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Analytical and numerical aspects of dynamic industrial chemical process analysis in fixed bed reactors

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ABSTRACT

Recent research in chemical plant operation shows increasing interest in dynamic process operation as part of designed operating strategy for reasons such as increased dependency on renewable energy, and process intensification. Conventional analyses of fixed bed reactors are developed for steady state optimization and may not be adequate for dynamic operation. In fact, the important metrics and targets in dynamic process design are not entirely clear. The first objective of this article is to provide a state-of-the-art survey categorize types of dynamic operation, and rank the available common modelling and analytical tools suitable for quantification of dynamic process variables. The article then examines a case study of 1D and 2D model differences in a methanol steam reforming reactor. The case study shows model prediction differences of up to 15% for conversion, and up to 50% for CO concentration at the outlet during extreme load changes. The study concludes that the complexity of analytical and numerical techniques for dynamic processes is notably higher compared to steady state analyses, but appropriate tools and procedures are currently lacking.

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 (Bashmakov et al., 2023). Variations of renewable power share in the grid can be followed for plant sustainability goals (Klüh et al., 2024; Bielefeld et al., 2024), and in Power-to-X processes for chemical energy storage and renewable fuel production (Tiggeloven et al., 2025; Chen and Yang, 2021). 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 must also 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 (Fischer and Freund, 2020; Zimmermann et al., 2022; Mbatha et al., 2026). 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 (Bielefeld et al., 2023; Cegla et al., 2023), while at present it is uncertain whether the traditional steady state design techniques are optimal, or even sufficient for the task (Stegehake et al., 2019; Wentrup et al., 2022).

This article 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 article 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.

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Table 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)	> 8 h	Mixed integer linear programming (MATLAB)	Start-up, shut-down, load following
	Tiggeloven et al. (2025)	> 10 h	Mixed integer linear programming (MATLAB)	Start-up, shut-down, load following
	Giannikopoulos et al. (2022)	> 25 h	Mixed integer linear programming	Load following
	Foslie et al. (2024)	> 150 h	Mixed integer linear programming (Julia)	Load following
	Caspari et al. (2019)	> 48 h	1D plug flow model (Aspen plus)	Load following
	Chen and Yang (2021)	–	1D plug flow model (Aspen plus)	Yearly operation with pre-defined steady states
	Klüh et al. (2024)	–	1D plug flow model (Aspen plus)	Yearly operation with pre-defined steady states
	Bielefeld et al. (2024)	–	Linear programming	Yearly operation with pre-defined steady states
Forced periodic operation (reactor scale)	Leipold et al. (2025)	36 s > t > 1 h	1D unsteady plug flow (Julia) + multi objective optimization	Multiple periodic oscillations
	Leipold et al. (2024)	> 1 h	1D unsteady plug flow (Julia) + multi objective optimization	Multiple periodic oscillations
	Nikolič et al. (2016)	> 45 min	Unsteady CSTR (Julia) + nonlinear frequency response method	Multiple periodic oscillations
On-demand (system scale)	Hollmann and Kabelac (2023)	> 3 min	1D plug flow model (MATLAB Simulink)	Load following
	van Biert et al. (2019)	> 1.5 h	1D isothermal plug flow model (MATLAB simulink)	Start-up, load following

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. 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 1.

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. (2020) and Luo et al. (2022). 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. (2023) and Cegla et al. (2023). 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. (2023) 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 (Tiggeloven et al., 2025) 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 (2021) 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. (2024) 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. (2024) 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. 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. (2022) 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. (2020) 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 h per 30 min 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. (2007) 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. (2019) 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 s.

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. (2007) note that loop reactors can better exploit the catalyst heat capacity. Both Barresi et al. (2007) and Sheintuch and Nekhamkina (2021) 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.

2.3. 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 cshemical 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 (van Biert et al., 2016) in response to strict emission regulations for ships (International Maritime Organisation, 2017), and problematic on-board hydrogen storage systems (van de et al., 2024). 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 (Rheenen et al., 2024). For example, partial or complete methane reforming is most common for solid oxide fuel cell systems (van Veldhuizen et al., 2023). 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 (Rheenen et al., 2024).

Such shipboard systems are medium sized in comparison with traditional chemical plants (Ma et al., 2024; Duong et al., 2024; Shi et al., 2024), 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 (RIX Industries, 2025), Mreformer (MMM Energy, 2025), and Amogy genset (Amogy Inc.) 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 (gCapitan Maritime News, 2025), and shipbuilder orders for hydrogen generators (PowerCell Sweden AB, 2025). 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 (Ma et al., 2024; Zhu et al., 2024). 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 (Seborg et al., 2011), which studies use to this day (Hollmann and Kabelac, 2023; van Biert et al., 2019).

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 reactor simulations steady and unsteady, and discusses how they are reflected among the recent unsteady modelling case studies.

3.1. Model characteristics

The reactor model characteristics vary based on the academic literature type, and publication date. Books on chemical reaction engineering

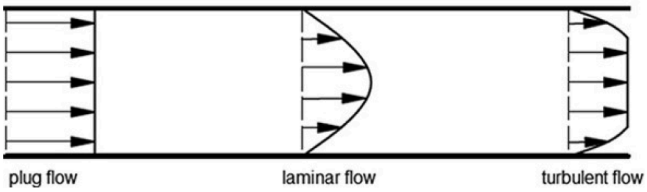


Fig. 1. Plug flow graphical representation. Reprinted from Bogatykh and Osterland (2019) with permission of Wiley, Copyright 2019.

tend to describe idealized approaches, mainly for reactor sizing using a steady state design approach. For example, Jakobsen (Jakobsen, 2014) shows only the simplest steady state approaches in the context of chemical reaction engineering, despite covering complex reactive flow models in great detail. Conesa (Conesa, 2019) 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 Fig. 1 are used extensively. More complex models and their applications for chemical reaction engineering are seldom described.

Scientific publications review model requirements for chemical engineering, often thoroughly exploring only one aspect. Zagoruiko et al. (2021) 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 and Santacesaria (2020) also advocate for capturing the macroscopic and microscopic gradients in the models depicted in Fig. 2, arguing that all processes interact with each other. They also find that internal diffusion limitations strongly influence process selectivity.

Stegehake et al. (2019) and Fabrik et al. (2022) 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. (2026) note in their review of CFD methods of modelling fuel production from CO2 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. (2022) 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 (Stegehake et al., 2019; Fabrik et al., 2022; Harkou et al., 2026; Micale et al., 2022) 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.

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 (Fischer and Freund, 2020; Zimmermann et al., 2022; Fischer and Freund, 2021), CO2 hydrogenation to methanol (Mbatha et al., 2026), or ammonia synthesis (Gottheil and Bremer, 2024). 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 Fig. 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. (2022) 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. Fig. 4

Giglio et al. (2021) 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 and Pashchenko (2023) 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 Fig. 4a and predicted the molar fraction reduction of produced hydrogen from 0.377 to 0.249 in 15 s of operation, as shown in Fig. 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. (2024) and Peltola et al. (2022). Kataria et al. stated 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. (2022) 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.

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. (2019) compare 1D to

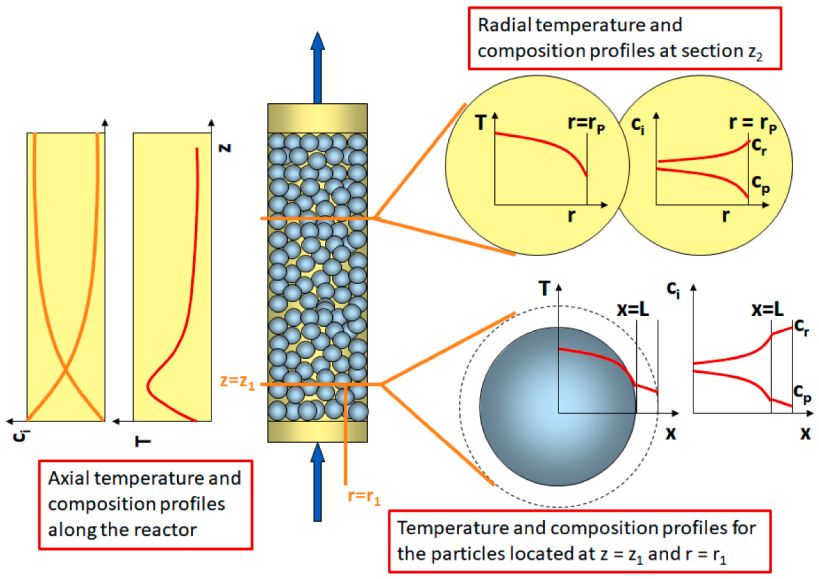
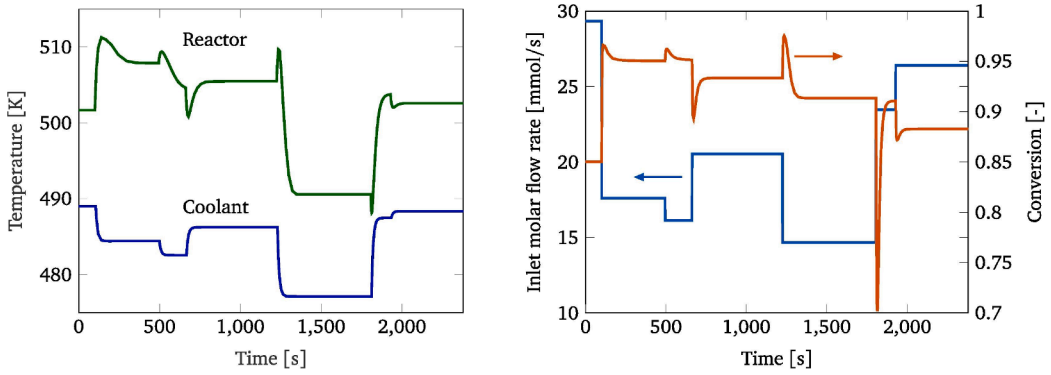


