R. R., Sinha, A. and Thirumalaiswamy, R. 'Digital twin in the chemical industry: A review'. In: *Digital Twins and Applications* 1.2 (2024), pp. 118–130. DOI: <https://doi.org/10.1049/dgt2.12019>.
- [232] Spatenka, S., Matzopoulos, M., Urban, Z. and Cano, A. 'From Laboratory to Industrial Operation: Model-Based Digital Design and Optimization of Fixed-Bed Catalytic Reactors'. In: *Industrial & Engineering Chemistry Research* 58.28 (2019), pp. 12571–12585. DOI: 10.1021/acs.iecr.9b01314.
- [233] Flores-Tlacuahuac, A., Saldívar-Guerra, E., de León, R. D., López-González, R. and Rodríguez-Guadarrama, L. A. 'Soft-sensor estimation via parameter fitting and dynamic optimization in an experimental batch butadiene homopolymerization reactor'. In: *Computers & Chemical Engineering* 183 (2024), p. 108587. ISSN: 0098-1354. DOI: <https://doi.org/10.1016/j.compchemeng.2024.108587>.
- [234] Zhu, J., Cui, X. and Araya, S. S. 'Comparison between 1D and 2D numerical models of a multi-tubular packed-bed reactor for methanol steam reforming'. In: *International Journal of Hydrogen Energy* 47.54 (2022), pp. 22704–22719. ISSN: 0360-3199. DOI: <https://doi.org/10.1016/j.ijhydene.2022.05.109>.
- [235] Grenko, B. *Methanol steam reformer code Git repository*. 2025. DOI: 10.5281/ZENODO.16941636.

- [236] Sahimi, M. 'Dispersion in Flow through Porous Media'. In: *Flow and Transport in Porous Media and Fractured Rock*. John Wiley & Sons, Ltd, 2011. Chap. 11, pp. 341–413. ISBN: 9783527636693. DOI: <https://doi.org/10.1002/9783527636693.ch11>.
- [237] Peppley, B. A., Amphlett, J. C., Kearns, L. M. and Mann, R. F. 'Methanolsteam reforming on Cu/ZnO/Al₂O₃ catalysts. Part 2. A comprehensive kinetic model'. In: *Applied Catalysis A: General* 179.1 (1999), pp. 31–49. ISSN: 0926-860X. DOI: [https://doi.org/10.1016/S0926-860X\(98\)00299-3](https://doi.org/10.1016/S0926-860X(98)00299-3).
- [238] Fogler, H. S. *Elements of Chemical Reaction Engineering*. 4th ed. Prentice Hall, Sept. 2005. ISBN: 0130473944.
- [239] Varma, A., Morbidelli, M. and Wu, H. *Parametric Sensitivity in Chemical Systems*. Cambridge Series in Chemical Engineering. Cambridge University Press, 1999.
- [240] Omojola, T. 'Concepts and tools for integrating multiscale dynamics into reaction kinetics'. In: *Physical Chemistry Chemical Physics* 27.33 (2025), pp. 17157–17177. ISSN: 1463-9084. DOI: [10.1039/d5cp00838g](https://doi.org/10.1039/d5cp00838g).
- [241] Driessen, R. T., Kersten, S. R. and Brilman, D. W. 'A Thiele Modulus Approach for Nonequilibrium Adsorption Processes and Its Application to CO₂ Capture'. In: *Industrial & Engineering Chemistry Research* 59.15 (2020), pp. 6874–6885. DOI: [10.1021/acs.iecr.9b05503](https://doi.org/10.1021/acs.iecr.9b05503).
- [242] Zhu, J., Araya, S. S., Cui, X. and Kær, S. K. 'The role of effectiveness factor on the modeling of methanol steam reforming over CuO/ZnO/Al₂O₃ catalyst in a multi-tubular reactor'. In: *International Journal of Hydrogen Energy* 47.14 (2022), pp. 8700–8715. ISSN: 0360-3199. DOI: <https://doi.org/10.1016/j.ijhydene.2021.12.223>.
- [243] Pérez-Gallego, D., Gonzalez-Ayala, J., Medina, A. and Calvo Hernández, A. 'Comprehensive review of dynamical simulation models of packed-bed systems for thermal energy storage applications in renewable power production'. In: *Heliyon* 11.4 (2025), e42803. ISSN: 2405-8440. DOI: <https://doi.org/10.1016/j.heliyon.2025.e42803>.
- [244] Grenko, B., de Jong, W., van de Ketterij, R. and van Biert, L. 'Dynamic modelling of methanol steam reforming to hydrogen in a packed bed reactor for shipboard fuel cells'. In: *Chemical Engineering Journal* 507 (2025), p. 160623. ISSN: 1385-8947. DOI: <https://doi.org/10.1016/j.cej.2025.160623>.
- [245] Kalz, K. F., Kraehnert, R., Dvoyashkin, M., Dittmeyer, R., Gläser, R., Krewer, U., Reuter, K. and Grunwaldt, J.-D. 'Future Challenges in Heterogeneous Catalysis: Understanding Catalysts under Dynamic Reaction Conditions'. In: *ChemCatChem* 9.1 (2017), pp. 17–29. DOI: <https://doi.org/10.1002/cctc.201600996>.
- [246] Hua, Z., Zheng, Z., Pahon, E., Péra, M.-C. and Gao, F. 'Remaining useful life prediction of PEMFC systems under dynamic operating conditions'. In: *Energy Conversion and Management* 231 (2021), p. 113825. ISSN: 0196-8904. DOI: <https://doi.org/10.1016/j.enconman.2021.113825>.
- [247] Nedstack Fuel Cell Technology. *PemGen CHP-FCPS-120*. Accessed: 2024-08-12. URL: <https://nedstack.com/en/pemgen-solutions/stationary-fuel-cell-power-systems/pemgen-chp-fcps-120>.
- [248] Bernardo, G., Araújo, T., da Silva Lopes, T., Sousa, J. and Mendes, A. 'Recent advances in membrane technologies for hydrogen purification'. In: *International Journal of Hydrogen Energy* 45.12 (2020). Hydrogen separation/purification via membrane technology, pp. 7313–7338. ISSN: 0360-3199. DOI: <https://doi.org/10.1016/j.ijhydene.2019.06.162>.

- [249] Element 1. *Element1 Hydrogen Purifier*. Accessed: 2024-08-13. URL: <https://www.e1na.com/hydrogen-purifier-module>.
- [250] Amin, M., Butt, A. S., Ahmad, J., Lee, C., Azam, S. U., Mannan, H. A., Naveed, A. B., Farooqi, Z. U. R., Chung, E. and Iqbal, A. 'Issues and challenges in hydrogen separation technologies'. In: *Energy Reports* 9 (Dec. 2023), pp. 894–911. ISSN: 23524847. DOI: 10.1016/j.egy.2022.12.014.
- [251] Lotri, A., Sekavnik, M. and Hoever, S. 'Effectiveness of heat-integrated methanol steam reformer and polymer electrolyte membrane fuel cell stack systems for portable applications'. In: *Journal of Power Sources* 270 (2014), pp. 166–182. ISSN: 0378-7753. DOI: <https://doi.org/10.1016/j.jpowsour.2014.07.072>.
- [252] Wang, Y., Wu, Q., Mei, D. and Wang, Y. 'Development of highly efficient methanol steam reforming system for hydrogen production and supply for a low temperature proton exchange membrane fuel cell'. In: *International Journal of Hydrogen Energy* 45.46 (2020), pp. 25317–25327. ISSN: 0360-3199. DOI: <https://doi.org/10.1016/j.ijhydene.2020.06.285>.
- [253] Yu, D., Van, N. T., Yun, J. and Yu, S. 'A Thermal Design of a 1 kW-Class Shell and Tube Methanol Steam Reforming System with Internal Evaporator'. In: *Processes* 2020, Vol. 8, Page 1509 8 (11 Nov. 2020), p. 1509. ISSN: 2227-9717. DOI: 10.3390/PR8111509.
- [254] Ribeirinha, P., Abdollahzadeh, M., Sousa, J. M., Boaventura, M. and Mendes, A. 'Modelling of a high-temperature polymer electrolyte membrane fuel cell integrated with a methanol steam reformer cell'. In: *Applied Energy* 202 (Sept. 2017), pp. 6–19. ISSN: 0306-2619. DOI: 10.1016/J.APENERGY.2017.05.120.
- [255] Lee, C.-H. and Yang, J.-T. 'Modeling of the Ballard-Mark-V proton exchange membrane fuel cell with power converters for applications in autonomous underwater vehicles'. In: *Journal of Power Sources* 196.8 (2011), pp. 3810–3823. ISSN: 0378-7753. DOI: <https://doi.org/10.1016/j.jpowsour.2010.12.049>.
- [256] Element 1. *S-Series Hydrogen Generator*. Accessed: 2024-08-13. URL: <https://www.e1na.com/s-series-hydrogen-generator>.
- [257] Wartsila Corporation. *Combustion engine vs. Aeroderivative gas turbine: Six elements of dispatching*. Accessed: 2024-09-18. URL: <https://www.wartsila.com/energy/learn-more/technology-comparison-engines-vs-aeros/six-elements-of-dispatching>.
- [258] MAN Energy Solutions. *MAN 175D: Four-stroke high-speed diesel engine compliant with IMO Tier II / IMO Tier III*. Tech. rep. MAN Energy Solutions, 2024. URL: https://man-es.com/applications/projectguides/4stroke/Propulsion/PG_P-II_175D.pdf.
- [259] Zhu, J., Araya, S. S., Cui, X., Sahlin, S. L. and Kær, S. K. 'Modeling and Design of a Multi-Tubular Packed-Bed Reactor for Methanol Steam Reforming over a Cu/ZnO/Al₂O₃ Catalyst'. In: *Energies* 13.3 (2020). ISSN: 1996-1073. DOI: 10.3390/en13030610.
- [260] Sari, A. and Sabziani, J. 'Modeling and 3D-simulation of hydrogen production via methanol steam reforming in copper-coated channels of a mini reformer'. In: *Journal of Power Sources* 352 (June 2017), pp. 64–76. ISSN: 03787753. DOI: 10.1016/j.jpowsour.2017.03.120.
- [261] Klenov, O., Makarshin, L., Gribovskiy, A., Andreev, D. and Parmon, V. 'CFD modeling of compact methanol reformer'. In: *Chemical Engineering Journal* 282 (Dec. 2015), pp. 91–100. ISSN: 13858947. DOI: 10.1016/j.cej.2015.04.006.

