

Full Length Article

Cyclic oxygen release and heat generation of oxygen storage materials using propane in a packed bed reactor

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ABSTRACT

The use of oxygen storage materials (OSMs) to supply oxygen for oxy-fuel combustion represents a promising approach for carbon capture. This qualitative proof-of-concept study investigates a process related to chemical looping with oxygen uncoupling (CLOU) using calcium-strontium-iron-manganese (CSFM)-type non-stoichiometric perovskite OSM mini-honeycombs in a small-scale packed bed reactor at atmospheric pressure. After preheating with a McKenna flat-flame burner, the stationary bed was alternately exposed to air and undiluted propane or methane without an intermediate purge or continuous external heating. Oxygen storage during charging is exothermic, whereas oxygen release during discharging is endothermic; simultaneous fuel combustion nevertheless produced a positive packed bed temperature response during both phases. The effects of starting temperature, fuel type, cyclic air-fuel ratio, volume flow rates, and phase durations were evaluated using packed bed temperature measurements and exhaust-gas analysis. Propane and methane exhibited opposing starting-temperature trends under the selected conditions: the effective test duration decreased with increasing starting temperature for propane but increased for methane, demonstrating the need for fuel-specific cyclic parameters. Sustained cyclic operation exceeding 50 min was achieved with propane. However, carbon monoxide and unburned hydrocarbons indicated incomplete fuel conversion, and a carbon dioxide-rich exhaust gas was not achieved. Because the total outlet flow was not measured, the temperature responses and exhaust gas concentrations are interpreted as comparative indicators rather than quantitative performance metrics. Overall, the results demonstrate the feasibility of short-cycle CLOU-related operation with stationary CSFM mini-honeycombs and undiluted propane while identifying empirical parameter ranges associated with the observed thermal response.

1. Introduction

Total annual industrial energy demand will continue to grow in the coming years. A significant share of this demand is attributable to the generation of process heat [1–3]. However, the electrification of existing processes and plants, as well as the conversion to carbon-free energy sources such as hydrogen, remain technically complex and costly in most cases. Therefore, the use of natural gas is expected to remain significant in the foreseeable future [2,4]. As the release of carbon dioxide during the combustion of carbon-based fuels cannot be completely avoided, carbon capture, utilization, and storage (CCUS) technologies represent a promising approach to decarbonization [5]. However, the

efficient application of these technologies requires a high degree of carbon dioxide purity in the exhaust gas stream [6,7]. This can be achieved by pre-combustion or post-combustion methods, as well as by oxy-fuel combustion [7].

This study investigates an oxy-fuel combustion concept in which oxygen is supplied by calcium-strontium-iron-manganese (CSFM)-type non-stoichiometric perovskite materials. In the present work, the term oxygen storage material (OSM) is used to emphasize their reversible oxygen storage and release function. Within the broader chemical-looping terminology, however, these materials are also known as perovskite-type oxygen carriers (OCs). These materials are particularly characterized by their fast oxygen exchange kinetics. By reversibly

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incorporating oxygen from air into the crystal lattice, the need for cost- and energy-intensive air separation can be avoided. In conventional chemical-looping combustion (CLC), the fuel is oxidized through its interaction with the solid oxygen carrier, whereas chemical looping with oxygen uncoupling (CLOU) involves the release of gas-phase oxygen from the carrier before its reaction with the fuel. Since CSFM releases gas-phase oxygen under the investigated discharge conditions, while additional direct interaction between the fuel and the solid cannot be excluded, the present process is positioned within the CLOU framework [8,9]. Alternating oxygen storage from air and oxygen release during the fuel phase provides the basis for cyclic operation with a sustained thermal response.

The CLOU-related process investigated here is operated in a lab-scale fixed (packed) bed reactor at atmospheric pressure. Since the rate of oxygen exchange depends on both temperature and oxygen partial-pressure gradients, a McKenna burner for preheating is located below the packed bed. Unlike many previously reported systems, neither the packed bed nor the incoming gases are externally heated during cyclic operation after the initial preheating step using the burner [10,11].

Ambient air is used to oxidize (charge) the OSM, while propane or methane is supplied during its reduction and oxygen-release (discharging) phase. In addition, neither the air nor the fuel streams are diluted with inert gases, in contrast to most previous studies [12–14].