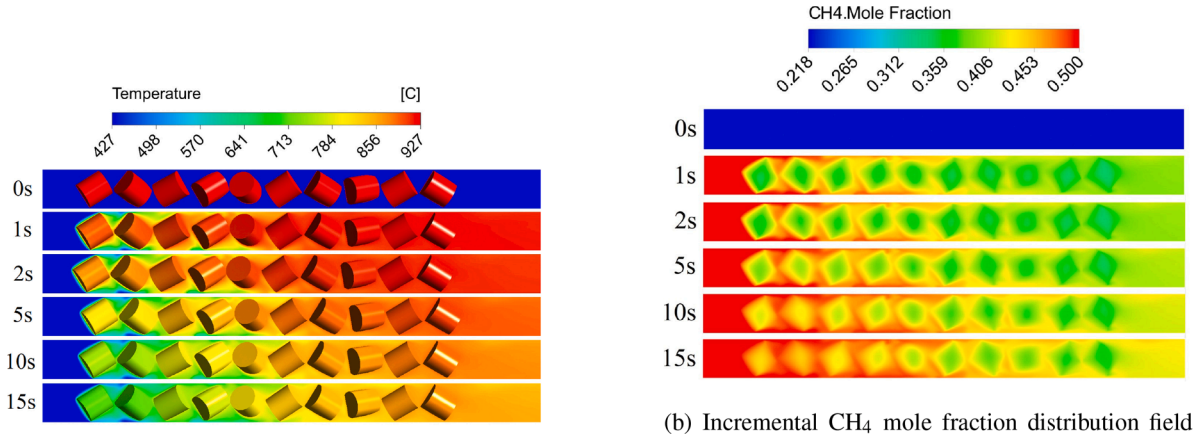
Fig. 2. Interparticle and intraparticle gradients of heat and concetration within a packed bed reactor. Reprinted from Tesser and Santacesaria (2020) with permission of MDPI, Copyright 2020.



(a) Average temperature in the reactor and coolant in response to varying inlet molar flow rate.

(b) Variations of inlet flow rate and resulting conversion at the outlet.

Fig. 3. 1D unsteady simulation of CO2 methanation in a wall-cooled fixed bed reactor with varying inlet molar flow rate. Reprinted from Fischer and Freund (2020) with permission of Elsevier, Copyright 2020.



(a) Incremental temperature field plots in time

(b) Incremental CH_4 mole fraction distribution field plots in time

Fig. 4. Unsteady 3D steam methane reforming simulation of a single reforming cycle after hot stand-by in a simplified packed bed geometry. Reprinted from Karpilov and Pashchenko (2023) with permission of Elsevier, Copyright 2023.

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. (2022) 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. (2024) 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. (2021) 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. (2025) 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. (2025) 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.

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 1. Instead, the available models affect the simulated domains and timescales, which is seen in CFD studies (Karpilov and Pashchenko, 2023). 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 Dixon (2025) 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.

3.5. Design speed-up with data driven approaches

Data driven approaches have been gaining popularity many applications. They have large potential use, considering the recent insights from Power-to-X review papers (Huerta-Rosas et al., 2025; Rentschler et al., 2024). 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 and Continillo (2021) 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. (2025) 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 (Grimm et al., 2024), temperature gradients (Hu et al., 2026), but also multiple simultaneous objectives (Han and Kim, 2024).

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.

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 (Stegehake et al., 2019; Wentrup et al., 2022) 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 H2, N2, O2, CO, CO2, NH3, 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.

Table 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	Fialkov et al. (2020), Harris and Lucy (2016)
MS	Real time with DIMS	High sensitivity	Complexity, cost, required operator skill, difficulty detecting H2, CH4, and most air components	Often used as complementary technique to GC	Langford (2022), Pleil et al. (2019), Ren et al. (2025), Dryahina et al. (2010)
FTIR	Real time	Fast in-line analysis, no sample preparation	Lower sensitivity than GC and MS, cannot detect H2, N2, and O2	Often used as complementary technique to GC	Guerrero-Pérez and Patience (2020), Giechaskiel and Clairotte (2021)
NDIR	mili(second) range	Fast analysis, lower cost and complexity than FTIR	Cannot detect H2, N2, and O2	Most often requires one sensor per specie	Jha (2022), Liang et al. (2023), Tan et al. (2020)
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	Das and Agrawal (2011), Majumder et al. (2025), Petrov and Matrosov (2016), Gao et al. (2019)
TDLAS	(mili)second range	No sample preparation, fast analysis, high potential sensitivity	Weak detection of H2 and N2, may need a sensor per detected specie	Sensitivity and analysis time are correlated	Avetisov et al. (2019), Liang et al. (2022), Wang et al. (2022), Sun et al. (2024), Liu et al. (2023), Nwaboh et al. (2017)

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

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 min 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. Fialkov et al. (2020) demonstrated analysis cycle time below 1 min 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 by case basis, since it also depends on the time-scale of the characterized transient event.

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) (Langford, 2022). These techniques are mostly used for analyses of breath or volatile organic compounds in the air (Pleil et al., 2019). Applications in chemical industry are scarce but present, with an example given by Ren et al. (2025) 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 $H3O+$, $NO+$, or $O2+$ do not react with hydrogen, methane, and species in ambient air (Dryahina et al., 2010); 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.

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 (Guerrero-Pérez and Patience, 2020), and analysis of hydrocarbon fuels and exhaust gas emissions (Giechaskiel and Clairotte, 2021). 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 H2, N2, and O2, 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.

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 CO2 levels in the air, breath, or emission monitoring systems (Jha, 2022). Quantification of gas concentrations is in the ppm range, and the analysis time can vary between milisecond and second scale (Liang et al., 2023). Multi-species detection systems with NDIR are possible, but better performing systems tend to be bulky and with high acquisition and maintenance costs (Liang et al., 2023; Tan et al., 2020). Same as in FTIR, the main limitation of NDIR for present purpose is the inability to detect gases without dipole moments.

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 (Das and Agrawal, 2011). 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 (Majumder et al., 2025). Raman has been recognized to be suitable for on-line natural gas analysis (Petrov and Matrosov, 2016; Gao et al., 2019), and several commercial solutions and implementation for natural gas analysis with run times of around 30 s are already on the market (Majumder et al., 2025). The technique is able to identify species of interest in fast analysis, making Raman spectroscopy a suitable analysis technique candidate.

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 H2 and N2. 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 (Avetisov et al., 2019; Liang et al., 2022). 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 (Wang et al., 2022; Sun et al., 2024). Successful demonstration of TLDAS in practice has been shown for processes with natural gas and typical accompanying species at low weight and instrumentation cost (Liu et al., 2023; Nwaboh et al., 2017). TLDAS therefore appears very useful for a multitude of dynamic process contexts.

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 (Sampaolo et al., 2022). 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 (Abina et al., 2023).

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 (Holmen et al., 2023). 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 (Morgan et al., 2017).

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 (Meyer et al., 2022; Mane et al., 2024).

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 (Spatenka et al., 2019).

Flores-Tlacuahuac et al. (2024) 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.

5. Case study: methanol steam reforming

Methanol steam reforming to hydrogen is recognized as one of the viable pathways for on-demand H2 production on board of ships for fuel cell applications (van Biert et al., 2016). 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 H2 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/Al2O3 composition are packed in a tube-in-shell heat exchanger, as shown in Fig. 5, where three dominant reforming reactions are sustained: methanol steam reforming (MSR), methanol decomposition (MD), and water gas shift (WGS), shown in Eqs. 1–3.

MSR	$CH_3OH + H_2O \Leftrightarrow CO_2 + 3\ H_2$	$\Delta H = 49.4$ kJ/mol	(1)
MD	$CH_3OH \Leftrightarrow CO + 2\ H_2$	$\Delta H = 90.5$ kJ/mol	(2)
WGS	$CO + H_2O \Leftrightarrow CO_2 + H_2$	$\Delta H = -41.1$ kJ/mol	(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.