- [262] Zhu, J. *Modelling of a Packed-Bed Methanol Steam Reformer for HT-PEM Fuel Cell Applications*. Ph.D.-serien for Det Ingeniør- og Naturvidenskabelige Fakultet, Aalborg Universitet. Aalborg Universitetsforlag, 2022. DOI: 10.54337/aaU513444640.
- [263] Yoon, H. C., Otero, J. and Erickson, P. A. 'Reactor design limitations for the steam reforming of methanol'. In: *Applied Catalysis B: Environmental* 75 (3-4 Sept. 2007), pp. 264–271. ISSN: 09263373. DOI: 10.1016/j.apcatb.2007.04.017.
- [264] **Grenko, B.** *Dynamic 2D methanol reformer*. Version v1.0. 2024. DOI: 10.5281/zenodo.13736015.
- [265] Pan, C., He, R., Li, Q., Jensen, J. O., Bjerrum, N. J., Hjulmand, H. A. and Jensen, A. B. 'Integration of high temperature PEM fuel cells with a methanol reformer'. In: *Journal of Power Sources* 145 (2 Aug. 2005), pp. 392–398. ISSN: 03787753. DOI: 10.1016/j.jpowsour.2005.02.056.
- [266] Chougule, A. and Sonde, R. R. 'Modelling and experimental investigation of compact packed bed design of methanol steam reformer'. In: *International Journal of Hydrogen Energy* 44 (57 Nov. 2019), pp. 29937–29945. ISSN: 03603199. DOI: 10.1016/j.ijhydene.2019.09.166.
- [267] Peters, R., Düsterwald, H. and Höhle, B. 'Investigation of a methanol reformer concept considering the particular impact of dynamics and long-term stability for use in a fuel-cell-powered passenger car'. In: *Journal of Power Sources* 86 (1-2 Mar. 2000), pp. 507–514. ISSN: 03787753. DOI: 10.1016/S0378-7753(99)00477-2.
- [268] Agrafiotis, C., von Storch, H., Roeb, M. and Sattler, C. 'Solar thermal reforming of methane feedstocks for hydrogen and syngas productionA review'. In: *Renewable and Sustainable Energy Reviews* 29 (2014), pp. 656–682. ISSN: 1364-0321. DOI: <https://doi.org/10.1016/j.rser.2013.08.050>.
- [269] Pinto, F., André, R. N., Franco, C., Carolino, C. and Gulyurtlu, I. 'Effect of syngas composition on hydrogen permeation through a PdAg membrane'. In: *Fuel* 103 (Jan. 2013), pp. 444–453. ISSN: 00162361. DOI: 10.1016/j.fuel.2012.05.060.
- [270] Zhang, N., Xiao, J., Bénard, P. and Chahine, R. 'Single- and double-bed pressure swing adsorption processes for H₂/CO syngas separation'. In: *International Journal of Hydrogen Energy* 44.48 (2019), pp. 26405–26418. ISSN: 0360-3199. DOI: <https://doi.org/10.1016/j.ijhydene.2019.08.095>.
- [271] Zhang, J., Zhang, C., Li, J., Deng, B., Fan, M., Ni, M., Mao, Z. and Yuan, H. 'Multi-perspective analysis of CO poisoning in high-temperature proton exchange membrane fuel cell stack via numerical investigation'. In: *Renewable Energy* 180 (2021), pp. 313–328. ISSN: 0960-1481. DOI: <https://doi.org/10.1016/j.renene.2021.08.089>.
- [272] Devrim, Y., Albostan, A. and Devrim, H. 'Experimental investigation of CO tolerance in high temperature PEM fuel cells'. In: *International Journal of Hydrogen Energy* 43.40 (2018), pp. 18672–18681. ISSN: 0360-3199. DOI: <https://doi.org/10.1016/j.ijhydene.2018.05.085>.
- [273] **Grenko, B.**, van Biert, L., van de Ketterij, R. and de Jong, W. 'Experimental validation of a dynamic 2D model for catalytic methanol steam reforming in a fixed bed reactor'. In: *Chemical Engineering Journal* 545 (Oct. 2026), p. 179613. ISSN: 1385-8947. DOI: 10.1016/j.cej.2026.179613.

- [274] Xu, C., Ju, F., Zheng, X., Liu, Y., Huang, J., Li, G., Li, Y., Zhu, L., Ye, L. and Pan, H. 'Computational Fluid Dynamics Modelling of Fixed-Bed Reactors Using Particle-Resolved Approach'. In: *Processes* 13.6 (June 2025), p. 1820. ISSN: 2227-9717. DOI: [10.3390/pr13061820](https://doi.org/10.3390/pr13061820).
- [275] Zhu, J., Yuan, Z., Wang, L., Dong, C., Lu, J. and Ding, J. '3D simulation in a fixed bed coupled pervaporation reactor for biodiesel production'. In: *Chemical Engineering Journal* 496 (Sept. 2024), p. 153854. ISSN: 1385-8947. DOI: [10.1016/j.cej.2024.153854](https://doi.org/10.1016/j.cej.2024.153854).
- [276] Daymo, E. A. and Hettel, M. 'Fixed bed reactor modeling with internal and external transport resistances: Comparing 3D PRCFD and 2D porous media simulations'. In: *Chemical Engineering Science* 321 (Feb. 2026), p. 122779. ISSN: 0009-2509. DOI: [10.1016/j.ces.2025.122779](https://doi.org/10.1016/j.ces.2025.122779).
- [277] Towler, G. and Sinnott, R. 'Heat transfer equipment'. In: *Chemical Engineering Design*. Elsevier, 2022. Chap. 19, pp. 823–951. ISBN: 9780128211793. DOI: [10.1016/b978-0-12-821179-3.00019-4](https://doi.org/10.1016/b978-0-12-821179-3.00019-4).
- [278] Eigenberger, G. and Ruppel, W. 'Catalytic Fixed-Bed Reactors'. In: *Ullmann's Encyclopedia of Industrial Chemistry*. John Wiley & Sons, Ltd, 2012. DOI: https://doi.org/10.1002/14356007.b04_199.pub2.
- [279] Idamakanti, M., Ledesma, E. B., Ratnakar, R. R., Harold, M. P., Balakotaiah, V. and Bollini, P. 'Electrified Catalysts for Endothermic Chemical Processes: Materials Needs, Advances, and Challenges'. In: *ACS Engineering Au* 4.1 (Dec. 2023), pp. 71–90. ISSN: 2694-2488. DOI: [10.1021/acsengineeringau.3c00051](https://doi.org/10.1021/acsengineeringau.3c00051).
- [280] Eppinger, T., Jurtz, N. and Kraume, M. 'Influence of Macroscopic Wall Structures on the Fluid Flow and Heat Transfer in Fixed Bed Reactors with Small Tube to Particle Diameter Ratio'. In: *Processes* 9.4 (Apr. 2021), p. 689. ISSN: 2227-9717. DOI: [10.3390/pr9040689](https://doi.org/10.3390/pr9040689).
- [281] Risthaus, K., Bürger, I., Linder, M. and Schmidt, M. 'Numerical analysis of the hydration of calcium oxide in a fixed bed reactor based on lab-scale experiments'. In: *Applied Energy* 261 (Mar. 2020), p. 114351. ISSN: 0306-2619. DOI: [10.1016/j.apenergy.2019.114351](https://doi.org/10.1016/j.apenergy.2019.114351).
- [282] Ermolaev, V. S., Gryaznov, K. O., Mitberg, E. B., Mordkovich, V. Z. and Tretyakov, V. F. 'Laboratory and pilot plant fixed-bed reactors for FischerTropsch synthesis: Mathematical modeling and experimental investigation'. In: *Chemical Engineering Science* 138 (Dec. 2015), pp. 1–8. ISSN: 0009-2509. DOI: [10.1016/j.ces.2015.07.036](https://doi.org/10.1016/j.ces.2015.07.036).
- [283] Pérez, J. F., Melgar, A. and Tinaut, F. V. 'Modeling of fixed bed downdraft biomass gasification: Application on lab-scale and industrial reactors: Modeling of fixed bed downdraft biomass gasification'. In: *International Journal of Energy Research* 38.3 (Apr. 2013), pp. 319–338. ISSN: 0363-907X. DOI: [10.1002/er.3045](https://doi.org/10.1002/er.3045).
- [284] Dou, B., Zhang, H., Cui, G., Wang, Z., Jiang, B., Wang, K., Chen, H. and Xu, Y. 'Hydrogen production by sorption-enhanced chemical looping steam reforming of ethanol in an alternating fixed-bed reactor: Sorbent to catalyst ratio dependencies'. In: *Energy Conversion and Management* 155 (Jan. 2018), pp. 243–252. ISSN: 0196-8904. DOI: [10.1016/j.enconman.2017.10.075](https://doi.org/10.1016/j.enconman.2017.10.075).
- [285] Spallina, V., Marinello, B., Gallucci, F., Romano, M. and Van Sint Annaland, M. 'Chemical looping reforming in packed-bed reactors: Modelling, experimental validation and large-scale reactor design'. In: *Fuel Processing Technology* 156 (Feb. 2017), pp. 156–170. ISSN: 0378-3820. DOI: [10.1016/j.fuproc.2016.10.014](https://doi.org/10.1016/j.fuproc.2016.10.014).

- [286] Chabot, G., Guilet, R., Cognet, P. and Gourdon, C. 'A mathematical modeling of catalytic milli-fixed bed reactor for FischerTropsch synthesis: Influence of tube diameter on Fischer Tropsch selectivity and thermal behavior'. In: *Chemical Engineering Science* 127 (May 2015), pp. 72–83. ISSN: 0009-2509. DOI: [10.1016/j.ces.2015.01.015](https://doi.org/10.1016/j.ces.2015.01.015).
- [287] Sheikh Al-Shabab, A. A., Silva, P. A. S. F., **Grenko, B.**, Tsoutsanis, P. and Skote, M. 'A Modular Multifidelity Approach for Multiphysics Oleo-Pneumatic Shock Absorber Simulations'. In: *Proceedings of the Cambridge Unsteady Flow Symposium 2024*. Springer Nature Switzerland, Dec. 2024, pp. 137–151. ISBN: 9783031690358. DOI: [10.1007/978-3-031-69035-8_8](https://doi.org/10.1007/978-3-031-69035-8_8).
- [288] Sheikh Al-Shabab, A. A., **Grenko, B.**, Silva, P. A. S. F., Antoniadis, A. F., Tsoutsanis, P. and Skote, M. 'Unsteady Multiphase Simulation of Oleo-Pneumatic Shock Absorber Flow'. In: *Fluids* 9.3 (Mar. 2024), p. 68. ISSN: 2311-5521. DOI: [10.3390/fluids9030068](https://doi.org/10.3390/fluids9030068).