To evaluate the effects of the operating conditions on cyclic oxygen storage and release, the packed bed temperature and the cyclic air-fuel ratio are varied. For this purpose, the temperature within the packed bed and the composition of the exhaust gas at the reactor outlet are measured and analyzed. The operational objective is to maintain a high and stable temperature level within the packed bed for as long as possible, thereby enabling sustained cyclic operation without additional heating.

Due to the small-scale reactor, the present study is explicitly scoped as a qualitative proof-of-concept investigation focusing on the packed bed temperature evolution, effective test duration, and the identification of empirical parameter ranges associated with maintaining the observed thermal response, while the limitations concerning fuel conversion and exhaust gas composition are evaluated qualitatively. Accordingly, the measured temperature responses, effective test duration, and outlet-gas concentrations are used as comparative indicators of reactor behavior; they do not provide experimentally determined oxygen-release capacities, fuel-conversion efficiencies, closed carbon balances, oxygen-utilization efficiencies, oxygen-uncoupling kinetics, or cycle-specific values of $\Delta\delta$. In general, achieving high fuel conversion and a carbon dioxide-rich exhaust gas suitable for subsequent carbon capture is a long-term objective of the reactor concept. Although perovskite oxygen carriers, CLOU, and packed bed chemical-looping reactors have previously been investigated [10–24], their combination with stationary CSFM mini-honeycombs under the operating conditions considered here has received little attention. The contribution of the present study lies in the atmospheric-pressure operation of a single packed bed using short cycles, direct switching between air and undiluted fuel without an intermediate purge phase, and no continuous external heating after initial preheating. Propane is investigated as the primary fuel and compared with methane to determine how fuel type, cyclic air-fuel ratio, operating temperature, volume flow rates, and phase durations affect the temperature evolution and effective test duration during cyclic operation. The results are intended to provide a basis for the future application of CSFM OSMs as stationary oxygen carriers in CLOU-related regenerative burner concepts.

2. Experimental set-up and materials

2.1. Materials and fuels

Previous studies of solid oxygen carrier materials for chemical-looping processes have extensively investigated Cu-, Fe-, and Ni-based

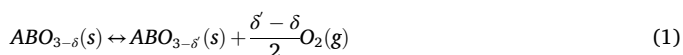
metal oxides [12,13]. These materials are conventionally referred to as oxygen carriers (OCs). Ilmenite (FeTiO_3) has also been widely investigated as a naturally occurring OC [17]. In addition, non-stoichiometric Ca-Mn-Ti-Fe-based perovskites have been investigated as OCs for chemical-looping applications [15]. This study investigates a non-stoichiometric perovskite OSM of the calcium-strontium-iron-manganese (CSFM) type with the nominal composition:



Consistent with the terminology introduced in Section 1, the material is referred to as an OSM to emphasize its reversible oxygen storage and release function, while it acts as a perovskite-type OC within the investigated CLOU-related process.

To provide a large gas-solid contact area, the CSFM OSMs were manufactured as mini-honeycombs containing 3×3 square channels. The nominal overall dimensions are $5.3 \times 5.3 \times 6.5$ mm, with minor variations between individual units resulting from the manufacturing process. The open porosity of the ceramic material is 41.5% and refers to the interconnected pore volume within the ceramic walls; it does not include the volume of the nine macroscopic honeycomb channels.

The operating principle of the OSM is based on the reversible storage and release of lattice oxygen through changes in its oxygen non-stoichiometry. The CSFM OSM is a mixed ionic and electronic conductor (MIEC). The transport of electrons and oxygen ions is driven by temperature and oxygen partial pressure gradients. At low external oxygen partial pressures, oxygen ions migrate through the lattice to the material surface, where they form oxygen molecules by releasing electrons. At higher external oxygen partial pressures, oxygen molecules at the material surface are transformed into ions by accepting electrons and incorporated (stored) into the lattice. At a given temperature, the equilibrium oxygen content of the OSM depends on the oxygen partial pressure of the surrounding atmosphere. During charging in air, the material approaches the oxidized state corresponding to an oxygen partial pressure of approximately 21 kPa. A subsequent decrease in the external oxygen partial pressure shifts the equilibrium toward a higher value of δ , resulting in the release of gas-phase oxygen. A key characteristic of CSFM-type OSMs is their ability to release oxygen at practically relevant rates even at comparatively high oxygen partial pressures. This reversible uncoupling of gas-phase oxygen enables the CSFM OSM to function as a perovskite-type oxygen carrier in the investigated CLOU-related process. The reversible oxygen exchange can be represented according to the following reaction:



with $\delta' > \delta$

A:	Large cations (alkaline earth or rare earth elements)
B:	Valence-variable 3d/4d transition metals