5.1. Numerical models

The utilized unsteady 2D packed bed reactor model is explained in detail in a previous publication (Grenko et al., 2025), and the code is available via Git repository (Grenko, 2025). The equations of mass and energy balance are:

$$\varepsilon \frac{\partial C_i}{\partial t} = -u_s \frac{\partial C_i}{\partial z} + D_{er}\left(\frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r}\frac{\partial C_i}{\partial r}\right) + \rho_c r_i, \tag{4}$$

$$\left(\varepsilon \rho_f c_{p,f} + (1-\varepsilon)\rho_s c_{p,s}\right)\frac{\partial T}{\partial t} = -u_s \rho_f c_{p,f}\frac{\partial T}{\partial z} + \lambda_{er}\left(\frac{\partial^2 T}{\partial^2 r} + \frac{1}{r}\frac{\partial T}{\partial r}\right) + \sum \eta_j \rho_c (-\Delta H_j) r_j S_c, \tag{5}$$

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} (m^2 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

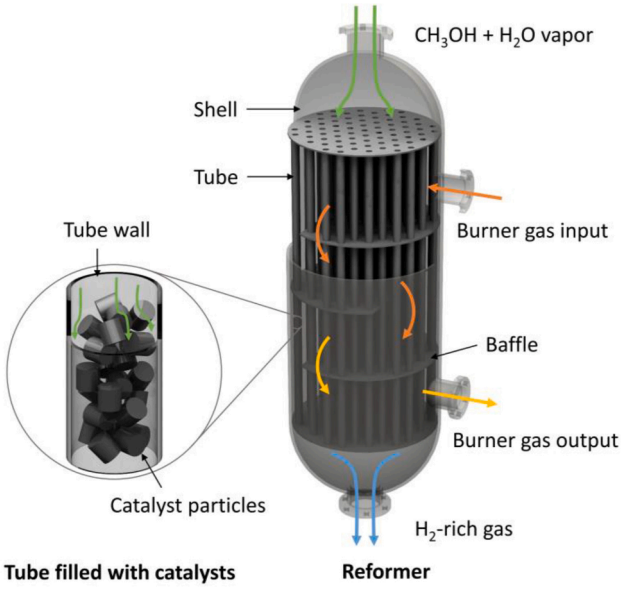


Fig. 5. Multi-tubular fixed bed methanol steam reforming reactor. Reprinted from Zhu et al. (2022b) with permission of Elsevier, Copyright 2022.

Table 3
Simulation boundary conditions.

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

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 (m^{-2} 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 3.

The model omits an axial dispersion term. Sahimi (2011) distinguishes between several dispersion regimes dependent on the Peclet number. Thus, the *power-law* regime between $5 < \text{Pe} < 300$ is dominated by convective transport with some molecular diffusion, while the *purely convective* regime falls between $300 < \text{Pe} < 10^5$. The characteristic flows for methanol steam reforming used in present simulations result in $\text{Pe} > 230$, 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. (1999), and the pressure drop is calculated with the Ergun equation (Fogler, 2005). The flue gas energy equation was adapted from Varma et al. (1999) for unsteady incompressible flow:

$$\rho_{fg} c_{p,fg} A_{pe} \frac{\partial T_{fg}}{\partial t} = -c_{p,fg} \dot{m} \frac{\partial T_{fg}}{\partial z} + d_{t,out} \pi N_t h_{s,fg} \Delta T_{fg}, \tag{6}$$

where rho_{fg} (kg m^{-3}) is the flue gas density, $c_{p,fg}$ (J kg^{-1} 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,

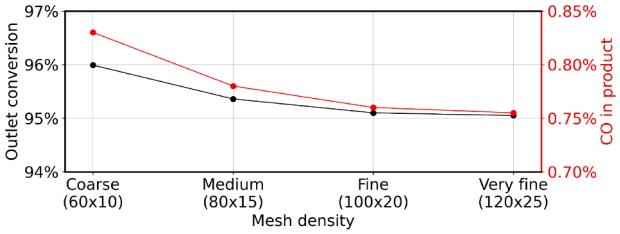


Fig. 6. Mesh independence study: effects of refining the mesh in axial and radial direction on the outlet methanol conversion and CO content in the product with the $d_{in} = 20$ mm reactor case.

N_t is the number of tubes in a reactor, and $h_{s,fg}$ (W m^{-2} K^{-1}) is the heat transfer coefficient from flue gas to the reactor tube outer wall.

Reactor tube wall temperature is computed according to:

$$\rho_w c_{p,w} \frac{\partial T_w}{\partial t} = k_w \frac{T_w}{\partial z} + U \Delta T_{fg,w} \frac{A_{t,out}}{V_t} - h_t \Delta T_{w,r} \frac{A_{t,in}}{V_t} \tag{7}$$

where ρ_w (kg m^{-3}) is the reactor tube density, $c_{p,w}$ (J kg^{-1} K^{-1}) is the reactor tube specific heat capacity, T_w (K) is the wall temperature, k_w (W m^{-1} K^{-1}) is the thermal conductivity of tube wall material, U (W m^{-2} K^{-1}) is the combined heat transfer coefficient, h_t (W m^{-2} 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:

$$U = \left(\frac{s_w}{k_w} \frac{d_{t,out}}{d_{lm}} + \frac{1}{h_s} \frac{d_{t,in}}{d_{t,out}} \right)^{-1}, \tag{8}$$

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 Fig. 6. The outlet methanol conversion and CO content in the reformate 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.

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 $4 \cdot 10^{-4}$ s. All cases were run simultaneously on a personal computer with Intel i7 processor. The resulting computational times for 20 min simulated time in unsteady cases were ≤30 h with 2D model, and ≤14 h with 1D model.

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 (Omojola, 2025). The reaction dynamics are not included in effectiveness factors either. In present study they are calculated with the Thiele modulus approach (Driessen et al., 2020), which

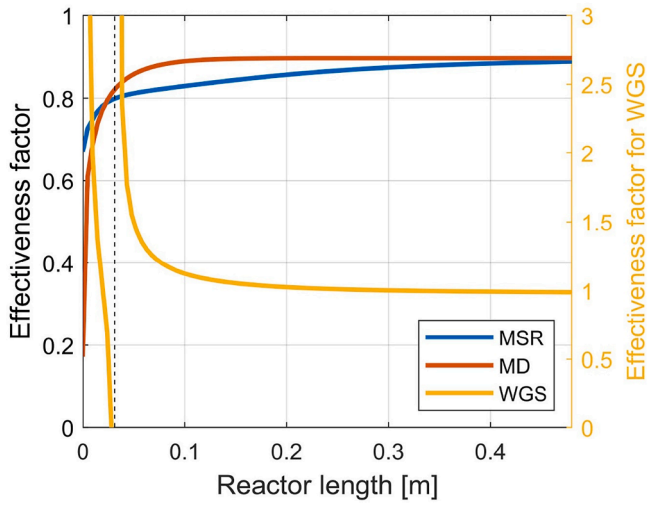


Fig. 7. Effectiveness factors for MSR, MD and WGS reactions along the methanol steam reforming reactor length. Reprinted from Zhu et al. (2022a) with permission of Elsevier, Copyright 2022.

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. (2022a) conclude the highest factor influence in the near-inlet zone, after which they quickly stabilize, as shown in Fig. 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.

Second, at present time the 2D model is only validated in steady state by Zhu et al. (2022b) as shown in Fig. 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 CH3OH conversion and CO content along the reactor length are shown in Fig. 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.

The sensitivity analysis 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 Fig. 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.

5.3. Simulated cases

The case study simulates a small tube-in-shell 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 4.

Table 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

Table 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 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 Fig. 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 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.

5.4. Results

Four unsteady cases were simulated with both models for each tube diameter: feed increase from $W_{cat.}/F_{CH_3OH} = 300\,\text{kg s mol}^{-1}$ to $150\,\text{kg s mol}^{-1}$, feed decrease from $W_{cat.}/F_{CH_3OH} = 150\,\text{kg s mol}^{-1}$ to $300\,\text{kg s mol}^{-1}$, feed increase to $W_{cat.}/F_{CH_3OH} = 300\,\text{kg s mol}^{-1}$ from reactor hot standby in non reactive conditions at 473 K, and feed increase to $W_{cat.}/F_{CH_3OH} = 150\,\text{kg s mol}^{-1}$ 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 Fig. 12. The plots for $d_{in} = 30$ cases in Fig. 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 Fig. 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.

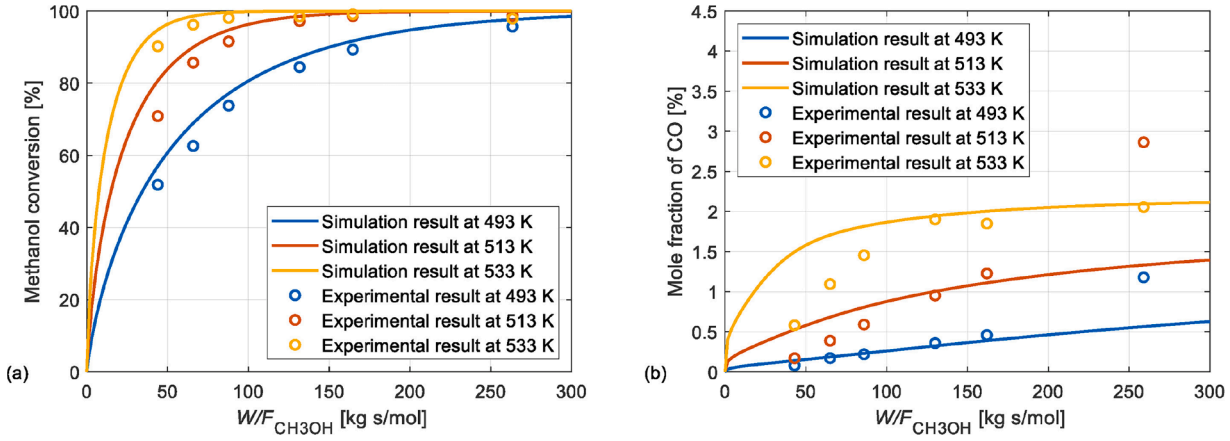


Fig. 8. Experimental validation of steady state methanol steam reforming model on a small packed bed experimental reactor (3.6 mL) with outlet methanol conversion and CO mole fraction. Reprinted from Zhu et al. (2022b) with permission of Elsevier, Copyright 2022.

