



Single pellet profile reactor for measuring concentration and temperature patterns in porous catalyst pellets

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ABSTRACT

Understanding coupled transport and reaction phenomena within porous catalyst pellets is crucial for the optimization of heterogeneous catalytic processes. Nonetheless, experimental access to intra-pellet concentration profiles under industrially relevant conditions remains limited. In this work, we present a second-generation single-pellet profile reactor (SPPR) that enables simultaneous measurement of intra-pellet concentration profiles and surface temperature distributions. The gas composition inside the pellet is measured using a movable sampling capillary and mass spectrometry analysis. The combination of an infrared thermography camera and a conical mirror inside the reactor enables the measurement of catalyst surface temperature. The reactor operates under industrially relevant conditions and allows investigations at different feed temperatures and feed ratios at steady-state. The capabilities of the setup are demonstrated for CO₂ methanation on a cylindrical 5 mm Ni/-Al₂O₃ catalyst pellet. Pronounced intra-pellet CO₂ concentration gradients are observed despite a stoichiometric educt feed ratio, whereas H₂ exhibits only minor gradients throughout the pellet. The infrared camera measurements reveal a surface temperature increase of up to 25 K with pronounced gradients in flow direction. Apart from these axial gradients, the pellet surface temperature is uniform at steady state. The presented reactor provides detailed operando insights into coupled mass and heat transport phenomena at the single-pellet scale and could offer a robust basis of experimental data for future model validation and knowledge-based catalyst optimization.

1. Introduction

How do the concentration profiles develop within a catalyst pellet? What appears to be a trivial question, is upon closer inspection, difficult to answer. Concentrations inside catalyst pellets are experimentally challenging to assess due to either low spin density of gases or optical inaccessibility [1,2]. Therefore, they are predominantly determined using simulations, for which landmark contributions have been provided by Jüttner [3], Damköhler [4], Thiele [5], Zeldowitsch [6], Schilson and Amundson [7], Aris [8], Luss [9] and Frank-Kamenetzki and Pawlowski [10]. However, this approach requires well-defined boundary conditions and relies heavily on simplifying assumptions. To obtain such boundary conditions, several reactor concepts have been developed. First, so-called stagnation flow reactors, as developed by McDaniel et al. [11], Taylor et al. [12], McGuire et al. [13,14] or Davari et al. [15], have been used to measure concentration profiles in the boundary layer adjacent to a catalyst pellet. This approach eliminates the need to assume a model for mass transfer in the external film

near the catalyst surface. However, it is restricted to flat geometries and the flow conditions deviate significantly from those encountered in industrial packed bed reactors.

Second, center-plane reactors, introduced by Hegedus and Petersen [16,17] and Cannestra et al. [18], employ a pellet with half the thickness of a real catalyst pellet, placed in a reactor featuring a chamber on the opposite side of the catalyst. The catalyst is sealed against the reactor walls, such that gas exchange between the center-plane chamber and the bulk gas occurs exclusively by mass transport through the porous catalyst. However, this configuration restricts diffusion to only parts of the pellet surface, as only one side is exposed to the reaction gases. Furthermore, these reactors provide only the center-plane concentration as a boundary condition. Thus, numerical simulations remain necessary to reconstruct the full concentration profile. In addition, this approach is limited to flat catalyst geometries.

Third, Chmelik et al. [2] developed a method to determine the effectiveness factor in porous catalyst pellets using Infrared (IR) micro

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imaging. This approach, however, requires specially prepared, optically transparent catalyst pellets made from glass. Consequently, their properties differ substantially from those of industrial catalyst pellets. Therefore, the results must be corrected and adapted before transfer to industrially relevant systems.

Finally, Sosna et al. [19] introduced the single-pellet reactor as a novel reactor concept that enables the measurement of concentration profiles inside a catalyst pellet using a fused silica capillary. However, this reactor was limited to temperatures below 200 °C and to flow rates corresponding to a particle Reynolds number of approximately 20. Beyond concentration profiles within catalyst pellets, the temperature distribution on the pellet surface is also of considerable interest, as hotspot formation can strongly affect local reaction rates and side-product formation. In this context, Pawlicki and Schmitz [20] reported the occurrence of multiple steady states using IR thermography. Furthermore, Westerterp et al. [21,22], Luss [23], Luss and Sheintuch [24] and Marwaha et al. [25] identified the formation of temperature fronts in catalytic fixed-bed reactors, which are of particular importance for the industrial application of heterogeneously catalyzed gas-solid reactions and an important element in numerous processes. However, only a limited number of studies have addressed the temperature distribution on the surface of individual catalyst pellets.

Annamalai et al. [26] developed a reactor equipped with a conical mirror that enables IR thermography measurements of the surface temperature of a single catalyst pellet during CO oxidation. The mirror allowed observation of both the top and the lateral surfaces of the pellet. They reported the formation of temperature patterns on the pellet surface, with variations occurring on timescales of several minutes, despite steady-state reactor operation. Later studies of pattern formation, especially also for dynamic feed conditions include Nett-Carrington and Herz [27] and Herz [28].

Given that intra-pellet concentration profiles remain difficult to access experimentally, this study aims to develop an advanced version of the single-pellet reactor proposed by Sosna et al. [19], capable of operation at temperatures up to 400 °C. This technique is combined with the IR thermography approach similar to Annamalai et al. [26] to simultaneously investigate concentration profiles inside a catalyst pellet and the surface temperature distribution. This combined approach provides improved insight into intra-pellet transport and reaction phenomena. For reactor development, CO₂ methanation was selected as a model reaction. As an exothermic process, it is well suited for observation by IR thermography and can extend reaction engineering insights gained by spatial profile reactors, as recently been shown by Küchen et al. [29]. Moreover, both reactant and product gases can be readily quantified by mass spectrometry. In addition, improving CO₂ methanation performance is directly relevant to power-to-gas technologies and supports the transition toward renewable energy systems [30,31]. Nonetheless, the reactor is not limited to this specific catalytic system. Besides other pellet shapes or sizes, different reaction systems such as Formox, selective catalytic reduction of NO_x, oxidation of SO₂ to SO₃ or with some improvements even methanol oxidation could be investigated. In the future, the new measuring system can produce data that can be used for model validation or derivation of empirical correlations and in turn improve heterogeneous catalytic processes by knowledge-based catalyst optimization. Possible optimization parameters include distribution of active component inside the pellet, pellet size and shape or pore network to just name a few. After changes were made to a catalyst pellet, the reactor could be used to test the effect of the optimized parameter experimentally, offering a valuable addition to simulation-based approaches.

2. Materials and methods

2.1. Catalyst

For reactor testing, CO₂ methanation over nickel on γ -Al₂O₃ catalyst was employed, as this system is widely used due to its low

Table 1

Physical catalyst properties.