A

Chapter 3 supplementary material

A.1. Steady state temperature fields

Internal temperature fields of four defined geometries

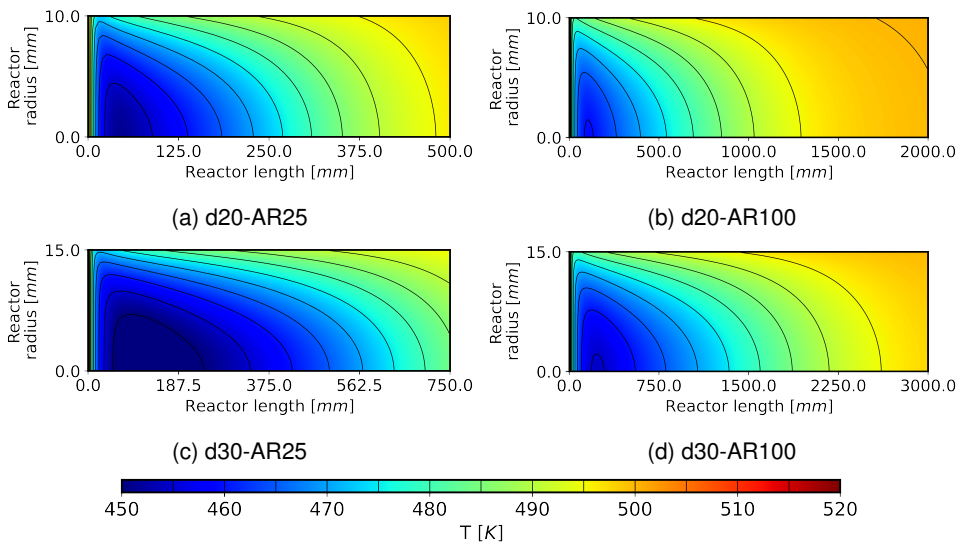


Figure A.1.: Internal reactor temperature fields at steady state 1

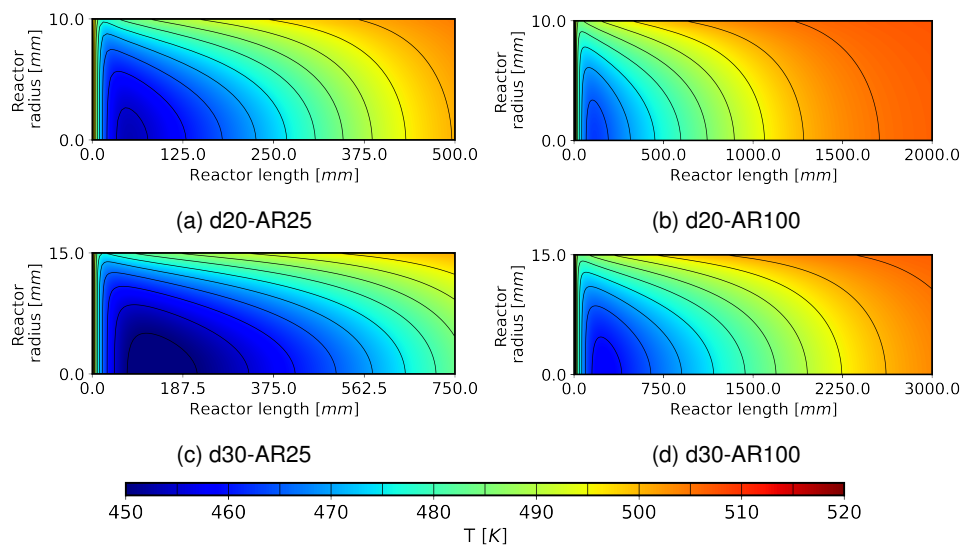


Figure A.2.: Internal reactor temperature fields at steady state 2

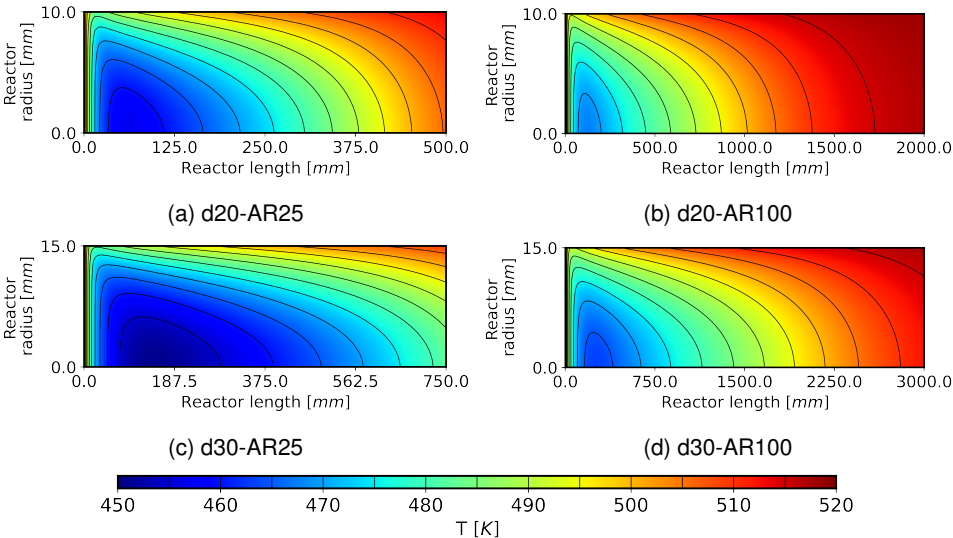


Figure A.3.: Internal reactor temperature fields at steady state 3

A.2. Reactor transient responses

Responses of four simulated reactors to input step functions

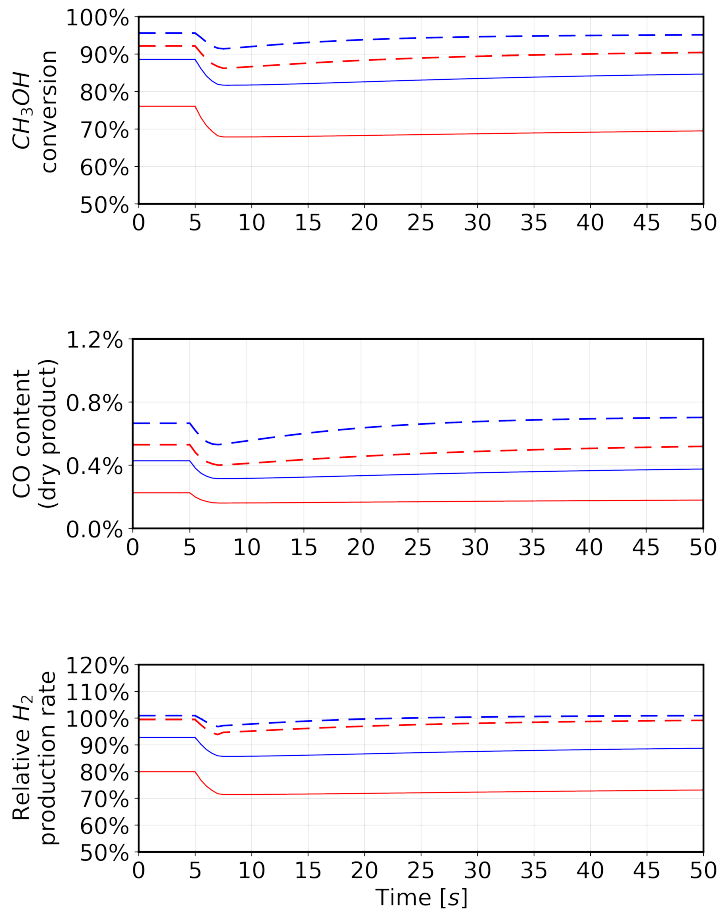


Figure A.4.: Transient response of four simulated reactors to increasing step between steady states 1-2

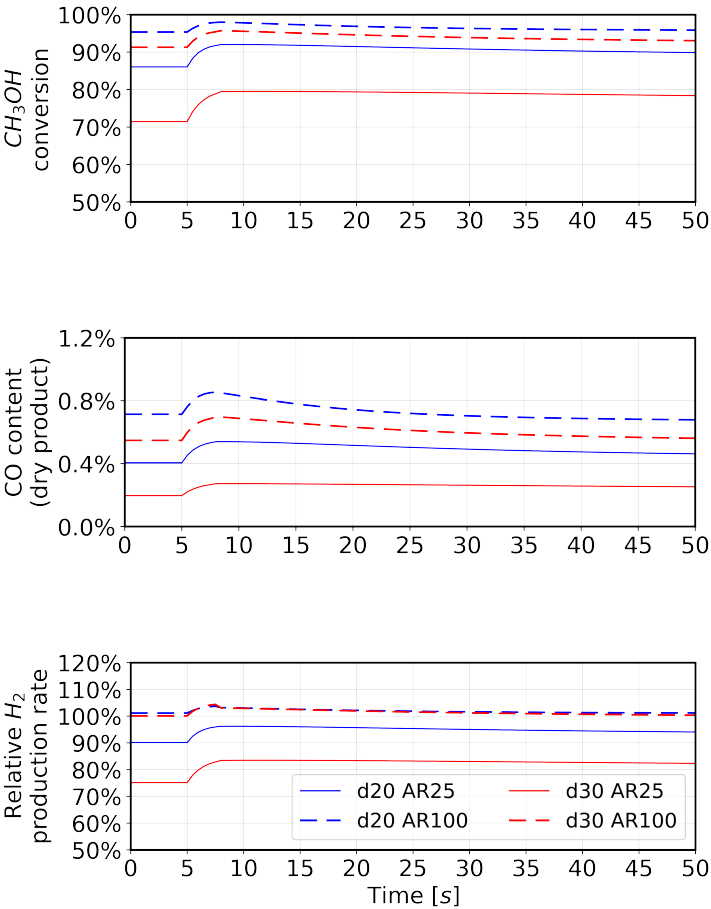


Figure A.5.: Transient response of four simulated reactors to decreasing step between steady states 2-1

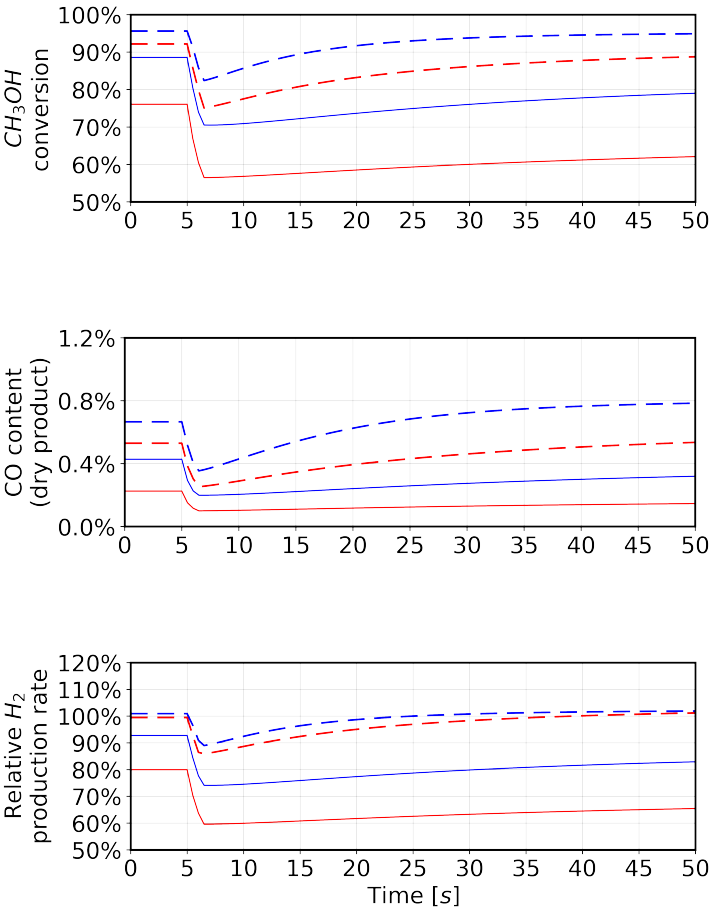


Figure A.6.: Transient response of four simulated reactors to increasing step between steady states 1-3

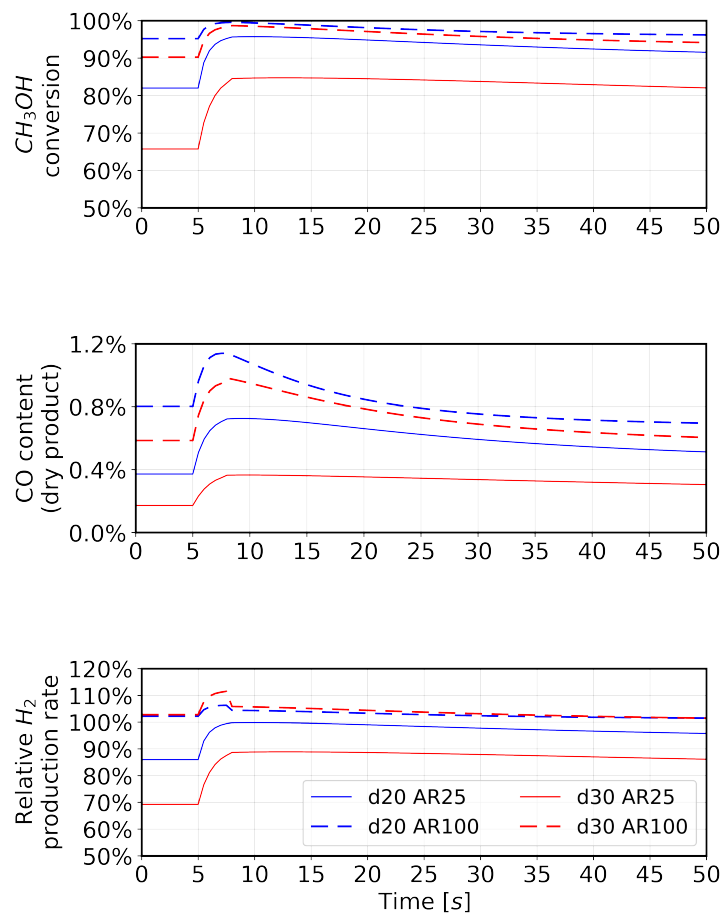


Figure A.7.: Transient response of four simulated reactors to decreasing step between steady states 3-1

B

Chapter 4 supplementary material

B.1. 2D dynamic model formulas

Presented equations are taken from the doctoral thesis of Zhu [262], in which detailed explanations can be found.