Table 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 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

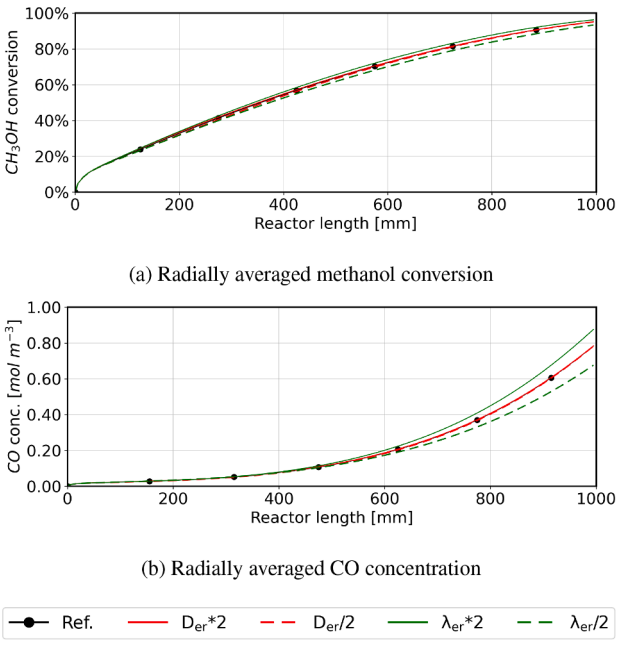


Fig. 9. Parameter sensitivity study: effects of doubling and halving the calculated radial mass (D_{er}) and heat (λ_{er}) effective dispersion coefficients on outlet methanol conversion and CO content along the reactor length.

The predictions of average reactor temperatures match closely in magnitude and trends between 1D and 2D models, as seen in Fig. 12b. However, the minimum and maximum reactor temperatures visibly differ in magnitude, as shown in Figs. 12c and 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.

Table 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

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.

Fig. 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

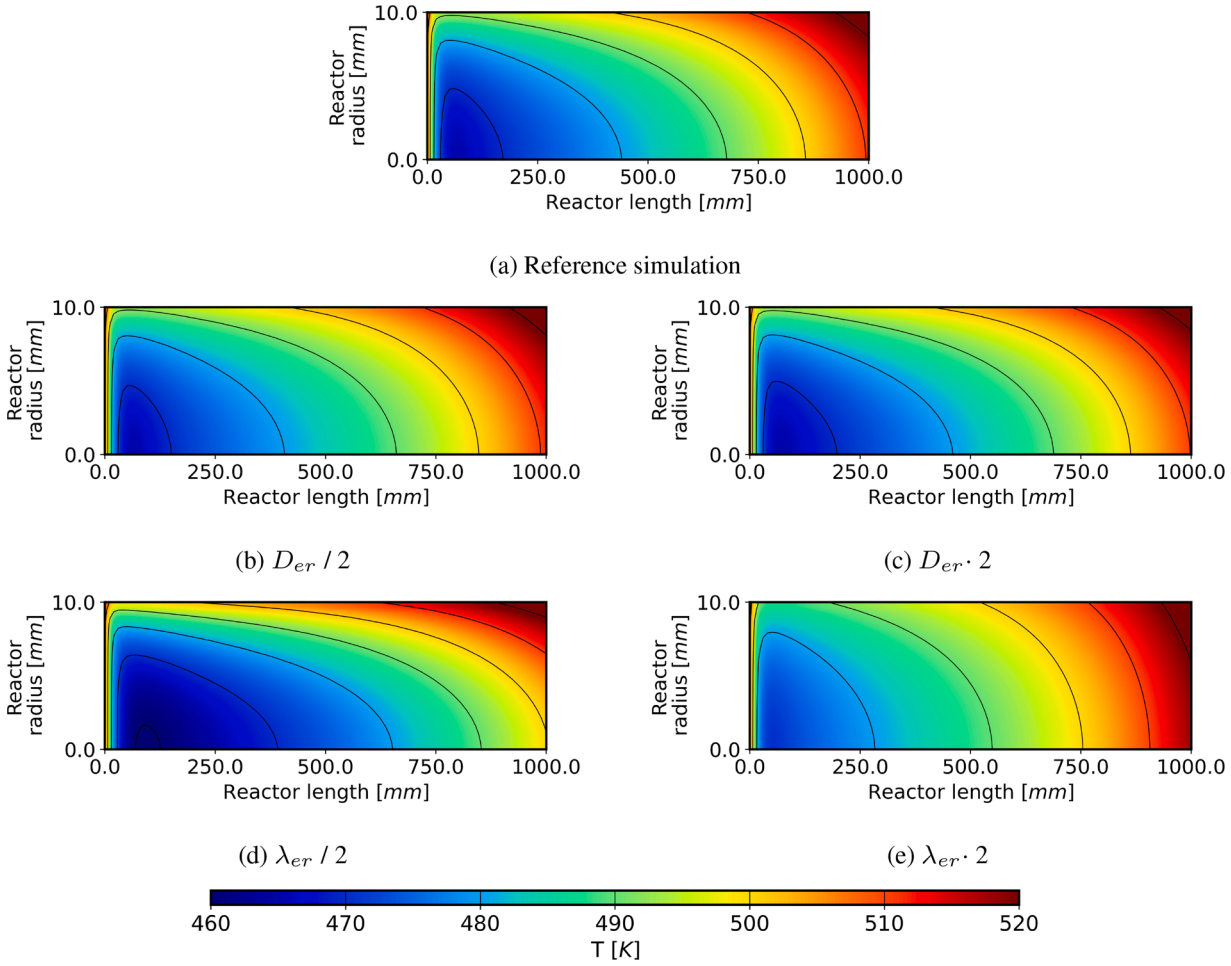


Fig. 10. Parameter sensitivity study: effects of doubling and halving the calculated radial mass (D_{er}) and heat (λ_{er}) effective dispersion coefficients on the internal temperature field.

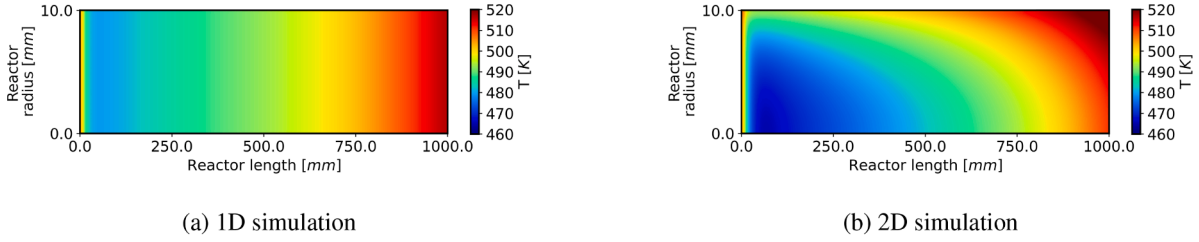


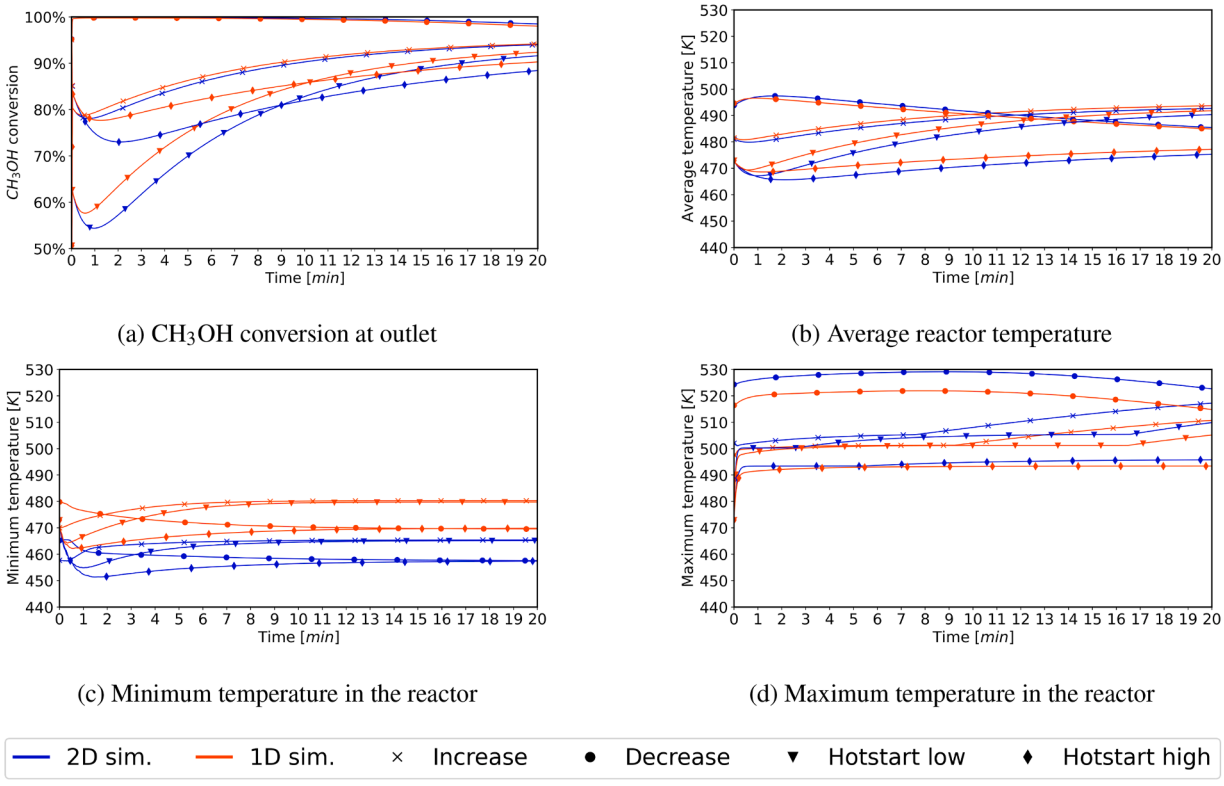
Fig. 11. The differences in temperature field plots between 1D and 2D simulations on a reactor with $d_{in} = 20$ mm at steady state with a throughput of $W_{cat}/F_{CH_3OH} = 150$ kg mol s^{-1}.

ones shown in Fig. 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.