Property	Value	Unit
Length	5	mm
Radius	2.5	mm
BET Area	199	m ² g ⁻¹
Pore Volume	0.426	cm ³ g ⁻¹
Density	1421	kg m ⁻³
Pore Diameter	8.796	nm
Porosity	0.618	
Thermal Conductivity [19]	0.1	W m ⁻¹ K ⁻¹

cost and high activity [32,33]. The γ -Al₂O₃ support was supplied as 5 mm × 5 mm cylinder (Sasol Germany GmbH, Hamburg, Germany). The catalyst was prepared by incipient wetness impregnation using nickel(II)-nitrate-hexahydrate as the metal precursor (Carl Roth GmbH, Karlsruhe, Germany), targeting a nickel weight loading of 10 % in the reactive catalyst. Based on the relative pore volume of the support, the required amount of precursor was calculated and dissolved in deionized water such that the desired weight loading was achieved in two impregnation steps. Prior to the first impregnation, the pellets were drilled with a 0.4 mm drill bit, rinsed, and soaked in nitric acid for 3 h. Subsequently, they were thoroughly rinsed with water and dried at 150 °C in an oven overnight. After drying, the pellets were placed in a microtiter tray and impregnated using a micropipette with a volume of precursor solution corresponding to the pore volume of a single pellet. The pellets were allowed to absorb the solution for 1 h, after which they were transferred to a Petri dish and dried overnight in a desiccator filled with silica gel. On the following day, the impregnation procedure was repeated, followed again by drying in the desiccator. This gentle drying procedure is required to obtain a homogeneous distribution of the active component, as rapid drying could adversely affect metal dispersion [34–36]. After the final drying step, the catalyst was stored in the desiccator until calcination, as Ni(NO₃)₂ · 6 H₂O is hygroscopic. Prior to the reaction experiments, the catalyst was calcined at 400 °C with a heating rate of 5 K min⁻¹ for 3 h in a gas mixture of 20 % O₂ and 80 % N₂, resulting in thermal decomposition of the nitrate precursor and formation of NiO. After cooling under argon flow, the pellets were stored in the desiccator until further use. As metallic nickel is the active form for CO₂ methanation, the catalyst was subsequently reduced for 5 h at 400 °C, heated with a rate of 5 K min⁻¹, in a 10 % H₂ in Ar mixture. The final loading was determined to be 6.8 wt % using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The catalysts properties are summarized in Table 1. The specific surface area and pore diameter were measured via Brunauer-Emmett-Teller (BET) and Non-Local Density Functional Theory (NLDFT) method using a Quantachrome Autosorb IQ2 (Anton Paar GmbH, Graz, Austria), while porosity, pore volume and density were determined by Mercury Intrusion Porosimetry (MIP) using a MicroActive AutoPore V 9600 (Micromeritics Instrument Corporation, Norcross, USA). Besides the pore size of 8.796 nm from NLDFT, the MIP shows a second, smaller peak at around 600 nm, corresponding to the pellet macropores. Both pore size distributions are shown in the supplementary information Figure S1 and Figure S2.

2.2. Reactor design and measurement concept

The reactor enabled the measurement of concentration profiles inside a single catalyst pellet and simultaneously recording the surface temperature distribution using IR thermography. It was initially designed for maximum flow rates of up to 10 L_N min⁻¹, corresponding to a particle Reynolds number of $Re_p = \frac{\rho v d_p}{\mu} \approx 100$. This flow rate was selected based on the available gas supply infrastructure in the laboratory and a stationary hydrodynamic regime. Different to this maximum design case, the first measurements shown here, were

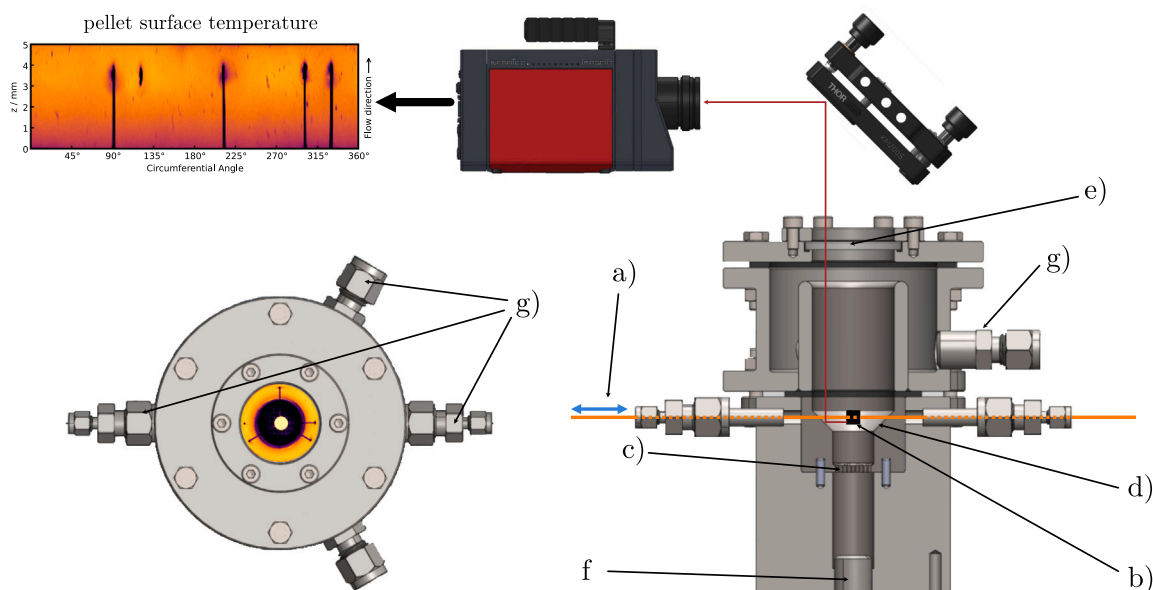


Fig. 1. Top view (left) and cross sectional view (right) of the reactor developed for single pellet profiling. (a) Movable capillary, (b) Catalyst pellet, (c) Flow distributor, (d) IR mirror, (e) IR window, (f) Inlet, (g) Outlets.

performed at $1 \text{ L}_\text{N} \text{ min}^{-1}$ ($\text{Re}_\text{p} \approx 10$) as a first starting point. Nonetheless, investigation of varying flow rates up to $10 \text{ L}_\text{N} \text{ min}^{-1}$ will be a possible subject of future studies. The reactor was operated at temperatures up to 400°C . Fig. 1 shows a cross sectional and top view of the reactor. The gas flow to the reactor was controlled by three mass flow controllers (MC-Series, Alicat Scientific, Tucson, USA), allowing precise dosing of CO_2 , H_2 and Ar. The bottom section of the reactor was equipped with electrical heating cartridges controlled by a PID controller (Eurotherm, Worthing, UK). A Type-K thermocouple positioned directly below the catalyst pellet was used to measure the gas-phase temperature in front of the pellet. The catalyst pellet was positioned at the center of the reactor and supported by three glass needles. This holding mechanism was designed to minimize disturbances to heat transfer and the local flow field around the pellet. The top of the reactor was sealed with an IR transparent sapphire window, providing optical access for thermographic measurements. Surrounding the pellet, a conical mirror made from polished stainless steel enabled IR thermography of both the top surface and the lateral surface of the catalyst pellet. To ensure that the flow around the pellet is stationary and not affected by stagnation zones caused by flow impingement on the sapphire window, Computational Fluid Dynamics (CFD) simulations were performed. Reaction chambers with length ranging from 20 mm to 100 mm were investigated, with the 100 mm configuration used as a reference case. A more detailed description of the simulations can be found in Section 3.1. Accordingly, the reaction chamber length was fixed to 60 mm. The inlet section of the reactor, which also serves to preheat the gas to reaction temperature, had a diameter of 15 mm, whereas the reaction chamber had a diameter of 30 mm. This geometry accounts for the conical mirror, which had an opening angle of 45° and a height of 7.5 mm.