The parameter δ represents the oxygen deficiency in the non-stoichiometric perovskite lattice [25]. A value of approximately 0.3 is representative of fully charged CSFM OSM under the relevant conditions, whereas δ may increase to approximately 0.5 during discharging and may reach values of up to 1.0 under strongly reducing conditions. These values describe characteristic material states and were not measured during the individual reactor cycles investigated in this study. Consequently, a change in δ of 0.2 is used as an assumed reference discharge range expected under typical operating conditions, whereas a change of 0.7 is used as the theoretical maximum range considered here. Based on these assumed changes in δ , the reactor packed with approximately 300 g of CSFM OSM has a calculated theoretical reference oxygen mass of 5.91 g for a change in δ from 0.3 to 0.5 and a calculated theoretical maximum reference oxygen mass of 20.69 g for a change from 0.3 to 1.0. The cycle-specific inlet-based stoichiometric oxygen demands of the investigated operating conditions and their ratios to

these theoretical OSM reference capacities are provided in Table S1 in the Supplementary Material. These ratios represent theoretical, inlet-based demand-to-capacity reference values and not experimentally determined degrees of OSM discharge. On a mass-specific basis, these values correspond to a theoretical reference oxygen capacity of 19.7 mg oxygen per 1 g OSM (0.62 mmol oxygen per 1 g OSM) for $\Delta\delta = 0.2$ and a theoretical maximum reference capacity of 68.9 mg oxygen per 1 g OSM (2.15 mmol oxygen per 1 g OSM) for $\Delta\delta = 0.7$. The amount of oxygen actually released during an individual discharging phase cannot be quantified from the present measurements because neither the time-dependent total exhaust gas flow rate nor the spatial distribution of δ within the packed bed was determined. Accordingly, neither the calculated capacities nor the demand-to-capacity ratios represent experimentally determined oxygen release, oxygen-utilization efficiency, actual OSM conversion, or cycle-specific $\Delta\delta$. Within the qualitative proof-of-concept scope of this study, the calculated capacities are therefore used only as theoretical reference values for contextualizing the fuel input and not as experimentally determined performance metrics.

The theoretical material-specific oxygen reference capacity used here is calculated from an assumed change in oxygen non-stoichiometry $\Delta\delta$ and is therefore not intrinsically dependent on the fuel. For identical assumed initial and final values of δ , the representative and theoretical maximum capacities stated above apply equally to propane and methane operation. Although the actual oxygen release cannot be quantified in the present study, the fuel type may affect the spatial and temporal extent of oxygen exchange during an individual cycle through differences in stoichiometric oxygen demand, local oxygen partial pressure, temperature evolution, and reaction kinetics.

The storage and release of oxygen result in geometric changes in the OSMs (less than 1% for CSFM OSM [26]). The associated lattice expansion and contraction are caused by changes in the oxygen vacancy concentration and the resulting variation in the crystal structure. Due to lattice expansion during the discharge phase, deep reduction of the OSM ($\delta > 1.0$) may induce mechanical stresses and promote crack formation. To minimize long-term material degradation, the operating parameters should therefore be selected to avoid such strongly reducing conditions.

In addition to the partial pressure of oxygen, temperature in particular has a significant impact on the exchange rate [12,27]. Oxygen storage and release are feasible at room temperature. However, the oxygen exchange rate is too low for CLOU-related combustion applications. For CSFM-type OSMs, a sufficiently rapid oxygen exchange occurs at temperatures between approximately 900 K and 1400 K. In the present application, a minimum operating temperature of approximately 850 K is required to initiate cyclic operation. This temperature range is comparable to reported operating ranges of previously investigated OCs such as CuO (900–1150 K), NiO (850–1550 K), and FeTiO₃ (800–1450 K) [11,14,17]. In contrast to some Cu-based OCs, which exhibit a comparatively low melting temperature of approximately 1360 K [17], CSFM-type OSMs exhibit high-temperature material stability up to about 1550 K. This property is expected to reduce the risk of thermally induced degradation. However, high-temperature material stability alone does not demonstrate long-term mechanical or redox-cycle durability under the investigated cyclic operating conditions.