6. Discussion

Dynamic reactor operation can hardly be addressed in a systematic way for all types of analyses. However, even the appropriateness of transient analyses is not clearly defined. The lack of such definitions expectedly disables the standardization of design and control of dynamic chemical processing systems.

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 determines the response to the expected product demand. Ultimately, the common theme across the operation types is that the importance of dynamic analysis is higher when transients are often expected.



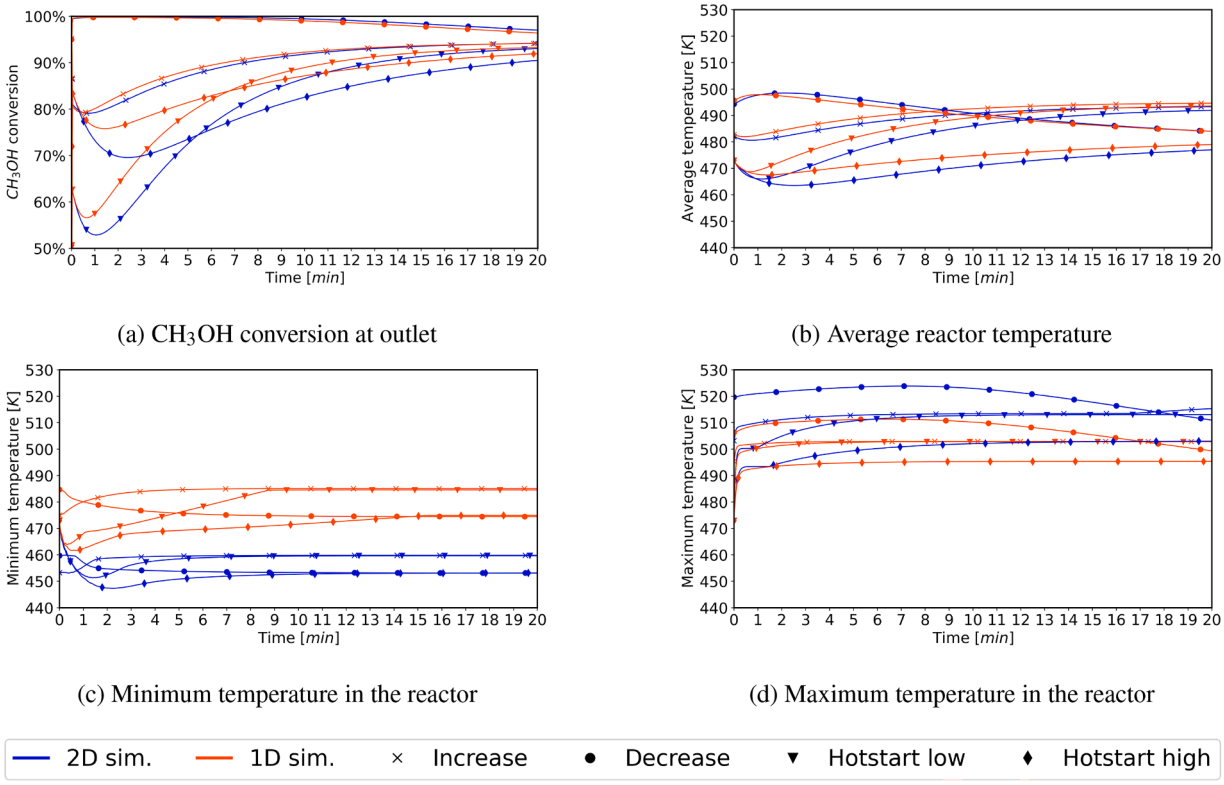
(a) CH_3OH conversion at outlet

(b) Average reactor temperature

(c) Minimum temperature in the reactor

(d) Maximum temperature in the reactor

Fig. 12. Comparison of output process variables in time for 1D and 2D simulations on d_{in} = 20mm reactor.



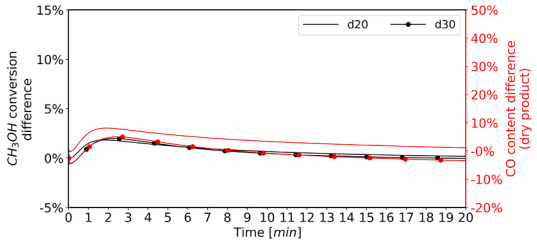
(a) CH_3OH conversion at outlet

(b) Average reactor temperature

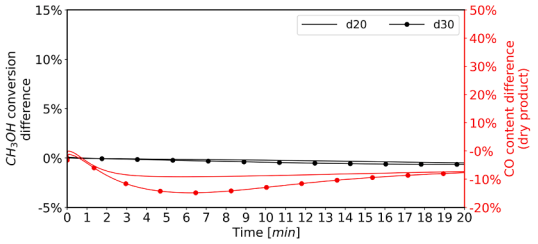
(c) Minimum temperature in the reactor

(d) Maximum temperature in the reactor

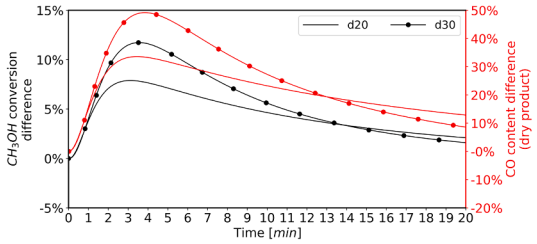
Fig. 13. Comparison of output process variables in time for 1D and 2D simulations on d_{in} = 30mm reactor.



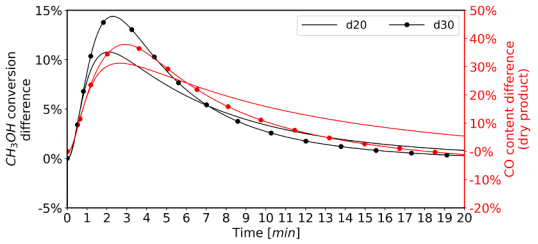
(a) Case 1: instantaneous feed increase from steady state W_{cat}/F_{CH_3OH}=300 to steady state W_{cat}/F_{CH_3OH}=150 kg mol s^{-1}



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



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



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

Fig. 14. Difference plots of 1D model relative to the 2D model in predicting methanol conversion and CO content at the reactor outlet.

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.

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. (2022), 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 (Pérez-Gallego et al., 2025), 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.

7. Conclusions

The unsteady operation of fixed bed reactor is analysed in this paper 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 study 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.

CRediT authorship contribution statement

Bojan Grenko: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization; **Wiebren de Jong:** Writing – review & editing, Supervision, Methodology, Investigation, Formal analysis, Conceptualization; **Robert van de Ketterij:** Writing – review & editing, Supervision, Formal analysis, Conceptualization; **Lindert van Biert:** Writing – review & editing, Supervision, Project administration, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Abina, A., Puc, U., Jazbinšek, M., Zidanšek, A., 2023. Analytical gas sensing in the terahertz spectral range. Micromachines 14 (11). https://doi.org/10.3390/mi14111987

Amogy Inc. Ammonia-to-power. Accessed: 2025-07-25. https://amogy.co/ammonia-to-power.

Argyris, P.A., de Leeuwe, C., Abbas, S.Z., Spallina, V., 2022. Mono-dimensional and two-dimensional models for chemical looping reforming with packed bed reactors and validation under real process conditions. Sustainable Energy Fuels 6 (11), 2755–2770. https://doi.org/10.1039/d2se00351a

Avetisov, V., Bjoroey, O., Wang, J., Geiser, P., Paulsen, K.G., 2019. Hydrogen sensor based on tunable diode laser absorption spectroscopy. Sensors 19 (23). https://doi.org/10.3390/s19235313

Barresi, A.A., Baldi, G., Fissore, D., 2007. Forced unsteady-state reactors as efficient devices for integrated processes: case histories and new perspectives. Ind. Eng. Chem. Res. 46 (25), 8693–8700. https://doi.org/10.1021/ie070477k

Bashmakov, I.A., Nilsson, L.J., Acquaye, A., Bataille, C., Cullen, J.M., de la Rue du Can, S., Fischedick, M., Geng, Y., Tanaka, K., 2023. Industry. Cambridge University Press. p. 1161–1244. https://doi.org/10.1017/9781009157926.013

Bielefeld, S., Cvetkovič, M., Ramirez, A.R., 2024. Electrification in the petrochemical industry: can flexibility enable low-carbon utility systems? In: Manenti, F., Reklaitis, G.V. (Eds.), 34th European Symposium on Computer Aided Process Engineering / 15th International Symposium on Process Systems Engineering. Elsevier. Vol. 53 of *Computer Aided Chemical Engineering*, pp. 2227–2232. https://doi.org/10.1016/B978-0-443-28824-1.50372-0