To obtain intra-pellet concentration profiles, a movable fused silica capillary (Outer Diameter (OD): $363 \mu\text{m}$, Inner Diameter (ID): $10 \mu\text{m}$, Polymicro Technologies, Phoenix, USA) was inserted into the reactor. The sampling capillary had a total length of 12 cm and was mounted on an electrically actuated linear drive (MT-S50, Thorlabs GmbH, Lübeck, Germany) to precisely move the capillary orifice to distinct positions inside the pellet. Behind the capillary, the sample gas stream was connected to the analytics with a transfer capillary (OD: $363 \mu\text{m}$, IDID: $150 \mu\text{m}$). A schematic of the sampling system and its dimensions is shown in Fig. 2.

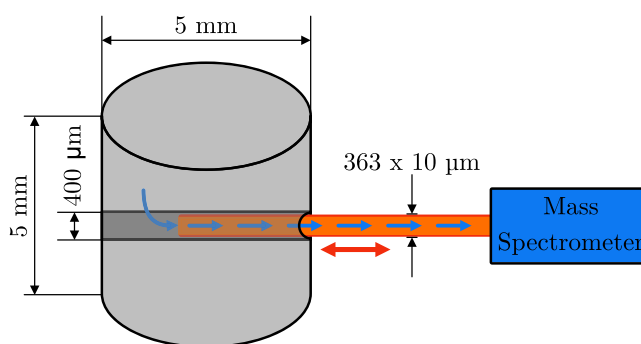


Fig. 2. Dimensions of the pellet and sampling capillary with schematic depiction of the sampling system. The dimensions of the pellet and capillary are not to scale.

2.3. Analytics

2.3.1. Concentration profiling

The sample extracted from the reactor was analyzed with a Quadrupole Mass Spectrometer (QMS) equipped with a Secondary Electron Multiplier (SEM) detector (HAL300S/3, Hiden Analytical, Warrington, England). To decrease the response time and reduce the background, the transfer line extended inside the vacuum chamber and ended directly in front of the ionizer, resulting in a response time of approximately 30 s. Due to the small sampling flow rate, resulting from the small ID capillary, the pressure inside the QMS chamber ranged from 1×10^{-7} mbar to 8×10^{-8} mbar. In the mass spectrometer, we quantified the different species by integrating the base peak of each component (H_2 : amu 2, CH_4 : amu 15, Ar: amu 40, CO_2 : amu 44, CO: amu 28) and normalizing each value to the peak area of argon (amu 40) as an internal standard. The CO signal at amu 28 overlaps with a fragment of CO_2 . Therefore, we subtracted the contribution of CO_2 from the integrated peak area at amu 28 before applying the calibration factor to determine the CO concentration. Because H_2O cannot be measured reliably by mass spectrometry under these conditions, we calculated its concentration. As shown in Section 3, only trace amounts of CO were formed via the Reverse Water-Gas Shift (RWGS) reaction. We therefore determined the amount of water stoichiometrically as twice the amount

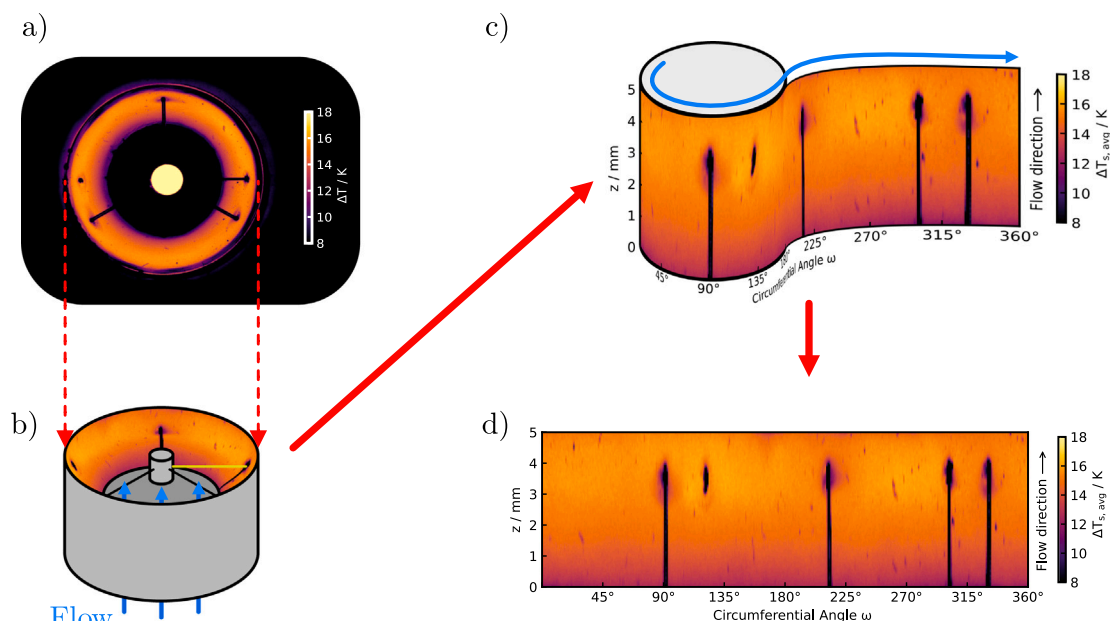


Fig. 3. Schematic of the transformation process. (a) Image obtained from temperature array with reference image data already subtracted. (b) Schematic of the IR reflection in the conical mirror. The direction of flow is depicted in blue. (c) Schematic of unwrapping the IR image from the cylinder's outer surface. (d) Final temperature field after subtraction and unwrapping as used in the following processing steps.

of methane formed at each measured point, given that the diffusion coefficients of both molecules are similar. We sampled each position for 2 min to ensure equilibrium in the QMS. These 2 min correspond to approximately 18 mass spectrometer cycles. We averaged the peak area over the last 10 cycles and divided it by the argon peak area for normalization. Using calibration curves, we converted the normalized peak areas into mole fractions.

2.3.2. IR Thermography

IR imaging was performed using a high resolution IR camera (Image IR 8380 hp, InfraTec GmbH, Dresden, Germany), equipped with a 50 mm telephoto lens and a macro adapter (CL WD300, InfraTec GmbH, Dresden, Germany), which reduced the minimum focus distance to 0.3 m. The camera was equipped with an Indium-Antimonide (InSb) Focal-Plane-Array (FPA) detector cooled to 77 K by a Stirling cooler.