The effective radial dispersion coefficient D_{er} ($\text{m}^2 \text{s}^{-1}$) of the packed bed is calculated with:

$$D_{er} = \frac{u_s d_p}{11 \left[1 + 19.4 \left(\frac{d_p}{d_{t,i}} \right)^2 \right]}, \quad (\text{B.1})$$

where u_s (m s^{-1}) is the superficial fluid velocity, d_p (m) is the catalyst particle diameter, and $d_{t,i}$ (m) is the inner diameter of reactor tube.

The radial thermal conductivity λ_{er} ($\text{W m}^{-1} \text{K}^{-1}$) is calculated with:

$$\frac{\lambda_{er}}{\lambda_f} = \frac{\lambda_r^0}{\lambda_f} + \frac{Pe_h^0}{Pe_{h,r}^\infty}, \quad (\text{B.2})$$

where λ_f is the thermal conductivity of the fluid, λ_r^0 is the effective stagnant thermal conductivity due to molecular heat conduction in the fluid and the solid phase, which is independent of the fluid velocity, Pe_h^0 is fluid Peclet number for heat transfer, and $Pe_{h,r}^\infty$ is Peclet radial heat transfer for fully developed turbulent flow.

Pe_h^0 is calculated as:

$$Pe_h^0 = \frac{u_s \rho_f c_{p,f} d_p^v}{\lambda_f} = Re Pr, \quad (\text{B.3})$$

where u_s (m s^{-1}) is the superficial fluid velocity, ρ_f (kg m^{-3}) is the fluid density, $c_{p,f}$ ($\text{J kg}^{-1} \text{K}^{-1}$) is the specific heat capacity of the fluid, and d_p^v (m) is the volume equivalent spherical catalyst particle diameter.

$Pe_{h,r}^\infty$ is calculated according to:

$$Pe_{h,r}^\infty = 8 \left[2 - \left(1 - \frac{2}{N} \right)^2 \right], \quad (\text{B.4})$$

where N is the aspect ratio, or the number of particles across the tube diameter:

$$N = \frac{d_{t,i}}{d_p^v}. \quad (\text{B.5})$$

The correlation for the stagnant thermal conductivity in packed beds λ_r^0 is given by:

$$\frac{\lambda_r^0}{\lambda_f} = (1 - \sqrt{1 - \varepsilon}) + \frac{2\sqrt{1 - \varepsilon}}{1 - B\kappa^{-1}} \left[\frac{B(1 - \kappa^{-1})}{(1 - B\kappa^{-1})^2} \ln\left(\frac{\kappa}{B}\right) - \frac{B - 1}{1 - B\kappa^{-1}} - \frac{B + 1}{2} \right], \quad (\text{B.6})$$

$$B = C_f \left(\frac{1 - \varepsilon}{\varepsilon} \right)^{\frac{10}{9}}, \quad (\text{B.7})$$

where C_f is a factor depending on catalyst particle shape: $C_f = 1.25$ for spherical particles; $C_f = 2.5$ for cylindrical particles, and $C_f = 2.5 \left(1 + \frac{d_i}{d_p} \right)$, ε is the packed bed void fraction, and κ is the ratio of the thermal conductivity of the solid catalyst particle and the gas fluid:

$$\kappa = \frac{\lambda_p}{\lambda_f}. \quad (\text{B.8})$$

The catalyst particle thermal conductivity is calculated with:

$$\lambda_p = 0.21 + 1.5 \cdot 10^{-4} T. \quad (\text{B.9})$$

The gas mixture thermal conductivity λ_f is calculated with:

$$\lambda_f = \sum_{i=1}^{N_C} \frac{x_i \lambda_i}{\sum_{j=1}^{N_C} x_j \Phi_{ij}}, \quad (\text{B.10})$$

$$\Phi_{ij} = \left(\frac{M_j}{M_i} \right)^{1/2} = \Phi_{ji}^{-1}. \quad (\text{B.11})$$

The individual thermal conductivity λ_i ($\text{mW m}^{-1} \text{K}^{-1}$) of gas component i is calculated with the Shomate equation, whose constants for each gas can be found on the [NIST Chemistry WebBook](#):

$$\lambda_i = a + b \cdot T + c \cdot T^2 + d \cdot T^3 + e \cdot \left(\frac{1}{T} \right)^2 \quad (\text{B.12})$$

The heat transfer coefficient of the tube side film h_t ($\text{W m}^{-2} \text{K}^{-1}$) is calculated with:

$$h_t = \left(0.4 Re^{1/2} + 0.2 Re^{2/3} \right) Pr^{0.4} \frac{1 - \varepsilon}{\varepsilon} \frac{\lambda_f}{d_p}, \quad (\text{B.13})$$

where Re is the Reynolds number, Pr is the Prandtl number, ε is the packed bed void fraction, and λ_f ($\text{W m}^{-1} \text{K}^{-1}$) is the thermal conductivity of gas mixture. Prandtl number and Reynolds number in packed beds are calculated respectively according to:

$$Pr = \frac{c_p \mu_f}{\lambda_f}, \quad (\text{B.14})$$

$$Re = \frac{d_p G}{\mu_f} \frac{1}{1 - \varepsilon}, \quad (\text{B.15})$$

where G ($\text{kg m}^{-2} \text{s}^{-1}$) is the fluid mass velocity, and μ_f (Pa s) is the gas mixture viscosity calculated with Wilke's method:

$$\mu_f = \frac{\sum_{i=1}^{N_C} \frac{x_i \mu_i}{\sum_{j=1}^{N_C} x_j \Phi_{ij}}}{\sum_{j=1}^{N_C} x_j \Phi_{ij}} \quad (\text{B.16})$$

The overall heat transfer coefficient U ($\text{W m}^{-2} \text{K}^{-1}$) includes resistances from the tube side gas film and within the reactor tube wall. It is calculated according to:

$$U = \left(\frac{1}{h_t} + \frac{s_w}{k_w} \frac{d_{t,out}}{d_{lm}} \right)^{-1}, \quad (\text{B.17})$$

where h_t ($\text{W m}^{-2} \text{K}^{-1}$) is the heat transfer coefficient of the tube side film (formula in the supplementary material), s_w (m) is the tube wall thickness, $d_{t,out}$ (m) is the outer tube diameter, and d_{lm} (m) is the log-mean reactor tube diameter.

The effectiveness factor η_j is calculated as a function of Thiele modulus. Besides in Zhu's dissertation, the expressions for all components of η_j are also given in an article of Zhu et al [242].

The factor η for reaction j is calculated by:

$$\eta = \frac{3}{\phi_1^2} (\phi_1 \coth \phi_1 - 1), \quad (\text{B.18})$$

where the Thiele modulus ϕ for a first order reaction is written as:

$$\phi_1^2 = \frac{r_j^s \rho_s r_p^2 S_c}{D_{i,ep} C_i^s}, \quad (\text{B.19})$$

where r_j^s ($\text{mol m}^{-2} \text{s}^{-1}$) is the rate of reaction j , ρ_s (kg m^{-3}) is the catalyst bed density, r_p (m) is the catalyst pellet radius, S_c ($\text{m}^2 \text{kg}^{-1}$) is the surface area per unit mass of fresh catalyst, $D_{i,ep}$ ($\text{m}^2 \text{s}^{-1}$) is the effective diffusivity of component i inside catalyst pellets, and C_i^s (mol m^{-3}) is the local concentration of component i .

The effective diffusivity inside catalyst pellet $D_{i,ep}$ is calculated based on ordinary bulk diffusivity $D_{i,M}$ ($\text{m}^2 \text{s}^{-1}$), and the Knudsen diffusivity $D_{i,K}$:

$$\frac{1}{D_{i,ep}} = \frac{1}{D_{i,M}} + \frac{1}{D_{i,K}}. \quad (\text{B.20})$$

The comprehensive Langmuir-Hinshelwood kinetic model used in this work is developed by Peppley et al. [237]. The kinetics are developed for the $\text{CuO/ZnO/Al}_2\text{O}_3$ catalyst, and include the reaction rates for methanol steam reforming (r_R), water gas shift (r_W), and methanol decomposition (r_D) reactions:

$$r_R = \frac{k_R K_{\text{CH}_3\text{O}}^* (p_{\text{CH}_3\text{OH}}/p_{\text{H}_2})^{1/2} (1 - p_{\text{H}_2}^3 p_{\text{CO}_2} / k_R p_{\text{CH}_3\text{OH}} p_{\text{H}_2\text{O}}) C_{S_1}^T C_{S_{1a}}^T}{\left(1 + K_{\text{CH}_3\text{O}}^* (p_{\text{CH}_3\text{OH}}/p_{\text{H}_2})^{1/2} + K_{\text{HCOO}}^* p_{\text{CO}_2} p_{\text{H}_2}^{1/2} + K_{\text{OH}}^* (p_{\text{H}_2\text{O}}/p_{\text{H}_2})^{1/2}\right) \left(1 + K_{\text{H}(1a)}^{1/2} p_{\text{H}_2}^{1/2}\right)} \quad (\text{B.21})$$

$$r_W = \frac{k_W^* K_{\text{OH}}^* (p_{\text{CO}} p_{\text{H}_2\text{O}}/p_{\text{H}_2})^{1/2} (1 - p_{\text{H}_2} p_{\text{CO}_2} / k_W p_{\text{CO}} p_{\text{H}_2\text{O}}) C_{S_1}^T}{\left(1 + K_{\text{CH}_3\text{O}}^* (p_{\text{CH}_3\text{OH}}/p_{\text{H}_2})^{1/2} + K_{\text{HCOO}}^* p_{\text{CO}_2} p_{\text{H}_2}^{1/2} + K_{\text{OH}}^* (p_{\text{H}_2\text{O}}/p_{\text{H}_2})^{1/2}\right)^2} \quad (\text{B.22})$$

$$r_D = \frac{k_D K_{\text{CH}_3\text{O}}^* (p_{\text{CH}_3\text{OH}}/p_{\text{H}_2})^{1/2} (1 - p_{\text{H}_2}^2 p_{\text{CO}} / k_D p_{\text{CH}_3\text{OH}}) C_{S_2}^T C_{S_{2a}}^T}{\left(1 + K_{\text{CH}_3\text{O}}^* (p_{\text{CH}_3\text{OH}}/p_{\text{H}_2})^{1/2} + K_{\text{OH}}^* (p_{\text{H}_2\text{O}}/p_{\text{H}_2})^{1/2}\right) \left(1 + K_{\text{H}(2a)}^{1/2} p_{\text{H}_2}^{1/2}\right)} \quad (\text{B.23})$$

Full description of the model development and terms can be found in the original publication.