Bielefeld, S., Cvetkovič, M., Ramírez, A., 2023. Should we exploit flexibility of chemical processes for demand response? differing perspectives on potential benefits and limitations. Front. Energy Res. Volume 11 - 2023. https://doi.org/10.3389/fenrg.2023.1190174

Bizon, K., Continillo, G., 2021. Efficient optimization of a multifunctional catalytic fixed-bed reactor via reduced-order modeling approach. Chem. Eng. Res. Des. 165, 214–229. https://doi.org/10.1016/j.cherd.2020.11.007

Bogatykh, I., Osterland, T., 2019. Characterization of residence time distribution in a plug flow reactor. Chem. Ing. Tech. 91 (5), 668–672. https://doi.org/10.1002/cite.201800170

Bruns, B., Herrmann, F., Polyakova, M., Grünewald, M., Riese, J., 2020. A systematic approach to define flexibility in chemical engineering. J. Adv. Manuf. Process. 2 (4). https://doi.org/10.1002/amp2.10063

Caspari, A., Offermanns, C., Schäfer, P., Mhamdi, A., Mitsos, A., 2019. A flexible air separation process: 2. optimal operation using economic model predictive control. AIChE J. 65 (11), e16721. https://doi.org/10.1002/aic.16721

Cegla, M., Semrau, R., Tamagnini, F., Engell, S., 2023. Flexible process operation for electrified chemical plants. Curr. Opin. Chem. Eng. 39, 100898. https://doi.org/10.1016/j.coche.2023.100898

Chen, C., Yang, A., 2021. Power-to-methanol: the role of process flexibility in the integration of variable renewable energy into chemical production. Energy Convers. Manage. 228, 113673. https://doi.org/10.1016/j.enconman.2020.113673

Conesa, J.A., 2019. Forced Unsteady State Operation of Chemical Reactors. John Wiley & Sons, Ltd. chapter 7. pp. 157–171. https://doi.org/10.1002/9783527823376.ch7

Das, R.S., Agrawal, Y.K., 2011. Raman spectroscopy: recent advancements, techniques and applications. Vib. Spectrosc. 57 (2), 163–176. https://doi.org/10.1016/j.vibspec.2011.08.003

Dixon, A.G., 2025. Fixed bed heat transfer parameter estimation –a new look at an old problem. Chem. Eng. Sci. 302, 120874. https://doi.org/10.1016/j.ces.2024.120874

Driessen, R.T., Kersten, S. R.A., Brilman, D. W.F., 2020. A thiele modulus approach for nonequilibrium adsorption processes and its application to CO2 capture. Ind. Eng. Chem. Res. 59 (15), 6874–6885. https://doi.org/10.1021/acs.iecr.9b05503

Dryahina, K., Smith, D., španěl, P., 2010. Quantification of methane in humid air and exhaled breath using selected ion flow tube mass spectrometry. Rapid Commun. Mass Spectrom. 24 (9), 1296–1304. https://doi.org/10.1002/rcm.4513

Duong, P.A., Ryu, B.R., Nam, T.T., Lee, Y.H., Jung, J., Lee, J.-K., Kang, H., 2024. Comparative study of thermodynamic performances: ammonia vs. methanol SOFC for marine vessels. Chem. Eng. Technol. 47 (9), e202400118. https://doi.org/10.1002/ceat.202400118

Fabrik, M., Salama, A., Ibrahim, H., 2022. State-of-the-art in methane-reforming reactor modeling: challenges and new insights. Rev. Chem. Eng. 38 (8), 991–1022. https://doi.org/10.1515/revce-2020-0038

Fatahillah, M.R., Monjezi, R., Ouyang, Y., Thybaut, J.W., Poelman, D., Heynderickx, G.J., 2024. Computational fluid dynamics simulation of a high-throughput catalytic fixed-bed reactor for total oxidation of methane. Ind. Eng. Chem. Res. 63 (7), 3290–3300. https://doi.org/10.1021/acs.iecr.3c03611

Fialkov, A.B., Lehotay, S.J., Amirav, A., 2020. Less than one minute low-pressure gas chromatography - mass spectrometry. J. Chromatogr. A 1612, 460691. https://doi.org/10.1016/j.chroma.2019.460691

Fischer, K.L., Freund, H., 2020. On the optimal design of load flexible fixed bed reactors: integration of dynamics into the design problem. Chem. Eng. J. 393, 124722. https://doi.org/10.1016/j.cej.2020.124722

Fischer, K.L., Freund, H., 2021. Intensification of load flexible fixed bed reactors by optimal design of staged reactor setups. Chem. Eng. Process. Process Intensif. 159, 108183. https://doi.org/10.1016/j.cep.2020.108183

Fischer, K.L., Langer, M.R., Freund, H., 2019. Dynamic carbon dioxide methanation in a wall-cooled fixed bed reactor: comparative evaluation of reactor models. Ind. Eng. Chem. Res. 58 (42), 19406–19420. https://doi.org/10.1021/acs.iecr.9b02863

Flores-Tlacuahuac, A., Saldívar-Guerra, E., de León, R.D., López-González, R., Rodriguez-Guadarrama, L.A., 2024. Soft-sensor estimation via parameter fitting and dynamic optimization in an experimental batch butadiene homopolymerization reactor. Comput. Chem. Eng. 183, 108587. https://doi.org/10.1016/j.compchemeng.2024.108587

Fogler, H.S., 2005. Elements of Chemical Reaction Engineering. Prentice Hall. 4 edition.

Foslie, S.S., Knudsen, B.R., Bjarghov, S., Korpås, M., 2024. Faster decarbonization of heavy industries in low-carbon power grids: using process flexibility for handling grid congestions. Energy Environ. Sci. 17 (22), 8838–8854. https://doi.org/10.1039/d4ee03888f

Gao, Y., Dai, L.-K., Zhu, H.-D., Chen, Y.-L., Zhou, L., 2019. Quantitative analysis of main components of natural gas based on raman spectroscopy. Chin. J. Anal. Chem. 47 (1), 67–76. https://doi.org/10.1016/S1872-2040(18)61135-1

gCapitan Maritime News. Hydrogen-powered towboat project receives key USCG approval. Accessed: 2025-07-25. https://tinyurl.com/49wwjdzw.

Giannikopoulos, I., Skouteris, A., Allen, D.T., Baldea, M., Stadtherr, M.A., 2022. Network-based analysis of electrified chemical processing with renewable energy sources. In: Montastruc, L., Negny, S. (Eds.), 32nd European Symposium on Computer Aided Process Engineering. Elsevier. Vol. 51 of *Computer Aided Chemical Engineering*, pp. 937–942. https://doi.org/10.1016/B978-0-323-95879-0.50157-0

Giechaskiel, B., Clairotte, M., 2021. Fourier transform infrared (FTIR) spectroscopy for measurements of vehicle exhaust emissions: a review. Appl. Sci. 11 (16). https://doi.org/10.3390/app11167416

Giglio, E., Pirone, R., Bensaid, S., 2021. Dynamic modelling of methanation reactors during start-up and regulation in intermittent power-to-gas applications. Renew. Energy 170, 1040–1051. https://doi.org/10.1016/j.renene.2021.01.153

Gottheil, L., Bremer, J., 2024. Enabling load-flexible ammonia synthesis via polytropic fixed-bed reactors. In: Manenti, F., Reklaitis, G.V. (Eds.), 34th European Symposium on Computer Aided Process Engineering / 15th International Symposium on Process Systems Engineering. Elsevier. Vol. 53 of *Computer Aided Chemical Engineering*, pp. 1891–1896. https://doi.org/10.1016/B978-0-443-28824-1.50316-1

Grenko, B., 2025. Methanol steam reformer code git repository. https://doi.org/10.5281/ZENODO.16941636

Grenko, B., de Jong, W., van de Ketterij, R., van Biert, L., 2025. Dynamic modelling of methanol steam reforming to hydrogen in a packed bed reactor for shipboard fuel cells. Chem. Eng. J. 507, 160623. https://doi.org/10.1016/j.cej.2025.160623

Grimm, M., Paul, S., Chainais, P., 2024. Process-constrained batch bayesian approaches for yield optimization in multi-reactor systems. Comput. Chem. Eng. 189, 108779. https://doi.org/10.1016/j.compchemeng.2024.108779

Guerrero-Pérez, M.O., Patience, G.S., 2020. Experimental methods in chemical engineering: Fourier transform infrared spectroscopy-FTIR. Can. J. Chem. Eng. 98 (1), 25–33. https://doi.org/10.1002/cjce.23664

Han, J.-R., Kim, Y.-H., 2024. Cfd-based multi-objective bayesian optimization approach for compact and efficient hydrogen production in steam reforming reactor. J. Ind. Eng. Chem. 139, 378–389. https://doi.org/10.1016/j.jiec.2024.05.015

Harkou, E., Adamou, P., Al-Salem, S.M., Atanasova, N., Tang, J., Manos, G., Villa, A., Dimitratos, N., Constantinou, A., 2026. Computational fluid dynamics (CFD) modelling as a power multiplier tool for the design improvement of gaseous and liquid fuels: current status, challenges and perspectives. Fuel 404, 136401. https://doi.org/10.1016/j.fuel.2025.136401

Harris, D.C., Lucy, C.A., 2016. Quantitative Chemical Analysis. W.H. Freeman & Company, New York, NY. 9 edition.