This setup provided a frame filling image of the pellet and the surrounding conical mirror, thereby maximizing spatial resolution. For accurate IR thermography measurements, the emissivity of the measured surfaces must be considered, since neglecting it can lead to misinterpretation of the radiation intensity and thus incorrect temperature reading [37–39].

In general, determining the exact emissivity over the entire temperature range and for each surface is difficult. Therefore, Moates et al. [40], Holzwarth et al. [37], Rajagopalan et al. [41] and Loskyll et al. [38] developed a method termed emissivity-corrected Infrared Thermography (ecIRT). Originally introduced for high-throughput catalysis research, we adapted this approach to determine the temperature distribution on the surface of a single catalyst pellet without the need of determining the emissivity at each position inside the reactor. This approach is based on reference image subtraction. We first recorded a background image at reaction temperature under Ar and H₂ flow in the absence of CO₂ to suppress methanation and further reduction. After introducing H₂ and thereby initiating the reaction, we recorded an IR image every 10 s. We then subtracted the reference image pixel wise from each image acquired during the reaction. Assuming that the emissivity of the pellet, the reflectivity of the mirror and transparency of the IR window remained constant throughout the reaction. The resulting differential images were independent of emissivity and reflected only the temperature changes induced by the chemical reaction.

A representative differential image is shown in Fig. 3a). This image includes not only the temperature distribution on the top surface of the pellet but also the lateral surface observed via the conical mirror. Therefore, further processing was required to obtain a rectangular, “unwrapped” representation of the pellet’s outer surface. The reflected temperature distribution appeared as an annular region (orange in Fig. 3a).

Slight misalignment of the camera or mirror caused the annular region to deviate from a perfect circle. For each experiment, we selected one image and visually fitted ellipses to the inner and outer boundaries of the annulus. Each ellipse was defined by five parameters: the center coordinates (x_c, y_c), semi-major and semi-minor axes (a, b) defining the eccentricity of the ellipses and the in-plane rotation angle θ . For uniformly spaced angular positions, we computed corresponding points on both ellipses and defined a normalized radial coordinate. This procedure transformed the elliptical coordinate system into a pseudo-Cartesian system, in which the vertical axis represents the radial distance from the inner ellipse and the horizontal axis represents the angular position. Although deviations from circular geometry were small, this approach yielded a more accurate representation of the pellet’s outer surface. An example of such an “unwrapped” view of the cylinder’s outer surface is shown in Fig. 3(d).

3. Results and discussion

3.1. CFD Assisted Reactor Design

The reaction chamber diameter was designed based on a maximum flow rate of 10 L_N min^{−1} and a pursued particle Reynolds number of 100. However, the length of the chamber needed to be determined by simulations. Too long and the absorption of IR radiation by the gas would become significant, while too short lets the influence of the stagnation flow zone in front of the window significantly influence the pellet perturbation. Hence, CFD simulations were performed to choose the optimal chamber length using Siemens Simcenter STAR-CCM+ (Version 19.02.012). A detailed description of the simulation methodology can be found in Reinold et al. [42]. Reaction chamber lengths of 20 mm, 60 mm and 100 mm were simulated where 100 mm served as a reference case, where no influence of the stagnation zone on

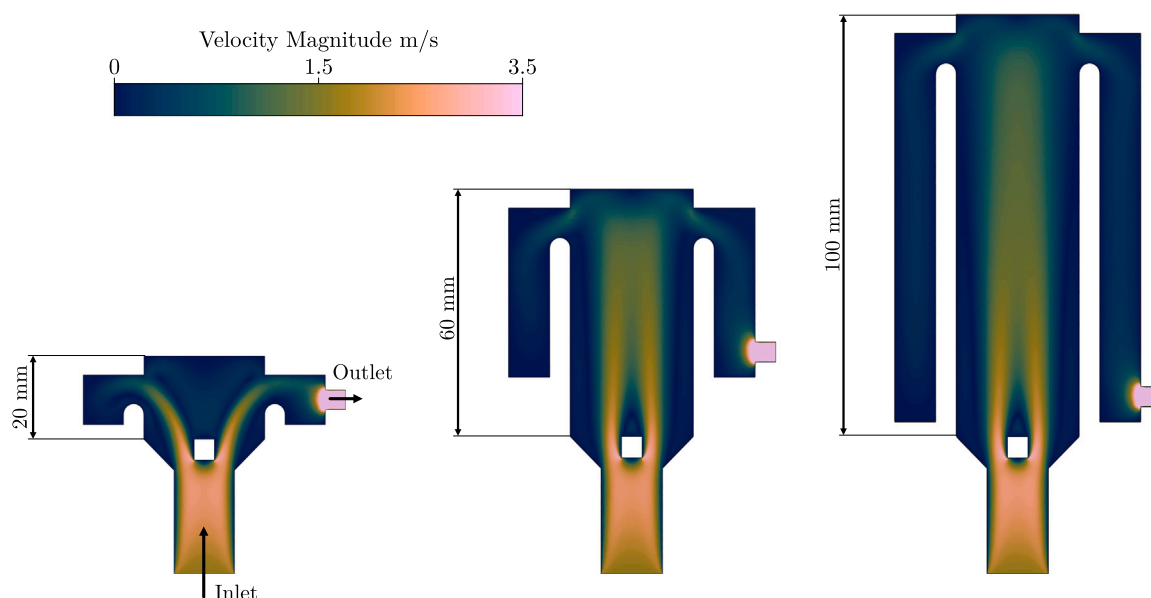


Fig. 4. CFD simulation to determine the optimum reactor length at a flow rate of $10 \text{ L}_\text{N} \text{ min}^{-1}$. Left: 20 mm reaction chamber length. Center: 60 mm length. Right: 100 mm length as reference case.

the pellet perturbation was expected. The results are shown in Fig. 4. It is apparent that the flow fields between the 60 mm and the 100 mm simulations are visually very similar, indicating that the stagnation zone is still of minor influence even for the shorter geometry. Furthermore, as shown in Figure S3, the axial velocity and profiles along the reactor closely agree and show that the flow is fully developed by 60 mm. Based on these simulation results, the length of the reaction chamber behind the pellet was chosen to be 60 mm. The entrance region of the reactor, upstream of the pellet, was not affected by these investigations.

3.2. Concentration profile measurements

This section presents the intra-pellet molar concentration profiles measured at four feed temperatures and CO_2/H_2 feed ratios. The measurements were performed at 290°C , 320°C , 350°C and 380°C and ratios of 1:4, 1:3, 1:2 and 1:1 with 1:4 corresponding to the stoichiometric ratio according to reaction (R1).