B.2. Unsteady validation

Temperature probe measurements against simulated values

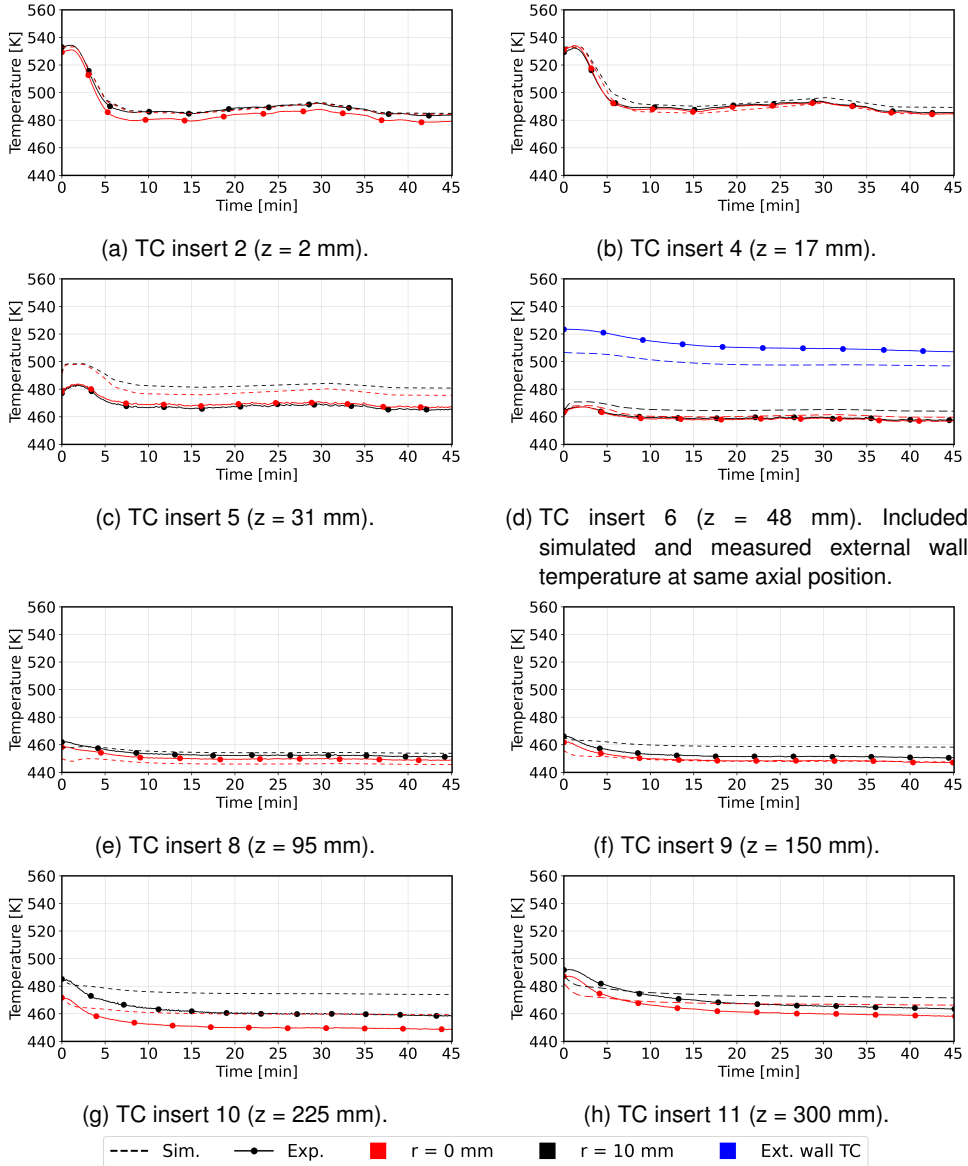


Figure B.1.: Thermocouple measurements and simulation in time: reactor response to flow increase $W_{cat.}/F_{CH_3OH}$ 200-120 kg s mol⁻¹ at $P_{el,in} = 150$ W

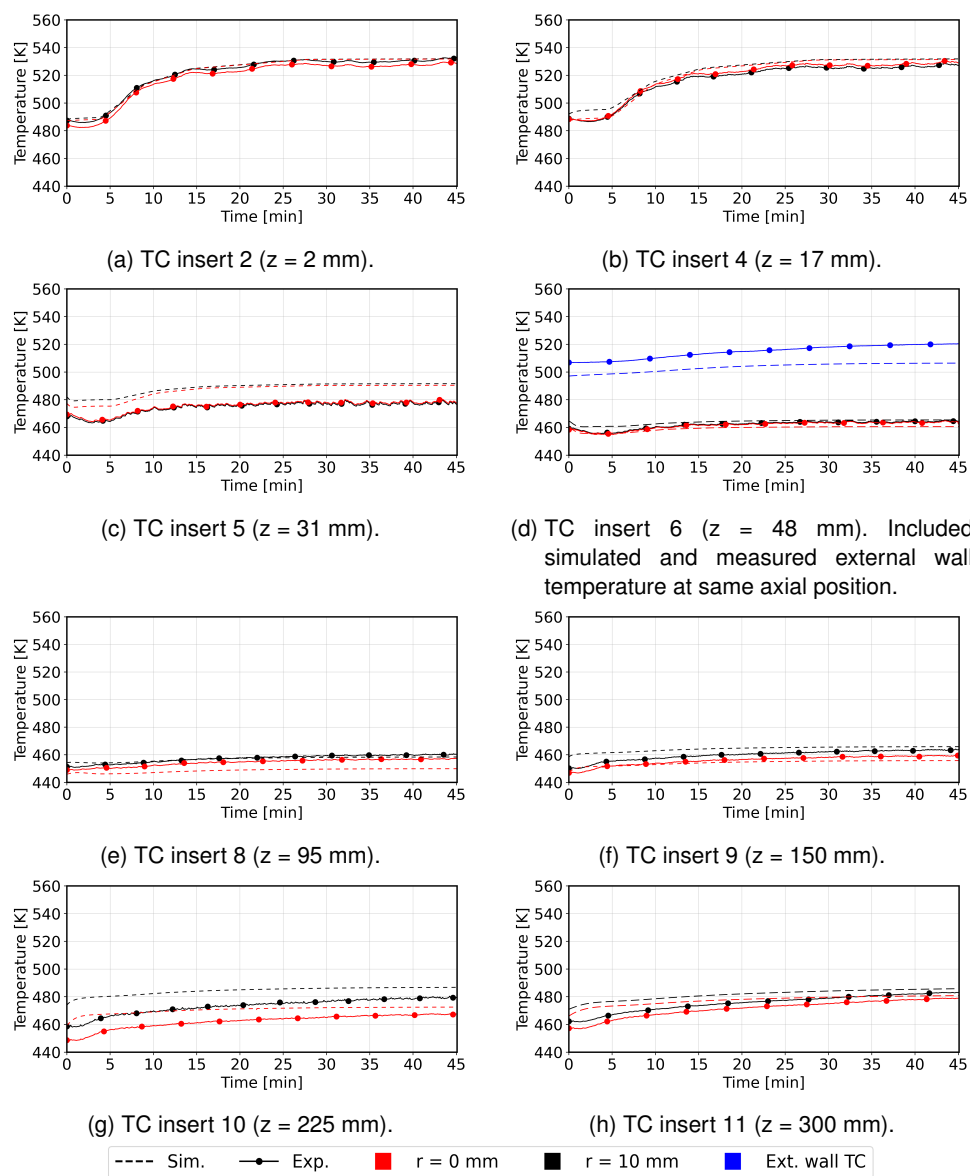


Figure B.2.: Thermocouple measurements and simulation in time: reactor response to flow decrease $W_{cat.}/F_{CH_3OH}$ 120-200 kg s mol⁻¹ at $P_{el,in} = 150$ W

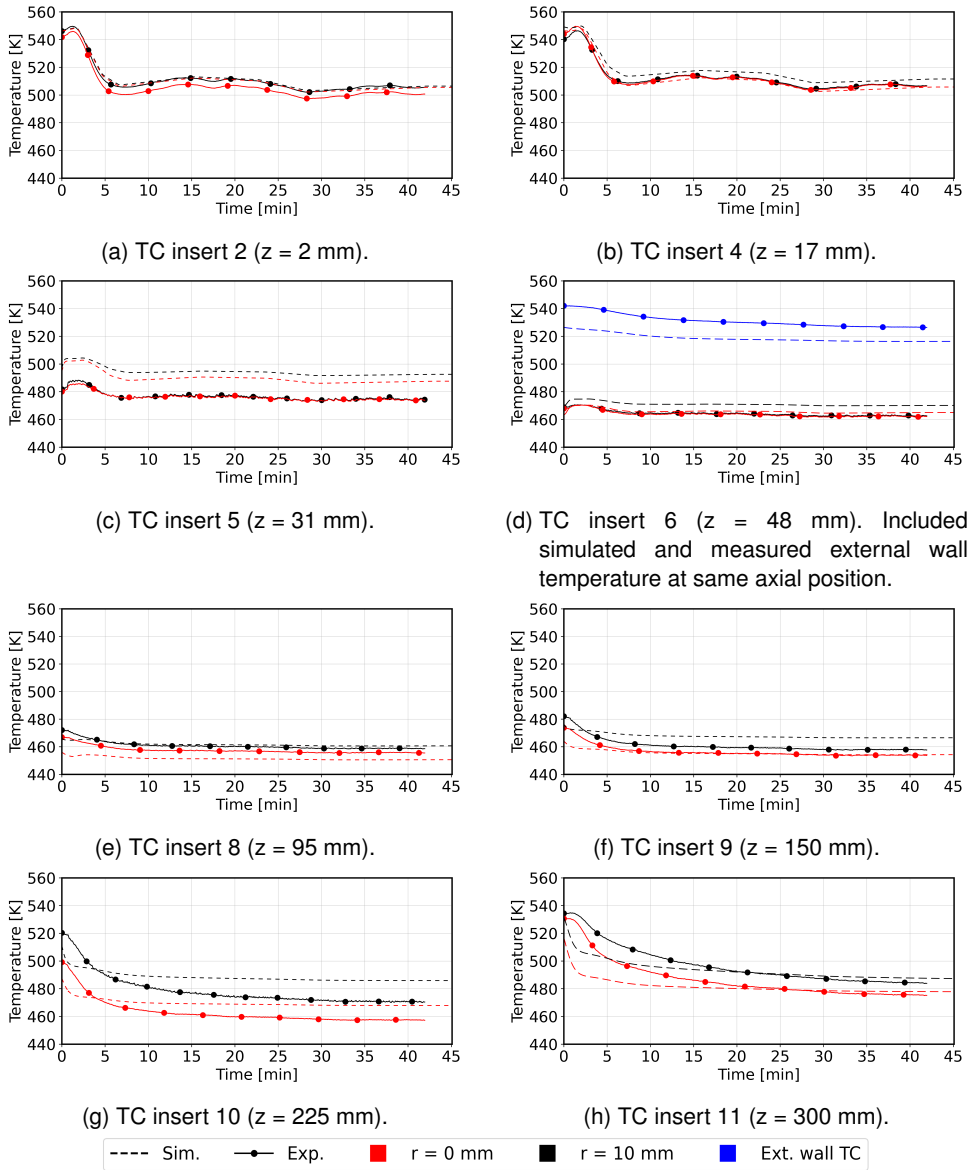


Figure B.3.: Thermocouple measurements and simulation in time: reactor response to flow increase $W_{cat.}/F_{CH_3OH}$ 200-120 kg s mol⁻¹ at $P_{el,in} = 187$ W