Hollmann, J., Kabelac, S., 2023. Steady-state and transient operation of solid oxide fuel cell systems with anode off-gas recirculation within a highly constrained operating range. Energies 16 (23). https://doi.org/10.3390/en16237827

Holmen, A., Yang, J., Chen, D., 2023. Steady-State Isotopic Transient Kinetic Analysis (SSITKA). Springer International Publishing. chapter 41. p. 935–965. https://doi.org/10.1007/978-3-031-07125-6_41

Hu, T., Qin, L., Zhou, L., Zheng, X., Zhu, L.-T., 2026. Analysis and optimization of methanol production and temperature gradient in CO2 hydrogenation fixed bed reactors using CFD and bayesian optimization. Chem. Eng. Sci. 321, 123030. https://doi.org/10.1016/j.ces.2025.123030

Huerta-Rosas, B., Juarez-García, M., Núñez-López, J.M., Alcocer-García, H., Segovia-Hernández, J.G., Sánchez-Ramírez, E., 2025. Power-to-x technologies for net-zero: bridging process innovation, system integration, and policy. Process Integr. Optim. Sustainability . https://doi.org/10.1007/s41660-025-00570-3

International Maritime Organisation, 2017. MARPOL Consolidated edition 2017. International Maritime Organisation. 6 edition. ISBN:9789280116571.

Jakobsen, H.A., 2014. Chemical Reaction Engineering. Springer International Publishing. chapter 11. pp. 789–807. https://doi.org/10.1007/978-3-319-05092-8_6

Jha, R.K., 2022. Non-dispersive infrared gas sensing technology: a review. IEEE Sens. J. 22 (1), 6–15. https://doi.org/10.1109/JSEN.2021.3130034

Karpilov, I., Pashchenko, D., 2023. Steam methane reforming over a preheated packed bed: heat and mass transfer in a transient process. Therm. Sci. Eng. Prog. 42, 101868. https://doi.org/10.1016/j.tsep.2023.101868

Kataria, P., Yeo, W.S., Nandong, J., 2024. Reviewing the dynamic modeling aspects of chemical looping hydrogen production. Int. J. Hydrogen Energy 82, 1282–1299. https://doi.org/10.1016/j.ijhydene.2024.08.033

Kiefer, F., Nikolic, M., Borgschulte, A., Dimopoulos Eggenschwiler, P., 2022. Sorption-enhanced methane synthesis in fixed-bed reactors. Chem. Eng. J. 449, 137872. https://doi.org/10.1016/j.cej.2022.137872

Klüh, D., Anetjärvi, E., Melin, K., Vakkilainen, E., 2024. Comparative techno-economic assessment of methanol production via directly and indirectly electrified biomass gasification routes. Energy Convers. Manage. 314, 118649. https://doi.org/10.1016/j.enconman.2024.118649

Langford, V., 2022. Real-time monitoring of volatile organic compounds in ambient air using direct-injection mass spectrometry. LCGC North Am. 40, 174–179. https://doi.org/10.56530/lcgc.na.nf7066t5

Leipold, J., Nikolic, D., Seidel-Morgenstern, A., Kienle, A., 2024. Multi-objective optimization of forced periodic operation of methanol synthesis in a fixed-bed reactor. In: Manenti, F., Reklaitis, G.V. (Eds.), 34th European Symposium on Computer Aided Process Engineering / 15th International Symposium on Process Systems Engineering. Elsevier. Vol. 53 of *Computer Aided Chemical Engineering*, pp. 1603–1608. https://doi.org/10.1016/B978-0-443-28824-1.50268-4

Leipold, J., Nikolic, D., Seidel-Morgenstern, A., Kienle, A., 2025. Optimization of methanol synthesis under forced periodic operation in a non-isothermal fixed-bed reactor. Comput. Chem. Eng. 196, 109040. https://doi.org/10.1016/j.compchemeng.2025.109040

Li, H., Tian, H., Chen, S., Sun, Z., Liu, T., Liu, R., Assabumrungrat, S., Saupsor, J., Mu, R., Pei, C., Gong, J., 2020. Sorption enhanced steam reforming of methanol for high-purity hydrogen production over cu-mgo/al2o3 bifunctional catalysts. Appl. Catal. B 276, 119052. https://doi.org/10.1016/j.apcatb.2020.119052

Liang, J.-G., Jiang, Y., Wu, J.-K., Wang, C., von Gratowski, S., Gu, X., Pan, L., 2023. Multiplex-gas detection based on non-dispersive infrared technique: a review. Sens. Actuators A 356, 114318. https://doi.org/10.1016/j.sna.2023.114318

Liang, T., Qiao, S., Liu, X., Ma, Y., 2022. Highly sensitive hydrogen sensing based on tunable diode laser absorption spectroscopy with a 2.1 μm diode laser. Chemosensors 10 (8). https://doi.org/10.3390/chemosensors10080321

Liu, Y., Shang, Q., Chen, L., Wang, E., Huang, X., Pang, X., Lu, Y., Zhou, L., Zhou, J., Wang, Z., Lyu, Y., 2023. Application of portable CH4 detector based on TDLAS technology in natural gas purification plant. Atmosphere 14 (12). https://doi.org/10.3390/atmos14121709

Luo, J., Moncada, J., Ramirez, A., 2022. Development of a conceptual framework for evaluating the flexibility of future chemical processes. Ind. Eng. Chem. Res. 61 (9), 3219–3232. https://doi.org/10.1021/acs.iecr.1c03874

Ma, Y., Wang, Z., Liu, H., Tang, H., Ji, Y., Han, F., 2024. Efficient and sustainable power propulsion for all-electric ships: an integrated methanol-fueled SOFC-sCO2 system. Renew. Energy 230, 120822. https://doi.org/10.1016/j.renene.2024.120822

Majumder, D., Janani, R., Scrimshire, A., Stone, A., Brooks, W., Holcroft, C., Werner, R., Green, S., Wheeler, N., Bingham, P.A., 2025. Raman gas sensing technology: a new horizon? Sens. Actuators Rep. 9, 100311. https://doi.org/10.1016/j.snr.2025.100311

Mane, S., Dhote, R.R., Sinha, A., Thirumalaiswamy, R., 2024. Digital twin in the chemical industry: a review. Digital Twins Appl. 1 (2), 118–130. https://doi.org/10.1049/dgt2.12019

Marín, P., Díez, F.V., Ordóñez, S., 2019. Reverse flow reactors as sustainable devices for performing exothermic reactions: applications and engineering aspects. Chem. Eng. Process. Process Intensif. 135, 175–189. https://doi.org/10.1016/j.cep.2018.11.019

Mbatha, S., Cui, X., Debiagi, P., Panah, P.G., Everson, R.C., Musyoka, N.M., 2026. 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. Chem. Eng. Sci. 319, 122280. https://doi.org/10.1016/j.ces.2025.122280

Meyer, D., Schumacher, J., Friedland, J., Güttel, R., 2022. Frequency response analysis of the unsteady-state CO/CO2 methanation reaction: an experimental study. Ind. Eng. Chem. Res. 61 (5), 2045–2054. https://doi.org/10.1021/acs.iecr.1c04547

Micale, D., Ferroni, C., Uglietti, R., Bracconi, M., Maestri, M., 2022. Computational fluid dynamics of reacting flows at surfaces: methodologies and applications. Chem. Ing. Tech. 94 (5), 634–651. https://doi.org/10.1002/cite.202100196

MMM Energy. M reformer hydrogen generator. Accessed: 2025-07-25. https://www.methanolreformer.com/.

Moghaddam, E.M., Foumeny, E.A., Stankiewicz, A.I., Padding, J.T., 2021. Multiscale modelling of wall-to-bed heat transfer in fixed beds with non-spherical pellets: from particle-resolved CFD to pseudo-homogenous models. Chem. Eng. Sci. 236, 116532. https://doi.org/10.1016/j.ces.2021.116532

Morgan, K., Maguire, N., Fushimi, R., Gleaves, J.T., Goguet, A., Harold, M.P., Kondratenko, E.V., Menon, U., Schuurman, Y., Yablonsky, G.S., 2017. Forty years of temporal analysis of products. Catal. Sci. Technol. 7 (12), 2416–2439. https://doi.org/10.1039/c7cy00678k

Nikolič, D., Felischak, M., Seidel-Morgenstern, A., Petkovska, M., 2016. Periodic operation with modulation of inlet concentration and flow rate part II: adiabatic continuous stirred-tank reactor. Chem. Eng. Technol. 39 (11), 2126–2134. https://doi.org/10.1002/ceat.201600187

Nwaboh, J.A., Pratzler, S., Werhahn, O., Ebert, V., 2017. Tunable diode laser absorption spectroscopy sensor for calibration free humidity measurements in pure methane and low CO2 natural gas. Appl. Spectrosc. 71 (5), 888–900. https://doi.org/10.1177/0003702816658672

Omojola, T., 2025. Concepts and tools for integrating multiscale dynamics into reaction kinetics. Phys. Chem. Chem. Phys. 27 (33), 17157–17177. https://doi.org/10.1039/d5cp00838g

Peltola, P., Alobaid, F., Tynjälä, T., Ritvanen, J., 2022. Overview of fluidized bed reactor modeling for chemical looping combustion: status and research needs. Energy Fuels 36 (17), 9385–9409. https://doi.org/10.1021/acs.energyfuels.2c01680

Peppley, B.A., Amphlett, J.C., Kearns, L.M., Mann, R.F., 1999. Methanol–steam reforming on Cu/ZnO/Al2O3 catalysts. part 2. a comprehensive kinetic model. Appl. Catal. A 179 (1), 31–49. https://doi.org/10.1016/S0926-860X(98)00299-3

Petrov, D.V., Matrosov, I.I., 2016. Raman gas analyzer (RGA): natural gas measurements. Appl. Spectrosc. 70 (10), 1770–1776. https://doi.org/10.1177/0003702816644611

Pleil, J.D., Hansel, A., Beauchamp, J., 2019. Advances in proton transfer reaction mass spectrometry (PTR-MS): applications in exhaled breath analysis, food science, and atmospheric chemistry. J. Breath Res. 13 (3), 039002. https://doi.org/10.1088/1752-7163/ab21a7

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. https://tinyurl.com/4p88kj6b.