The resulting molar concentration profiles across the Ni/- Al_2O_3 pellet are displayed in Fig. 5. Mole fractions were calculated as described in Section 2.3. The gray-shaded area in Fig. 5 indicates the pellet interior, with the sampling position plotted relative to the pellet center. Although samples were obtained only at discrete positions, connecting lines are shown to guide the eye, they do not represent fitted data. The concentration profiles are strongly influenced by both, feed temperature and educt feed ratio. Furthermore, a slight asymmetry is observed, as the concentration profiles are shifted toward the side from which the capillary was inserted. As demonstrated in CFD simulations reported by Sosna et al. [19], this effect originates from additional gas fluxes through the open side of the channel in the catalyst pellet. This flux leads to a slightly increased educt supply from that side and consequently affects the local gas composition. As reported by Sosna et al. [19], this tends to decrease the measured gradients of all species, flattening their profiles. The annular gap of $\sim 20 \mu\text{m}$ and corresponding Knudsen number $\text{Kn} = \frac{k_B T}{\sqrt{2\pi d^2 P l}}$ of 0.003 to 0.007 at reaction conditions is no longer in the mass selective Knudsen diffusion regime. Consequently, H_2 is not preferentially transported through the channel, by diffusion in the continuum regime or convective flow. Nonetheless, the profiles are flattened by gas entering through the

open channel and annular gap as shown by Sosna et al. [19]. As this effect is consistent across all operating conditions, it does not affect the comparative interpretation of the presented concentration profiles.

Across all investigated operating conditions, CO was detected only in trace amounts, indicating that RWGS reaction has a negligible influence on the system. In contrast, pronounced trends are observed for the other species. The concentration profiles deviate markedly from stoichiometric CO_2 and H_2 consumption, with a significantly stronger decrease in CO_2 than in H_2 . At the stoichiometric feed ratio (1:4), the CO_2 concentration at the pellet center approaches zero, whereas the H_2 concentration remains above 50 % at all temperatures. This arises from the higher diffusivity of hydrogen in the pores, which results in a flatter hydrogen concentration gradient throughout the pellet. The effect becomes more pronounced when the feed ratio exceeds the stoichiometric CO_2 concentration, confirming that profiles are strongly influenced by differences in diffusivities of the individual species. In addition, increasing the CO_2 feed concentration enhances CH_4 formation up to a ratio of 1:2, beyond which only minor additional conversion is observed. This trend indicates that the reaction inside the pellet is more strongly influenced by the CO_2 concentration than by the H_2 concentration, which remains abundant due to its high diffusivity. At an equimolar feed ratio (1:1), however, the CO_2 concentration at the pellet center decreases to approximately 15 %, indicating that both CO_2 and H_2 become limiting. Together, these observations suggest that the optimum feed ratio for methane formation lies between 1:1 and 1:2.

Similar trends are observed for the variation of the feed temperature. Increasing the feed temperature initially enhances methane formation. Although CO_2 methanation is exothermic and therefore thermodynamically favored at lower temperatures, increasing temperature initially increases methane formation up to approximately 350°C to 380°C due to accelerated kinetics at elevated temperatures. Above 350°C , further temperature increase does not lead to higher CH_4 formation, indicating the onset of thermodynamic limitations and increasing transport resistances. These findings are consistent with previous experimental and modeling studies such, as reported by Gao et al. [43] and Schmider et al. [44].

As the small amount of methane produced by a single pellet is diluted by the abundance of reactant feed gas its concentration in the outlet gas stream is very low. Consequently, conventional direct measurement of the conversion in the outlet is not possible. However, to assess the reaction rate across the investigated conditions, the species

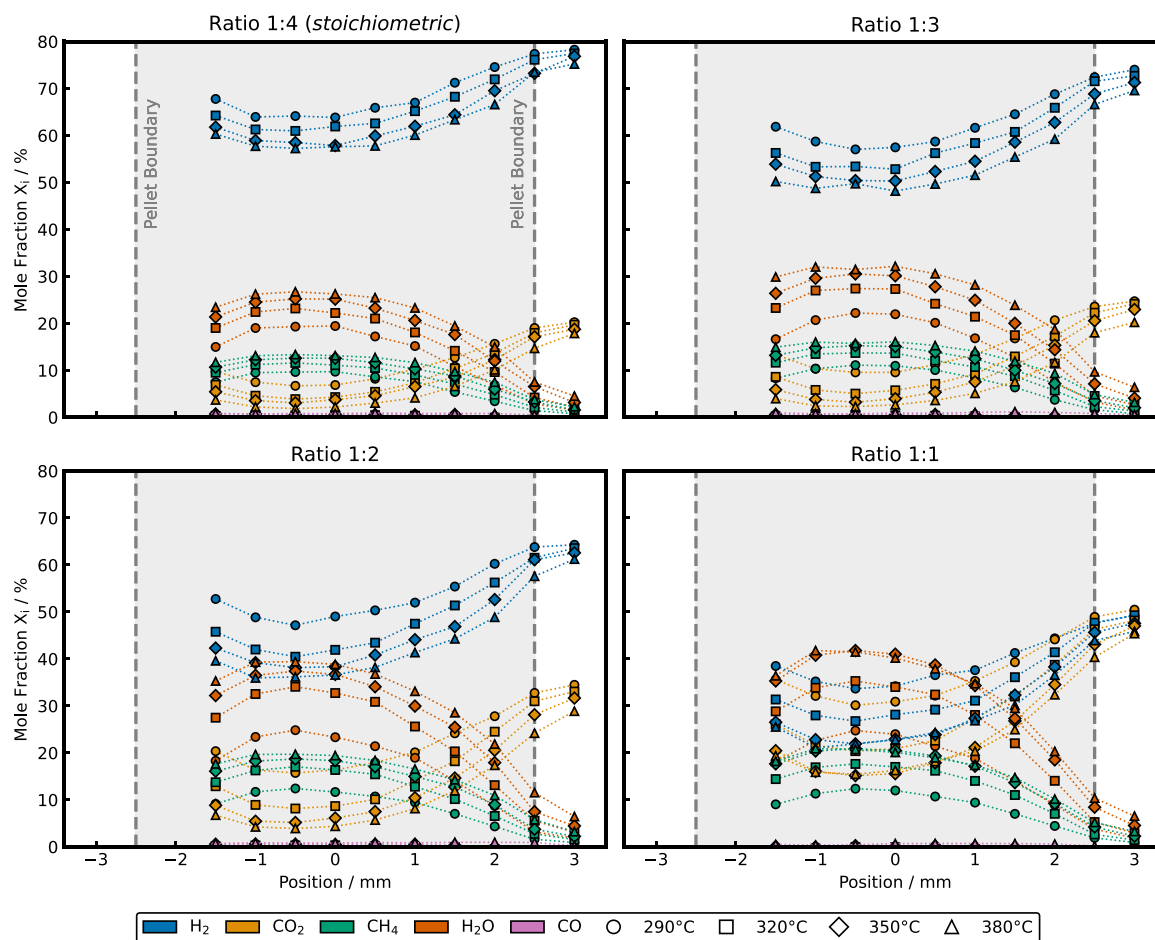


Fig. 5. Molar concentration profiles of reactants during CO_2 methanation inside the $\text{Ni}/\text{Al}_2\text{O}_3$ pellet at different feed temperatures and CO_2 to H_2 feed ratios. The region inside the pellet is indicated by the gray area and corresponding dashed lines. The position is plotted relative to the pellet center. The connecting lines do not resemble actual data but are rather considered to guide the eye.

flux over the pellet surface could be used. For that, the measured profiles are fitted using a quadratic fit. Analytical derivation yields the concentration gradient at the pellet surface, which can be converted into a flux using Fick's first law while considering the effective diffusion coefficient calculated from the Knudsen diffusion coefficient, measured porosity and the tortuosity of the catalyst. These values are shown in Fig. 6. The quadratic fit for each profile and corresponding gradients are displayed in Figure S4. Additionally, we calculated the average concentration of methane for each case by integration of the concentration profiles and division by the pellet diameter as shown in Figure S5. Overall, the data reveal that the intra-pellet CH_4 formation is predominantly limited by local CO_2 availability rather than by H_2 , even for CO_2 -rich feed compositions. The observed trends demonstrate the coupled influence of mass transport and chemical kinetics within a single catalyst pellet. These results highlight the importance of accounting for intra-pellet transport phenomena in the development and optimization of industrial catalysts. Furthermore, it is shown that the presented single-pellet profile reactor is capable of accurately resolving intra-pellet concentration profiles that have not been previously measured.