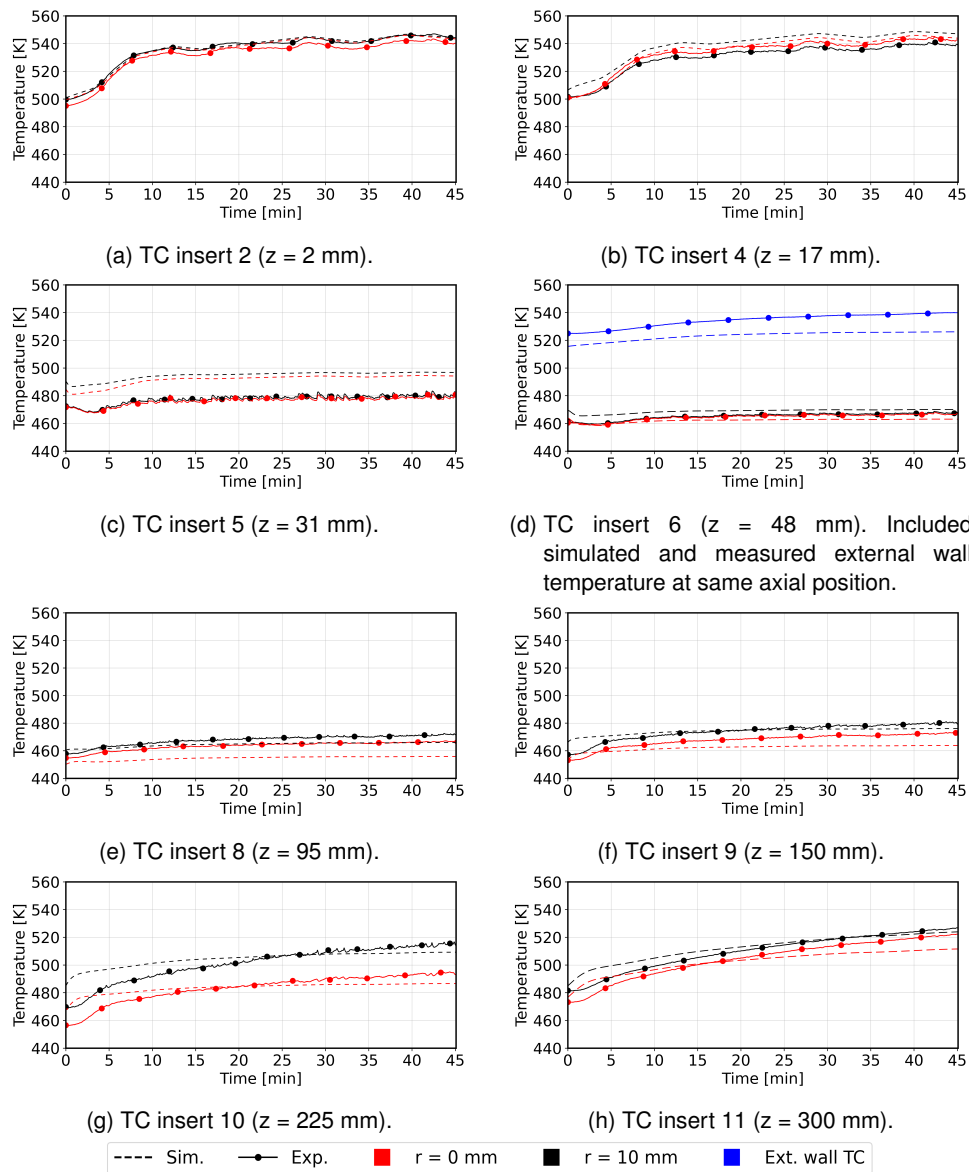


Figure B.4.: Thermocouple measurements and simulation in time: reactor response to flow decrease $W_{cat.}/F_{CH_3OH}$ 120-200 kg s mol⁻¹ at $P_{el,in} = 187$ W

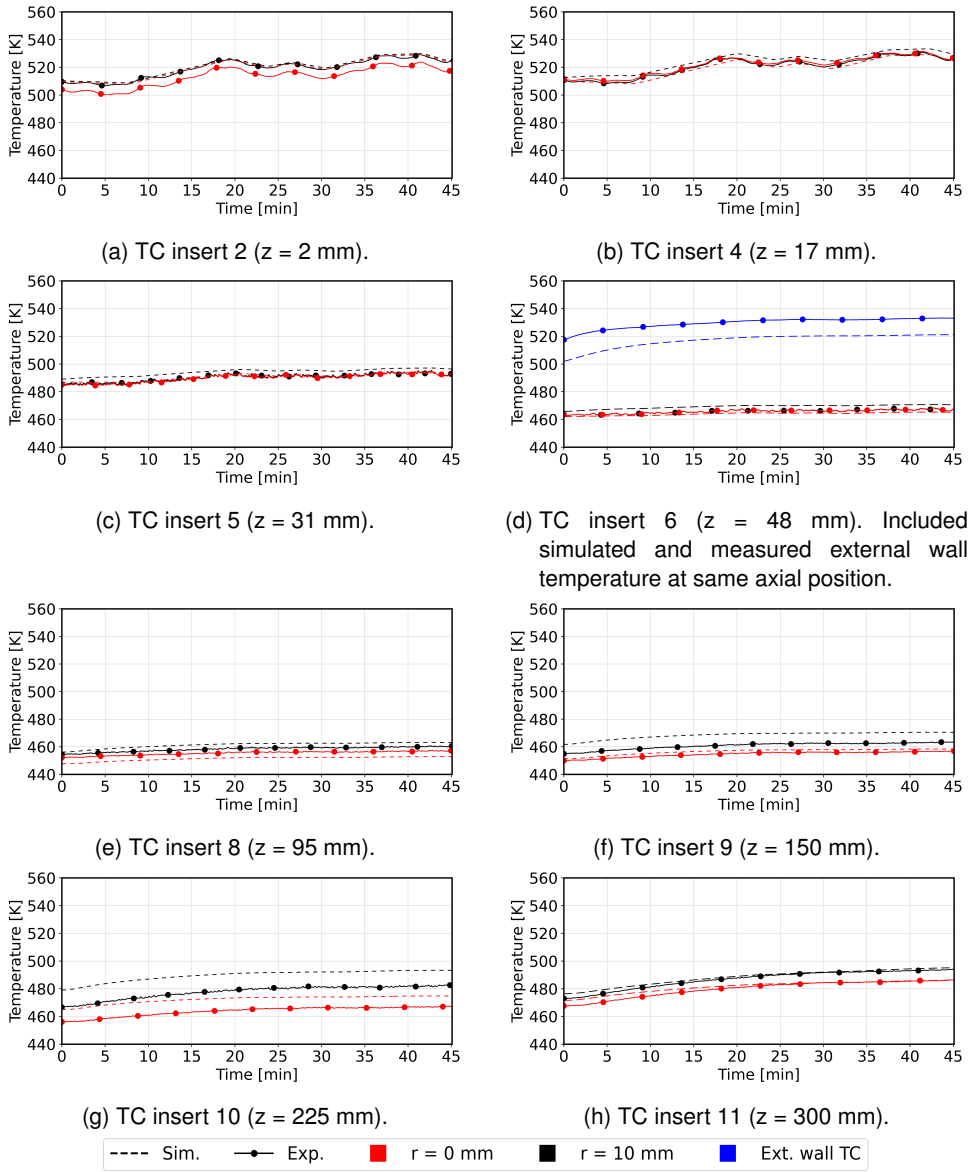


Figure B.5.: Thermocouple measurements and simulation in time: reactor response to heating increase $P_{el,in}$ 150-187 W at $W_{cat.}/F_{CH_3OH} = 150$ kg s mol⁻¹

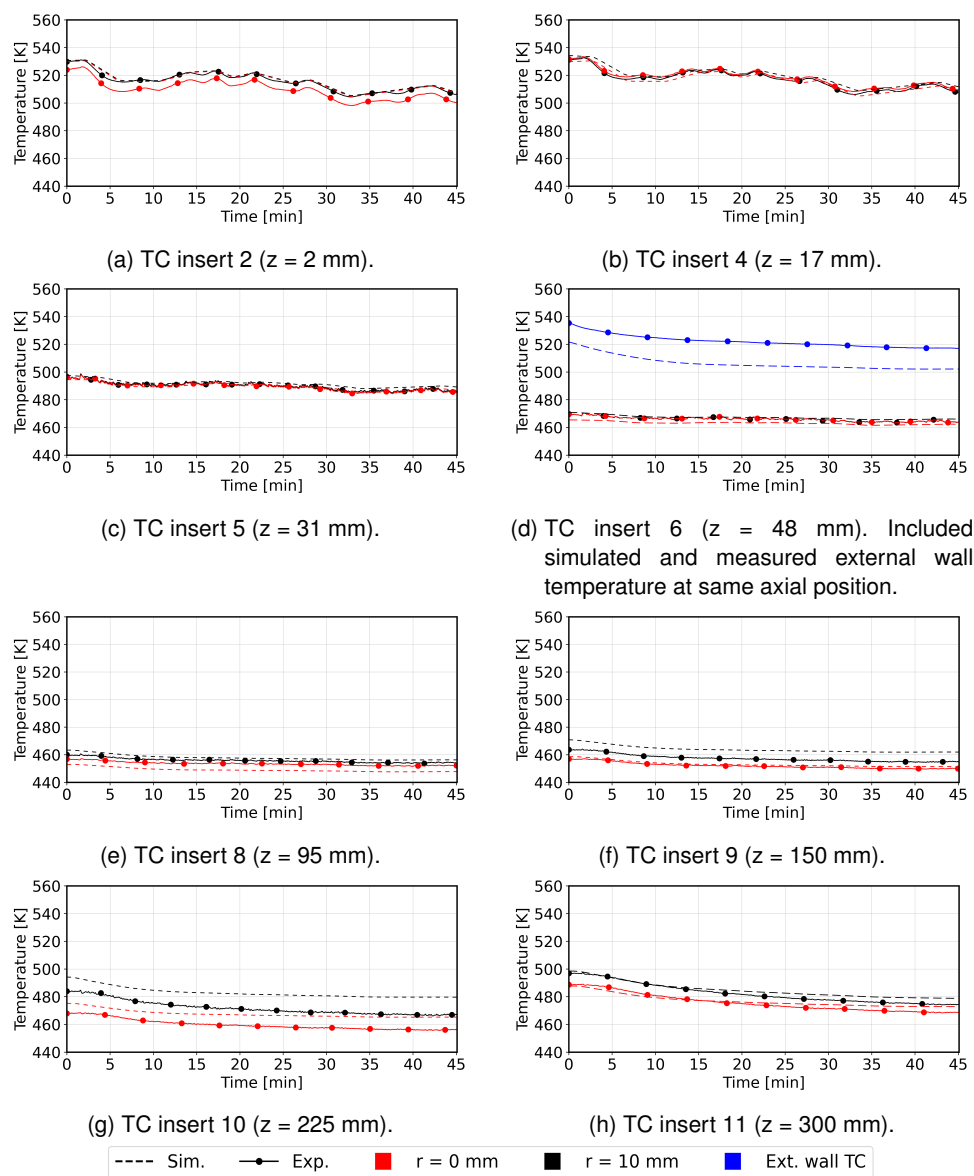


Figure B.6.: Thermocouple measurements and simulation in time: reactor response to heating decrease $P_{el,in}$ 187-150 W at $W_{cat.}/F_{CH_3OH} = 150 \text{ kg s mol}^{-1}$