Pérez-Gallego, D., Gonzalez-Ayala, J., Medina, A., Calvo Hernández, A., 2025. Comprehensive review of dynamical simulation models of packed-bed systems for thermal energy storage applications in renewable power production. Heliyon 11 (4), e42803. https://doi.org/10.1016/j.heliyon.2025.e42803

Ren, M., Wan, Y., Ji, Y., Chen, J., 2025. Trace detection of natural gas leakage using novel hollow-electrode radiofrequency glow discharge ion-source mass spectrometry. Anal. Methods 17, 4403–4410. https://doi.org/10.1039/D5AY00302D

Rentschler, P., Klahn, C., Dittmeyer, R., 2024. The need for dynamic process simulation: a review of offshore power-to-x systems. Chem. Ing. Tech. 96 (1-2), 114–125. https://doi.org/10.1002/cite.202300156

Rheenen, E.S.V., Padding, J.T., Slootweg, J.C., Visser, K., 2024. Hydrogen carriers for zero-emission ship propulsion using PEM fuel cells: an evaluation. J. Mar. Eng. Technol. 23 (3), 166–183. https://doi.org/10.1080/20464177.2023.2282691

RIX Industries. M2H2 series mobile hydrogen generator. Accessed: 2025-07-25. https://www.rixindustries.com/hydrogen-generation-systems.

Sahimi, M., 2011. Dispersion in Flow through Porous Media. John Wiley & Sons, Ltd. chapter 11. pp. 341–413. https://doi.org/10.1002/9783527636693.ch11

Sampaolo, A., Patimisco, P., Giglio, M., Zifarelli, A., Wu, H., Dong, L., Spagnolo, V., 2022. Quartz-enhanced photoacoustic spectroscopy for multi-gas detection: a review. Anal. Chim. Acta 1202, 338894. https://doi.org/10.1016/j.aca.2021.338894

Seborg, D.E., Mellichamp, D.A., Edgar, T.F., 2011. Process Dynamics and Control. Wylie Series in Chemical Engineering, John Wiley & Sons. third edition.

Sheintuch, M., Nekhamkina, O., 2021. Dynamics and control of loop reactors: a review. Math. Model. Nat. Phenom. 16, 43. https://doi.org/10.1051/mmnp/2021035

Shi, J., Wu, Q., Mei, D., Liu, H., Wang, Y., 2024. Development of pure hydrogen generation system based on methanol steam reforming and PD membrane. Int. J. Hydrogen Energy 69, 147–157. https://doi.org/10.1016/j.ijhydene.2024.04.359

Spatenka, S., Matzopoulos, M., Urban, Z., Cano, A., 2019. From laboratory to industrial operation: model-based digital design and optimization of fixed-bed catalytic reactors. Ind. Eng. Chem. Res. 58 (28), 12571–12585. https://doi.org/10.1021/acs.iecr.9b01314

Stegehake, C., Riese, J., Grünewald, M., 2019. Modeling and validating fixed-bed reactors: a state-of-the-art review. ChemBioEng Rev. 6 (2), 28–44. https://doi.org/10.1002/cben.201900002

Sun, J., Chang, J., Wang, C., Shao, J., 2024. Tunable diode laser absorption spectroscopy for detection of multi-component gas: a review. Appl. Spectrosc. Rev. 59 (8), 1086–1107. https://doi.org/10.1080/05704928.2024.2302608

Tan, X., Zhang, H., Li, J., Wan, H., Guo, Q., Zhu, H., Liu, H., Yi, F., 2020. Non-dispersive infrared multi-gas sensing via nanoantenna integrated narrowband detectors. Nat. Commun. 11 (1). https://doi.org/10.1038/s41467-020-19085-1

Tesser, R., Santacesaria, E., 2020. Revisiting the role of mass and heat transfer in gas-solid catalytic reactions. Processes 8 (12). https://doi.org/10.3390/pr8121599

Tiggeloven, J.L., Faaij, A. P.C., Kramer, G.J., Gazzani, M., 2023. Optimization of electric ethylene production: exploring the role of cracker flexibility, batteries, and renewable energy integration. Ind. Eng. Chem. Res. 62 (40), 16360–16382. https://doi.org/10.1021/acs.iecr.3c02226

Tiggeloven, J.L., Faaij, A. P.C., Kramer, G.J., Gazzani, M., 2025. Optimizing emissions reduction in ammonia-ethylene chemical clusters: synergistic integration of electrification, carbon capture, and hydrogen. Ind. Eng. Chem. Res. 64 (8), 4479–4497. https://doi.org/10.1021/acs.iecr.4c03817

van Biert, L., Godjevac, M., Visser, K., Aravind, P.V., 2016. A review of fuel cell systems for maritime applications. J. Power Sources 327, 345–364. https://doi.org/10.1016/j.jpowsour.2016.07.007

van Biert, L., Godjevac, M., Visser, K., Aravind, P.V., 2019. Dynamic modelling of a direct internal reforming solid oxide fuel cell stack based on single cell experiments. Appl. Energy 250, 976–990. https://doi.org/10.1016/j.apenergy.2019.05.053

van de, K. R.G., Geertsma, R., Grasman, A., Pothaar, M., Coraddu, A., 2024. Alternative fuels, propulsion and power systems for the future navy - a route towards reduced emissions and signatures, and fossil fuel independence. In: Frerks, G., Geertsma, R., Klomp, J., Middendorp, T. (Eds.), Climate Security and the Millitary: Concepts, Strategies, and Partnerships. Leiden University Press. Vol. 2023 of *LUP NL ARMS*. chapter 14. https://doi.org/10.24415/9789400604780-019

Varma, A., Morbidelli, M., Wu, H., 1999. Parametric Sensitivity in Chemical Systems. Cambridge Series in Chemical Engineering, Cambridge University Press.

van Veldhuizen, B., van Biert, L., Aravind, P.V., Visser, K., 2023. Solid oxide fuel cells for marine applications. Int. J. Energy Res. 2023 (1), 5163448. https://doi.org/10.1155/2023/5163448

Wang, M., Bu, S., Zhou, B., Gong, B., Li, Z., Chen, D., 2025. Physics-informed neural networks for effective diffusion characteristics inversion in packed bed at low flow rates. Int. J. Heat Mass Transf. 244, 126970. https://doi.org/10.1016/j.ijheatmasstransfer.2025.126970

Wang, Q., Sun, P., Zhang, Z., Zhang, L., Pang, T., Wu, B., Xia, H., Guo, Q., Sigrist, M.W., Culshaw, B., 2022. Multi-component gas measurement aliasing spectral demodulation method for interference separation in laser absorption spectroscopy. Sens. Actuators B Chem. 369, 132292. https://doi.org/10.1016/j.snb.2022.132292

Weng, J., Wen, S., Shu, Z., Jiang, J., Ye, G., Zhou, X., 2025. A 2D continuum model based on particle-resolved CFD for packed-bed reactors. Ind. Eng. Chem. Res. 64 (16), 8516–8530. https://doi.org/10.1021/acs.iecr.5c00351

Wentrup, J., Pesch, G.R., Thöming, J., 2022. Dynamic operation of fischer-tropsch reactors for power-to-liquid concepts: a review. Renew. Sustainable Energy Rev. 162, 112454. https://doi.org/10.1016/j.rser.2022.112454

Zagoruiko, A.N., Bobrova, L., Vernikovskaya, N., Zazhigalov, S., 2021. Unsteady-state operation of reactors with fixed catalyst beds. Rev. Chem. Eng. 37 (1), 193–225. https://doi.org/10.1515/revce-2019-0017

Zhu, J., Araya, S.S., Cui, X., Kær, S.K., 2022a. The role of effectiveness factor on the modeling of methanol steam reforming over CuO/ZnO/Al2O3 catalyst in a multi-tubular reactor. Int. J. Hydrogen Energy 47 (14), 8700–8715. https://doi.org/10.1016/j.ijhydene.2021.12.223

Zhu, J., Cui, X., Araya, S.S., 2022b. Comparison between 1D and 2D numerical models of a multi-tubular packed-bed reactor for methanol steam reforming. Int. J. Hydrogen Energy 47 (54), 22704–22719. https://doi.org/10.1016/j.ijhydene.2022.05.109

Zhu, Y., He, Z., Xuan, T., Huang, Y., Zhong, W., 2024. Analysis and optimization of energy conversion for an on-board methanol reforming engine with thermochemical recuperation. Fuel 378, 132767. https://doi.org/10.1016/j.fuel.2024.132767

Zimmermann, R.T., Bremer, J., Sundmacher, K., 2022. Load-flexible fixed-bed reactors by multi-period design optimization. Chem. Eng. J. 428, 130771. https://doi.org/10.1016/j.cej.2021.130771