3.3. IR thermography

This section aims to determine whether distinct temperature patterns or hotspots form during the reaction. Furthermore, we examine how changes in feed temperature and educt feed ratios influence the

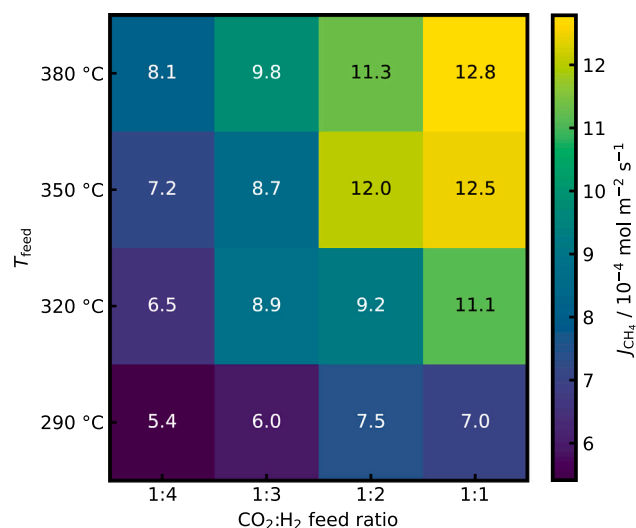


Fig. 6. Absolute species molar flux across at the pellet surface for all investigated conditions as a measure of reaction rate.

pellet surface temperature as a measure of reaction rate or catalytic activity. For the subsequent analysis, it is essential to determine whether

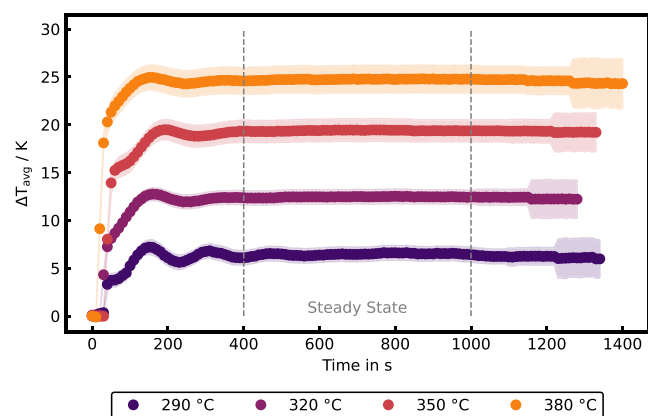


Fig. 7. Average pellet surface temperature increase over the course of a profile measurement at a ratio of 1:1 and temperatures of 290 °C to 380 °C. The dashed lines indicate the time that was considered as steady state and averaged for the further processing.

the temperature of the pellet outer surface reaches a steady state or whether temperature fluctuations persist under steady state conditions. Thus, the outer pellet surface is used to evaluate the temperature distribution. The outer surface temperature field is obtained by unwrapping the mirrored image as explained in Section 2.3.2. Fig. 7 shows the temporal evolution of the averaged temperature rise on the pellet outer surface due to reaction. For this analysis, the subtracted IR images taken every 10 s were unwrapped and the entire temperature field was spatially averaged to yield a single value representing the mean temperature increase caused by the reaction. The profiles shown are at a feed ratio of 1:1. After the start of the measurement, an oscillation in the average temperature increase is observed for all feed temperatures. This oscillation however is more pronounced and of longer duration for 290 °C. In addition, an initial spike is observed in all cases. After around 400 s, the system reaches a steady state until a sudden drop in ΔT can be observed close to the end of the measurement. This is caused by tilting of the pellet when the sampling capillary is retracted, causing a change in the reflection on the mirror which cannot be corrected by the applied data processing. The observed temperature oscillations are likely caused by the control behavior of the heating system and the experimental setup rather than by intrinsic reaction dynamics. The feed temperature in the reactor is regulated by a thermocouple placed in the gas stream, which controls the power supplied to the heating block and thus its temperature. Prior to each experiment, a background IR image is recorded under non reacting conditions which means that H_2 and Ar are flown through the reactor in the absence of CO_2 to stop the reaction from occurring. Under these conditions, the gas flow is slightly lower than under actual reaction conditions. When starting the flow of CO_2 , more gas flows through the heating block causing the gas stream temperature to drop slightly and the heating power to be increased. As the thermal mass of the heating block is high, the control response is slow. Therefore, it takes some time for the feed temperature to stabilize. This behavior is consistent with the observation that the effect becomes more noticeable with a feed ratio of 1:1, as in this case more CO_2 is present in the inlet gas stream and the change in flow rate between reacting and non-reacting conditions is larger. Overall, after an initial startup phase, the average temperature increase on the surface is stable. Therefore, using the time-averaged temperature increase between 400 s to 1000 s for further interpretation is justified. Having established that a steady-state temperature is reached, the following analysis focuses on spatial temperature variations and their correlation with reaction conditions and methane production.

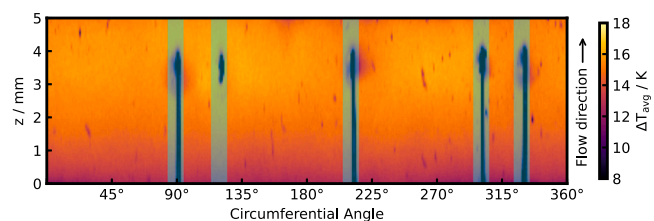


Fig. 8. Exemplarily time-averaged temperature field as used for the following data processing at 350 °C and a ratio of 1:4. The sampling capillary and needles used to hold the pellet are clearly visible. The mask that was applied to account for the holding needles, capillary and other end of the hole is marked in light blue.

3.3.1. Time averaged temperature field

Averaging the temperature as described above yields a temperature field, as shown in Fig. 8, for a feed temperature of 350 °C and a stoichiometric feed ratio. The needles holding the pellet are clearly visible, as well as the sampling capillary entering from one side and the opening in the mirror used to insert a side orifice capillary. In addition to these experimental features, spatial variations are observed. Small localized spots appear across the entire image. These features originate either from imperfections in the mirror surface or holes and pores on the pellet surface resulting from the manufacturing process. Aside from these artifacts, no distinct temperature patterns or hotspots are observable. To account for the cold regions formed by the needles and capillary, the area $\pm 5^\circ$ around these spots was masked and not used for further data processing. This mask is shown in Fig. 8. As the glass needles are not taking part in the reaction and have a low thermal conductivity, they have a temperature similar to the gas feed and therefore do not appear in the subtracted temperature field. This effect is also visible in Fig. 8, where the temperature increase is below 8 K.