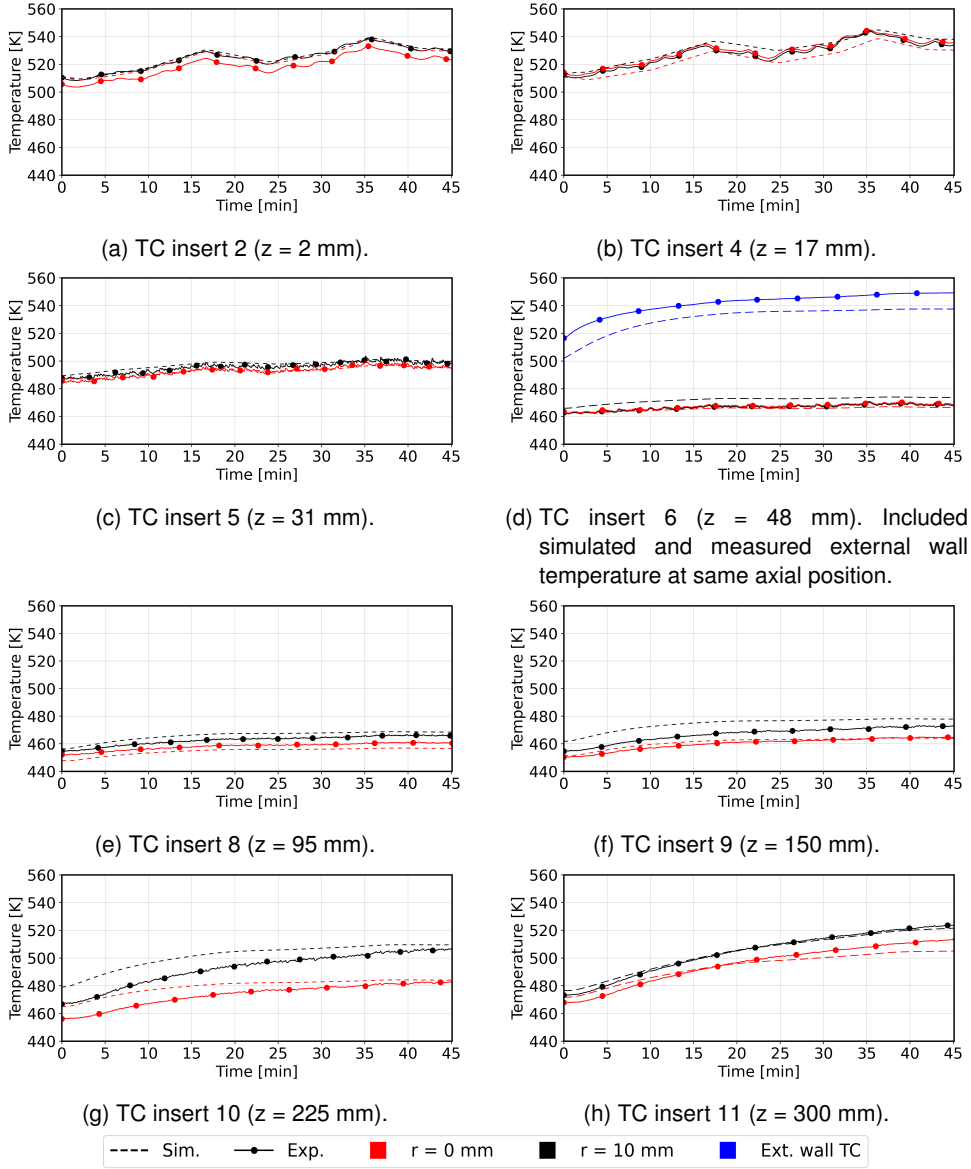


Figure B.7.: Thermocouple measurements and simulation in time: reactor response to heating increase $P_{el,in}$ 150-224 W at $W_{cat.}/F_{CH_3OH} = 150 \text{ kg s mol}^{-1}$

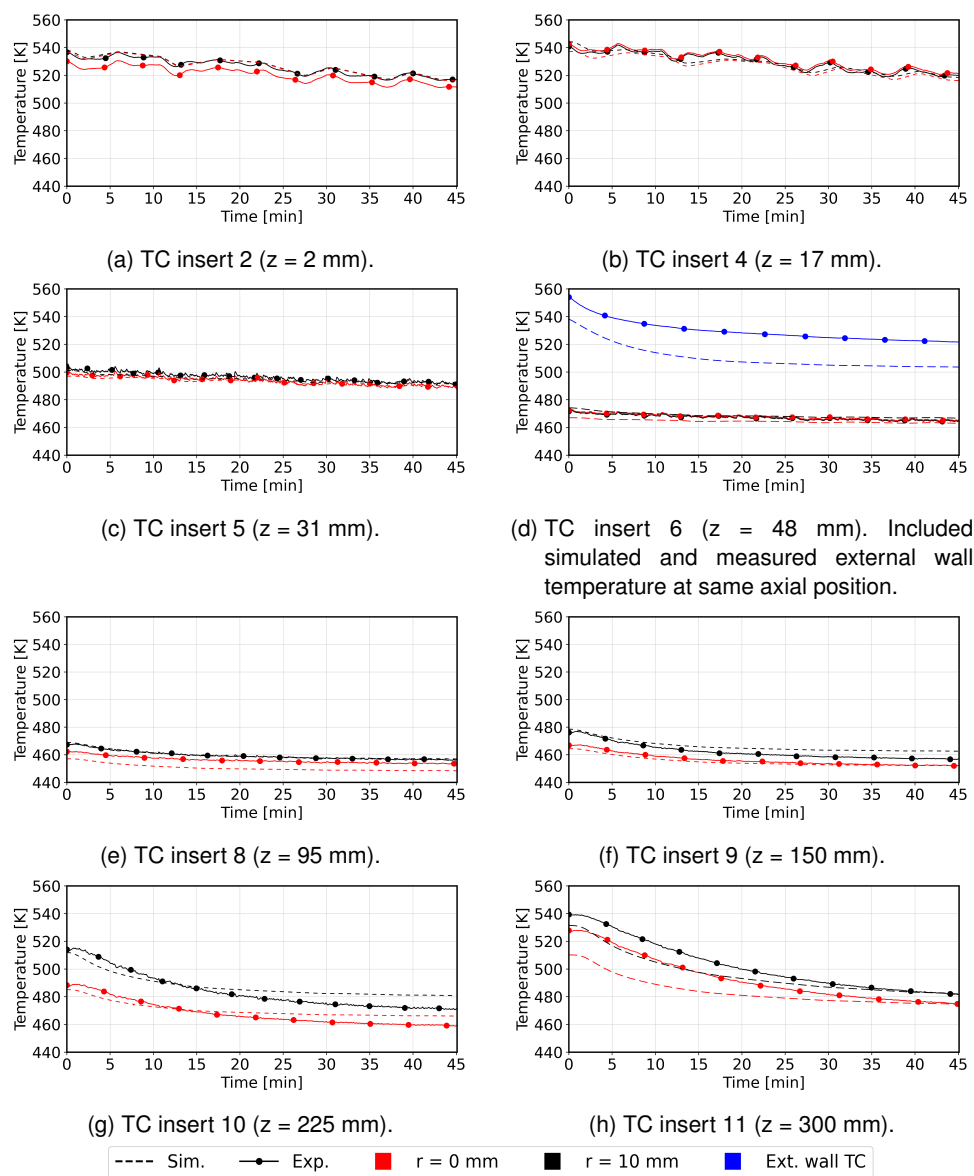


Figure B.8.: Thermocouple measurements and simulation in time: reactor response to heating decrease $P_{el,in}$ 224-150 W at $W_{cat.}/F_{CH_3OH} = 150 \text{ kg s}^{-1}$

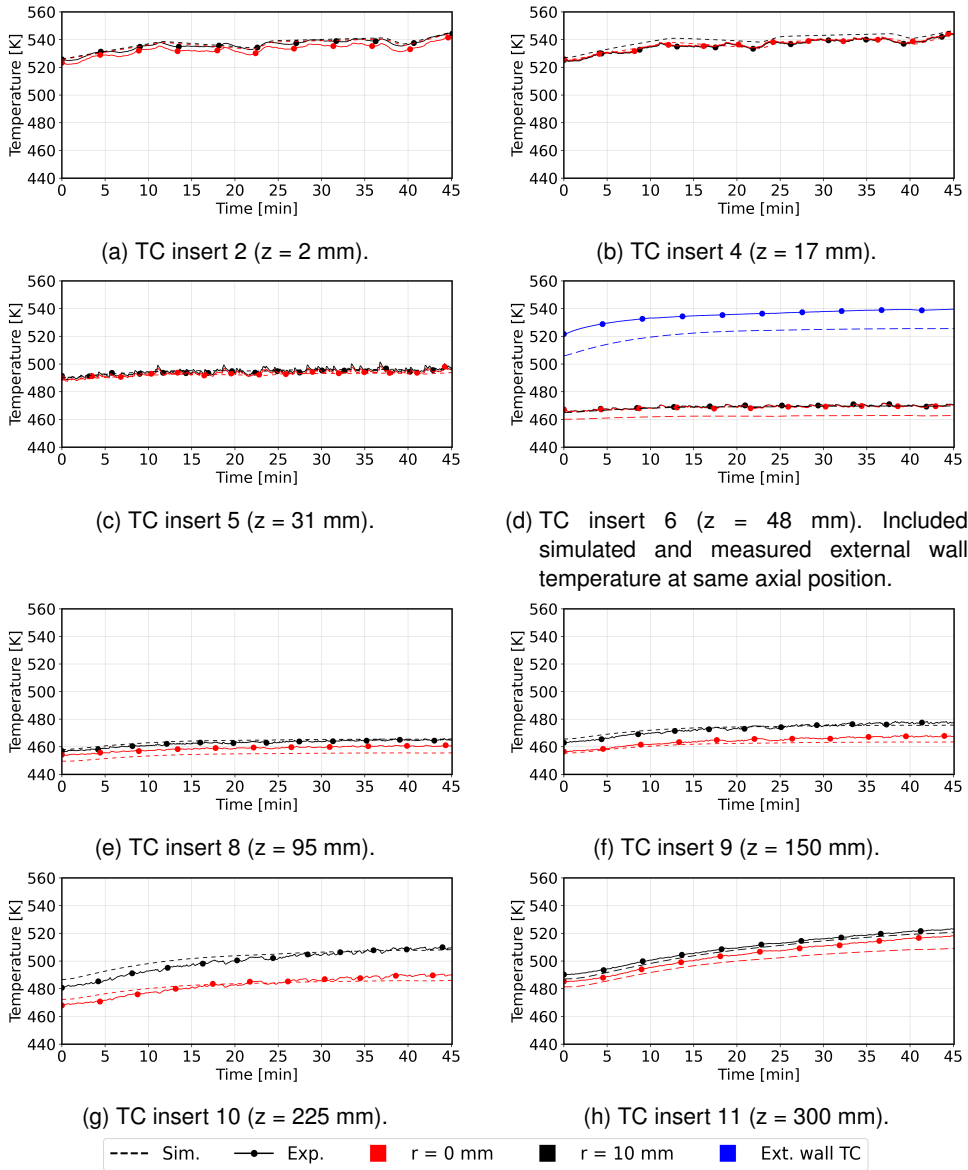


Figure B.9.: Thermocouple measurements and simulation in time: reactor response to heating increase $P_{el,in}$ 150-184 W at $W_{cat.}/F_{CH_3OH} = 200$ kg s mol⁻¹