3.3.2. Axial temperature along the Pellet's outer surface

Having confirmed steady-state conditions during a defined section of the experiment, the spatial distribution of the pellet surface temperature is analyzed. The analysis aims to identify any spatial gradients that persist over time, such as axial or radial gradients. Furthermore, the influence of feed temperature and feed ratio on the surface temperature increase is investigated. For this purpose, time-averaged temperature maps are used. Fig. 9 shows the circumferentially averaged temperature field at a feed temperature of 350 °C and four feed ratios. The temperature is plotted along the x-axis, to keep the orientation comparable to the image shown in Fig. 8. From Fig. 9 it is apparent, that the temperature generally increases axially along the flow direction. Additionally, it also increases with feed ratio until a ratio of 1:2 is reached. Between a ratio of 1:2 and 1:1 however, only minor differences are observed. These findings are consistent with the observations made for the concentration profiles in Section 3.2. Between ratios of 1:1 and 1:2, no substantial differences in methane production are observable. Since (R1) is the dominant reaction and therefore the main heat source, no difference in surface temperature is expected for the same methane production. The IR temperature measurements confirm that the exothermic reaction causes a measurable surface temperature rise compared to the inlet feed temperature.

At the upper region of the pellet above 4 mm, the temperature decreases again. This is most likely an hydrodynamic effect, where the convective heat transport is locally enhanced due to flow separation at the trailing edge of the pellet. Additionally, the pellet geometry may deviate slightly from a perfect cylinder, leading to geometric distortions at the boundary, as the unwrapping procedure only accounts for misalignment of the camera. Despite these uncertainties, the overall trend in surface temperature remains clearly visible when disregarding the top and bottom regions. The pronounced axial temperature gradient

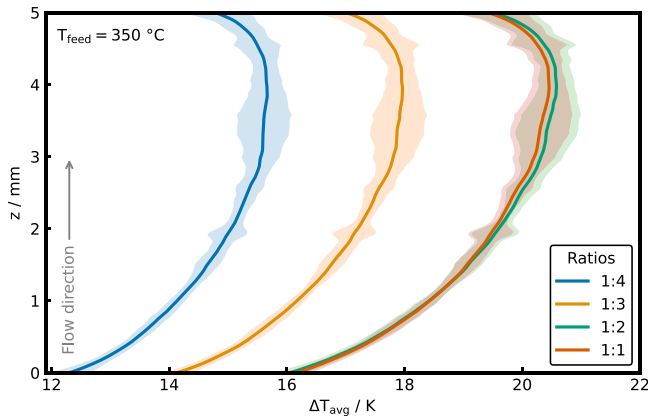


Fig. 9. Comparison of axial temperature profiles obtained by row averaging of the temperature field. The shaded area corresponds to the standard deviation. The depicted profiles were measured at a feed temperature of 350 °C and four different ratios.

indicates differences in heat removal in the axial direction. The feed gas enters the reactor colder than the pellet and hence, convectively cools the lower part of the pellet. As the gas warms up along the flow path, its cooling effect decreases, resulting in the observed gradient. Apart from these gradients and in contrast to the findings by Annamalai et al. [26] for CO oxidation, no pronounced temperature pattern formation was observed under steady-state conditions. The observed spatial trends are consistent across all investigated feed temperatures and the overall agreement between conditions demonstrates the reproducibility of the experiment.

3.3.3. Assessing the internal temperature gradient

Before comparing the surface temperature rise between different feed compositions and temperatures, the maximum temperature gradient inside the pellet will be calculated. The Prater number β can be used to assess the internal gradient to judge whether the surface temperature is representative of the bulk of the pellet.

$$\beta = \frac{c_s D_{\text{eff}} (-\Delta H_R)}{\lambda_{\text{eff}} T_s} = \frac{\Delta T_{\text{max}}}{T_s} \quad (1)$$

It is defined as the ratio of maximum temperature difference inside the pellet and the pellet surface temperature. The Knudsen diffusion coefficient is calculated as:

$$D_{K_{\text{CH}_4}}(T) = \frac{2}{3} r_{\text{pore}} \sqrt{\frac{8RT}{(\pi M_{\text{CH}_4})}} = 2.785 \times 10^{-6} \text{ m}^2 \quad (2)$$

Followed by the effective diffusion coefficient.

$$D_{\text{eff,CH}_4}(T) = \frac{\varepsilon}{\tau} D_{K_{\text{CH}_4}}(T) = 5.1 \times 10^{-7} \text{ m}^2 \text{ s}^{-1} \quad (3)$$

For the largest gradient case at $T_{\text{feed}} = 380^\circ\text{C}$ and a ratio of 1:4, this results in $\beta = 0.0037$. Assuming a temperature increase of 24.71 K, the surface temperature used for this calculation is 677.86 K and the maximum intra-pellet $\Delta T_{\text{max}} = 2.5$ K. This is roughly 10% of the highest observed temperature rise. Considering this, the measured surface temperature rise could be assumed to be representative for the bulk temperature of the pellet.

3.3.4. Pellet surface temperature for varying feed conditions

In the previous sections, the development of surface temperature increase over time and along the axial direction has been shown for selected feed temperatures and ratios. However, to systematically assess the influence of feed ratio and feed temperature on the temperature increase and, consequently, on the reaction rate, a more general approach is required. Accordingly, this section presents the average

Table 2

Ratio of thermal conductivities and measured temperature rise at 350 °C for a $\text{CO}_2\text{:H}_2$ feed ratio of 1:4 as the reference case.

Ratio	$\lambda_{\text{ratio}} = \frac{\lambda_{\text{g,ref}}}{\lambda_{\text{g,i}}}$	$\Delta T_{\text{ratio}} = \frac{\Delta T_{\text{s,i}}}{\Delta T_{\text{s,ref}}}$
1:4 → 1:3	0.08	0.14
1:4 → 1:2	0.22	0.31
1:4 → 1:1	0.58	0.30

surface temperature increase for all investigated feed temperatures and feed ratios. The average temperatures shown in the following figure are derived from the steady-state, time-averaged temperature fields described above. Fig. 10 shows a strip plot of the surface temperature rise for all investigated feed ratios and temperatures. As not the temperature of all 72k time averaged pixels per experiment could be plotted in the strip plot, 500 points per experiment were randomly sampled and plotted. The horizontal axis is categorical and data within each set are spread horizontally to improve visualization of clustered values. Note that no data are available for 380 °C and a ratio of 1:3, as the IR camera recording failed during the corresponding experiment. As a measure of uncertainty, the standard deviation of the time-averaged temperature field at a fixed spatial coordinate is used. The maximum temporal standard deviation in the steady-state region is approximately 0.2 K, which is within the resolution of the IR camera. The spatial standard deviation however, is considerably larger and is mainly caused by geometric variations rather than measurement uncertainty. It is apparent, that the temperature rise increases with rising feed temperature, indicating higher reaction rates and associated heat release at elevated temperatures. In addition, the temperature increase becomes larger with increasing CO_2 concentration in the feed (up to a ratio of 1:1). In general, the increase in average surface temperature with increasing CO_2 concentration could reflect the larger exothermic heat release and indicate higher reaction rate. However, interpretation of these finding requires care. Assuming only small intra-pellet temperature gradients, the temperature rises by balancing between chemical reaction heat release $\dot{Q}_{\text{rxn}}$ and heat removal by colder feed gas.

$$\Delta T_s = \frac{\dot{Q}_{\text{rxn}}}{(h A_s)} \quad (4)$$

The surface temperature rise is only a direct measure of catalyst activity or reaction rate, if heat removal stays consistent between feed ratios. As shown in the definition of the Nusselt number Eq. (5), the heat transfer coefficient is directly correlated with thermal conductivity λ and consequently changes drastically with composition.

$$h = \text{Nu} \frac{\lambda_g}{d_p} \quad (5)$$

Using CoolProp [45], we calculated the thermal conductivity coefficients for the pure feed gases. Utilizing the Mason–Saxena modification of the Wassiljewa equation, we calculated the thermal conductivity of the different feed gas mixtures λ_g [46] for the film temperature. At a feed temperature of 350 °C, λ_g decreases from 0.178 $\text{W m}^{-1} \text{K}^{-1}$ at 1:4 to 0.165 $\text{W m}^{-1} \text{K}^{-1}$, 0.146 $\text{W m}^{-1} \text{K}^{-1}$ and 0.112 $\text{W m}^{-1} \text{K}^{-1}$ for 1:3, 1:2 and 1:1 feed ratios respectively. Assuming constant heat release and feed temperature, Eqs. (4) and (5) combine to:

$$\frac{\Delta T_{\text{s,i}}}{\Delta T_{\text{s,ref}}} = \frac{h_{\text{ref}}}{h_i} = \frac{\text{Nu}_{\text{ref}}}{\text{Nu}_i} \frac{\lambda_{\text{g,ref}}}{\lambda_{\text{g,i}}} \quad (6)$$

As seen in Eq. (6), the ratio of ΔT is directly dependent on the ratio of the thermal conductivities when assuming constant pressure, feed temperature and geometry. If the measured ΔT ratio exceeds the ratio of thermal conductivities, the difference must be caused by more heat being released due to a higher reaction rate.

Table 2 shows the ΔT_{ratio} and λ_{ratio} exemplarily for 350 °C. It can be seen that increasing the ratio from 1:4 to 1:2 leads to a higher measured

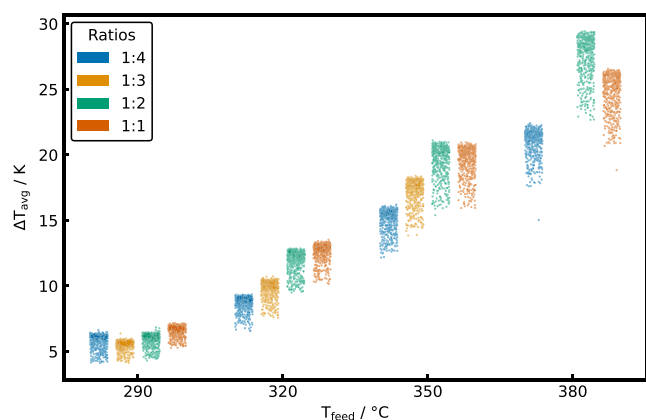


Fig. 10. Comparison of time averaged temperature rise of the pellet's lateral surface for all investigated feed temperatures and ratios as a strip plot. The amount of data was reduced by randomly sampling 500 points per experiment to maintain readability.

temperature increase than the change in mixture thermal conductivity would suggest. However, when comparing 1:1 to 1:4, the measured rise is below the predicted one. Consequently, a kinetic contribution to the temperature rise is indicated for the ratios 1:3 and 1:2. Nonetheless, as the thermal conductivity changes drastically and is therefore contributing to the temperature rise, it should not be used as a unique criterion to judge reaction rate. Instead, it should be used as an additional insight in close combination with the measured concentration profiles in Fig. 9 and especially the surface flux of methane as shown in Fig. 6. A comparison between different feed temperatures under a constant ratio is not affected by these effects, as the thermal conductivity and therefore the convective cooling exhibits a less sensitive temperature dependency. In conclusion, the observed temperature rise suggests that both, higher temperature and higher CO₂ concentration yield a higher temperature rise, some of which is attributed to higher reaction rate. This observation is in close agreement with the measured concentration profiles and the calculated surface flux of methane.

4. Conclusions

The presented results show that the composition inside the catalyst pellet deviates strongly from the bulk gas composition, with CO₂ being almost fully consumed while sufficient H₂ remains available. Furthermore it is shown that the feed ratio and feed temperature strongly influence methane formation and that optimal conditions may differ from a stoichiometric composition of the educt gases in the feed.

The IR thermography data corroborates these findings. A higher CO₂ feed concentration leads to a higher surface temperature. However, analysis of the external heat transport shows that the thermal conductivity of the feed gas mixture decreases significantly with decreasing H₂ concentration, strongly influencing the surface temperature rise. Therefore, the surface temperature rise should only be examined in close combination with the measured concentration profiles and should not serve as a judgment for catalytic activity on its own. Apart from the reported axial gradient, no evidence of other spatial temperature pattern formation was observed under steady-state operation conditions. Overall, the thermography data and spatial profiling provide a coherent picture of coupled mass and heat transport phenomena in the methanation catalyst. In the end, the presented reactor has shown to provide a new foundation for producing experimental in-situ data to help in future validation of intra-pellet kinetic and transport models and optimize catalysts based on experimental knowledge.

Besides the optimization, future work will focus on investigating the response of single catalyst pellets to dynamically changing operating conditions such as square wave feed modulation. Furthermore,

a Particle-Resolved Computational Fluid Dynamics (PRCFD) model of this exact reactor is currently under development and will be the core of a future publication. The PRCFD model will be useful in further investigating and quantifying the invasiveness of the measuring system, especially regarding the drilled channel and annular gap size depending effects.

CRediT authorship contribution statement

Mats Finkeldei: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis. **Philipp Reinold:** Writing – review & editing, Visualization, Validation, Investigation. **Oliver Korup:** Validation, Project administration, Conceptualization. **Gregor D. Wehinger:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Raimund Horn:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of Generative AI Usage

OpenAI ChatGPT (GPT-5), and Anthropic Claude (Sonnet 4.8) were used to improve language and formatting. The result was thoroughly reviewed and edited by the authors who take full responsibility for the published content of the article.

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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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.cej.2026.182393>.

Data availability

The experimental data and the associated data processing code supporting the findings of this study are openly available at <https://doi.org/10.15480/882.17442> and <https://doi.org/10.15480/882.17444>, respectively.

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