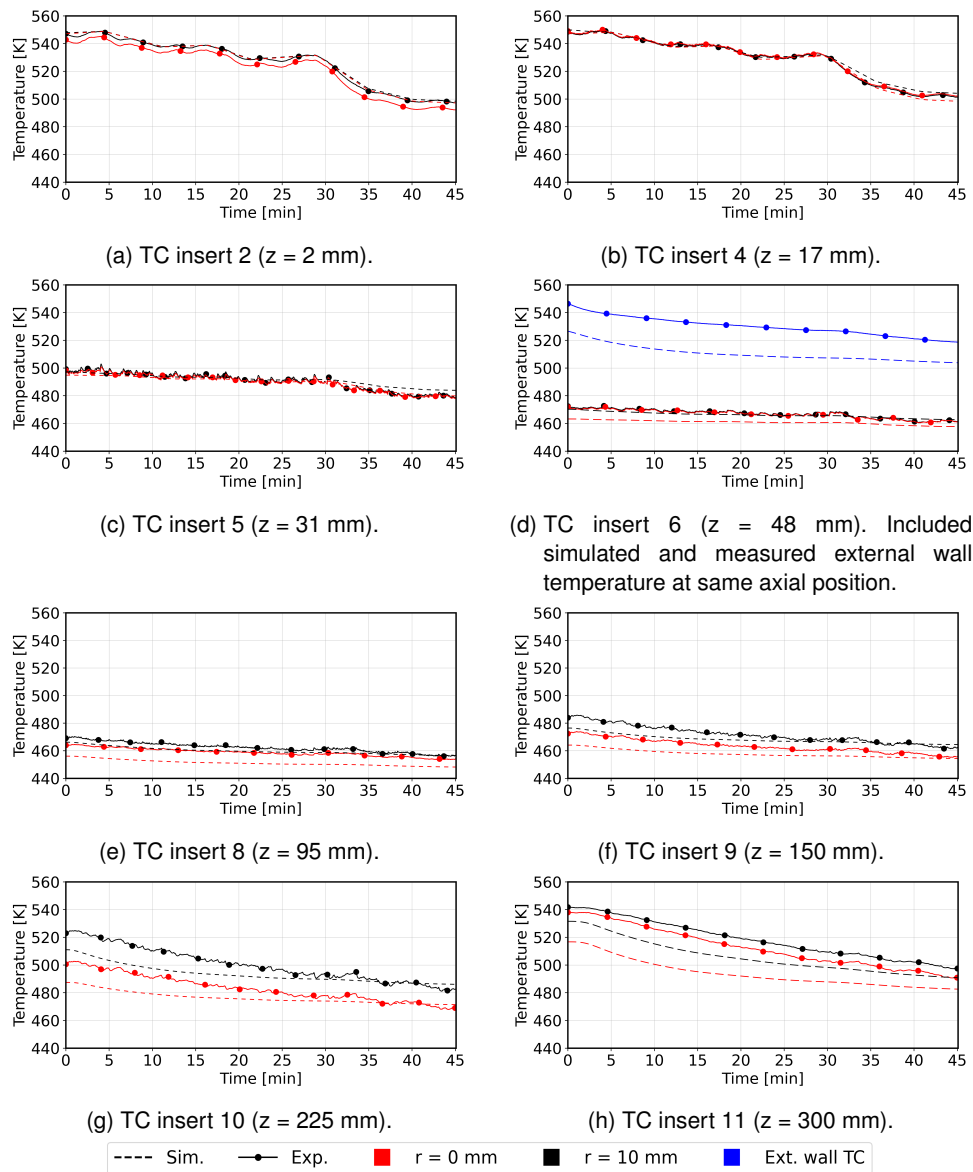


Figure B.10.: Thermocouple measurements and simulation in time: reactor response to heating decrease $P_{el,in}$ 184-150 W at $W_{cat.}/F_{CH_3OH} = 200$ kg s mol⁻¹

Acknowledgements

Some time ago, Joseph Campbell wrote that '*The privilege of a lifetime is being who you are*'. It seems to me that this privilege is made possible by the people around us: the close community that not only makes space for our individuality, but also gives it room to breathe, change, and grow. I am quite certain that I have found myself in such communities for the past several years. As the Count of Monte Cristo would say (yes, another quote): '*We are never quits with those who oblige us... for when we do not owe them money, we owe them gratitude*'. And thus I will never be quits with many, many people, so much so that I struggle to remember everyone I want to thank. So instead of listing names here, I wish to list things that made possible the privilege of being (and becoming) who I am. Dear reader, if you recognize yourself in anything written below, it is meant exactly for you.

To my supervisors, who cultivated my professional identity – I could not have imagined a better trio. Over the years I have discovered that you are not only excellent professionals, but genuinely great people. My updates were always met with interest while my doubts prompted advice and encouragement. I got all the input when I asked for it and all the independence when I wanted to work alone. You gave me your trust and allowed me to test boundaries. You saw what I could do long before I knew it. For all this and much more, I am deeply grateful to have had you on my side during this pilgrimage.

To the department staff – there is an old proverb that comes to mind: *it takes a village to raise a child*. In my case it takes two departments, and an entire laboratory with its staff. To all of you: thank you for taking good care of me as a worker and as a person. Thank you for taking care of our work environment. Thank you for answering a billion questions and helping me navigate through all bureaucratic and practical issues. Thank you for making my time here that much easier. You made the environment in which it all happened.

To the women in science and education – I have been continually impressed by the women who have been my professors, colleagues, friends, and students along my entire education path. The kind of strength, determination, and work quality that I have witnessed in the women around me have left a lasting impression on me. I cannot imagine my journey without the examples you have given me. Thank you for being a wonderful source of inspiration.

To everyone whose work crossed paths with mine – I am so very grateful that we had a chance to work together. My project ended up being shaped by other people much more than expected. Whether we met and worked together because of our research group/section, teaching, project, conferences, or by accident; all my interactions were fruitful in some way and honestly enjoyable. From the smallest advice to the biggest collaboration, working together brought much warmth to the workplace. All of this enriched the good days, and brightened the difficult days. My sincere thanks for the all the

pleasant moments of working together. One can only wish to again work with such people.

To all my friends in work and private life – There are so many of you I could not name everyone if I tried. Yes, I am that fortunate. In essence, I wish to thank you for anything that you shared with me: your time, laughs, pains, food, drinks, understanding, culture, advice, thoughts, ideas... Together we created so many fond memories that have enriched my time as a PhD candidate, which I will always remember. Thank you for the gift of your friendship. I am happy to have shared with you any extent of time in the past four years.

Za svo domaće društvo gdje god se nalazili – tko ima svoje ljude, doma je gdje god dođe. Tako je barem meni bilo na relaciji HR-NL proteklih godina. Ni moji stari ni novi prijatelji nikada nisu dopuštali da se zaborave dva iskonska hrvatska osjećaja: domoljublje i žgaravica. Za vas jedno posebno hvala na druženju, posjetama, pjesmama, hrani, kavicama, kritiziranju svega na svijetu, i svoj ostaloj nematerijalnoj kulturnoj baštini. Hvala što ste bili dio doma.

To my family – the encouragement I received could only be given by family. So how do I use words to thank those who are unconditionally proud and supportive of me? I can only try. My gratitude is equal to the support you have given me: limitless and everlasting.

Finally, the only people who know how much time we spend working are those waiting for us at home. In this one case, I cannot possibly list everything I am grateful for. Ida – simply thank you for everything. Bad days were never so bad with you around.

Curriculum Vitae

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Education

2022–2026 PhD Chemical Process Engineering
Delft University of Technology, the Netherlands
Thesis: Dynamic Methanol Reforming in Fixed Bed Reactors

2019–2020 MSc. Computational Fluid Dynamics
Cranfield University, United Kingdom
Thesis: Aerodynamic Analysis of Aerial Delivery of an Ocean-going Robot

2015–2019 BSc. Mechanical Engineering
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Thesis: Hydroelectric powerplant intake structure numerical analysis

Experience

2020-2021 Research Assistant
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2019 HVAC Design Assistant
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2017 Piping Manufacture Intern
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2016 Superstructure Dept. Intern
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Scientific contributions

Part of this dissertation

Journal publications

3. **Grenko, B.**, van Biert, L., van de Ketterij, R. and de Jong, W. *Experimental validation of a dynamic 2D model for catalytic methanol steam reforming in a fixed bed reactor* (2026). *Chemical Engineering Journal*
2. **Grenko, B.**, de Jong, W., van de Ketterij, R. and van Biert, L. *Analytical and numerical aspects of dynamic industrial chemical process analysis in fixed bed reactors* (2026). *Chemical Engineering Science*
1. **Grenko, B.**, de Jong, W., van de Ketterij, R. and van Biert, L. *Dynamic modelling of methanol steam reforming to hydrogen in a packed bed reactor for shipboard fuel cells* (2025). *Chemical Engineering Journal*

Conference presentations

3. **Grenko, B.**, de Jong, W., van de Ketterij, R., and van Biert, L. *Dynamic process modelling in H₂ economy: a case of methanol steam reforming*, at *Sustainable Energy and Process Technologies*, Eindhoven, the Netherlands; October 2025. (Oral presentation)
2. **Grenko, B.**, de Jong, W., van de Ketterij, R., and van Biert, L. *Variable hydrogen production from methanol for large transport applications*, at *European PhD Hydrogen Conference*, Trieste, Italy; April 2025. (Oral presentation)
1. **Grenko, B.**, van Biert, L., van de Ketterij, R., and de Jong, W. *Dynamic Methanol Steam Reforming To Hydrogen in a packed bed reactor for shipboard PEM fuel cells Methanol as a hydrogen carrier*, at *International Symposia on Chemical Reactor Engineering*, Turku, Finland; June 2024. (Poster presentation)

Additional contributions

4. Andriani, G., **Grenko, B.**, Pio, G., Vianello, C., Salzano, E., de Jong, W., van de Ketterij, R., van Biert, L., and Mocellin, P. *Model-based controllers of methanol steam reformers for hydrogen production: reduced-order modelling and experimental validation* (2026), 16th *Mediterranean Congress of Chemical Engineering*.
3. Sheikh Al-Shabab, A. A., Silva, P. A. S. F., **Grenko, B.**, Tsoutsanis, P. and Skote, M. A *Modular Multifidelity Approach for Multiphysics Oleo-Pneumatic Shock Absorber Simulations* (2024). *Proceedings of the Cambridge Unsteady Flow Symposium 2024*

2. La Colla, E., van Biert, L., **Grenko, B.** and Loeff, G. *Experimental and modelling studies on HVO-methanol mixtures separation for superyachts applications (2024). Conference Proceedings of INEC*
1. Sheikh Al-Shabab, A. A., **Grenko, B.**, Silva, P. A. S. F., Antoniadis, A. F., Tsoutsanis, P. and Skote, M. *Unsteady Multiphase Simulation of Oleo-Pneumatic Shock Absorber Flow (2024). Fluids*