The manufacturing process of the CSFM-type OSMs can be divided into two main steps: powder preparation and honeycomb fabrication.

The ceramic powders were synthesized using a conventional solid-state synthesis route involving the mixing of stoichiometric amounts of raw oxides and carbonates, calcination at 1370–1470 K and milling of the calcined powders to achieve a particle size in the range of 2–3 μm .

The CSFM-type OSM honeycombs were manufactured by stiff plastic extrusion. For this purpose, the ceramic powders were mixed with varying amounts of pore-forming agents, water, and organic additives such as binders and waxes. The resulting mixtures were plasticized using a conventional twin-shaft kneader. Extrusion was performed using a single-screw vacuum extruder with a screw diameter of 50 mm (ECT-

KEMA GmbH) and a specially designed die enabling the simultaneous shaping of eight honeycomb strands, each containing nine channels and a cross-section of $5.27 \times 5.27 \text{ mm}^2$. A screw rotation speed of 15 rpm was applied in all extrusion processes, resulting in extrusion pressures between 4000 kPa and 13000 kPa depending on the composition of the mixture. The extruded strands were automatically cut to equal lengths using a dedicated cutting device. After drying, the honeycombs were fired at 1300 K and 1570 K respectively.

Pure propane was used as the fuel during discharge of the OSM and associated oxy-fuel combustion in the present investigations. Comparative analyses were conducted using methane as a reference fuel. While previous studies have predominantly focused on methane, syngas, hydrogen, or diluted fuel streams [12,17–19], the application of CSFM-type OSMs as packed bed oxygen carriers in a CLOU-related process with undiluted propane under the cyclic packed bed operating conditions investigated here has received little attention.

Although methane and propane have comparable gravimetric lower heating values and adiabatic flame temperatures, their stoichiometric oxygen demands differ considerably. Complete combustion requires 2 mol of O₂ per mole of methane but 5 mol of O₂ per mole of propane. At an identical normalized volumetric flow rate, propane therefore imposes 2.5 times the oxygen demand and an approximately 2.5-fold nominal thermal input rate because of its correspondingly higher volumetric lower heating value. The objective is to investigate how these fuel-dependent differences influence the thermal response and exhaust-gas concentration trends during cyclic charging and discharging. Fuel-dependent operating conditions are therefore compared using the cyclic relative air-fuel ratio λ_{cycle} , which accounts for the different stoichiometric oxygen requirements. However, this normalization does not provide the amount of oxygen actually released from the OSM during an individual cycle.

Furthermore, the fuel-dependent temperature gradients that develop within the packed bed during cyclic operation are of special interest. The effect of propane's lower autoignition temperature compared with that of methane (739 K versus 810 K [28]) on the packed bed temperature evolution and the exhaust gas composition is investigated. In addition, the impact of differences in fuel reactivity is examined, particularly under fuel-rich operating conditions.

2.2. Experimental set-up and instrumentation

A modular cylindrical model reactor is used for the experimental investigation. The setup allows the analysis of the impact of various operating parameters (see Section 2.3) on the temperature evolution and exhaust gas composition during oxygen storage and release. The reactor is shown schematically in Fig. 1. The reactor is operated cyclically and contains a fixed (packed) bed of OSMs. In addition to its simpler design compared to a dual fluidized-bed reactor (DFB), it offers particular advantages by avoiding mechanical abrasion of the OSM particles. Particle attrition in DFB systems may raise both environmental and operational concerns and can result in material losses over extended operating periods [14].

In contrast to many reactor concepts reported in the literature, the present reactor is designed for operation nominally at atmospheric pressure [10,12,17,20]. Although operation at atmospheric pressure may reduce the oxygen exchange rate compared with pressurized systems, it simplifies the reactor design and may facilitate future scale-up and industrial implementation. Neither the absolute reactor pressure nor the differential pressure across the packed bed was measured during the tests. Consequently, the propagation of the reaction and temperature fronts was evaluated based on the axially distributed thermocouples and the exhaust-gas composition.

The central reactor module contains an OSM packed bed with a diameter of approximately 60 mm and a height of approximately 90 mm, comprising approximately 300 g of randomly packed CSFM mini-honeycombs and corresponding to a bulk density of approximately

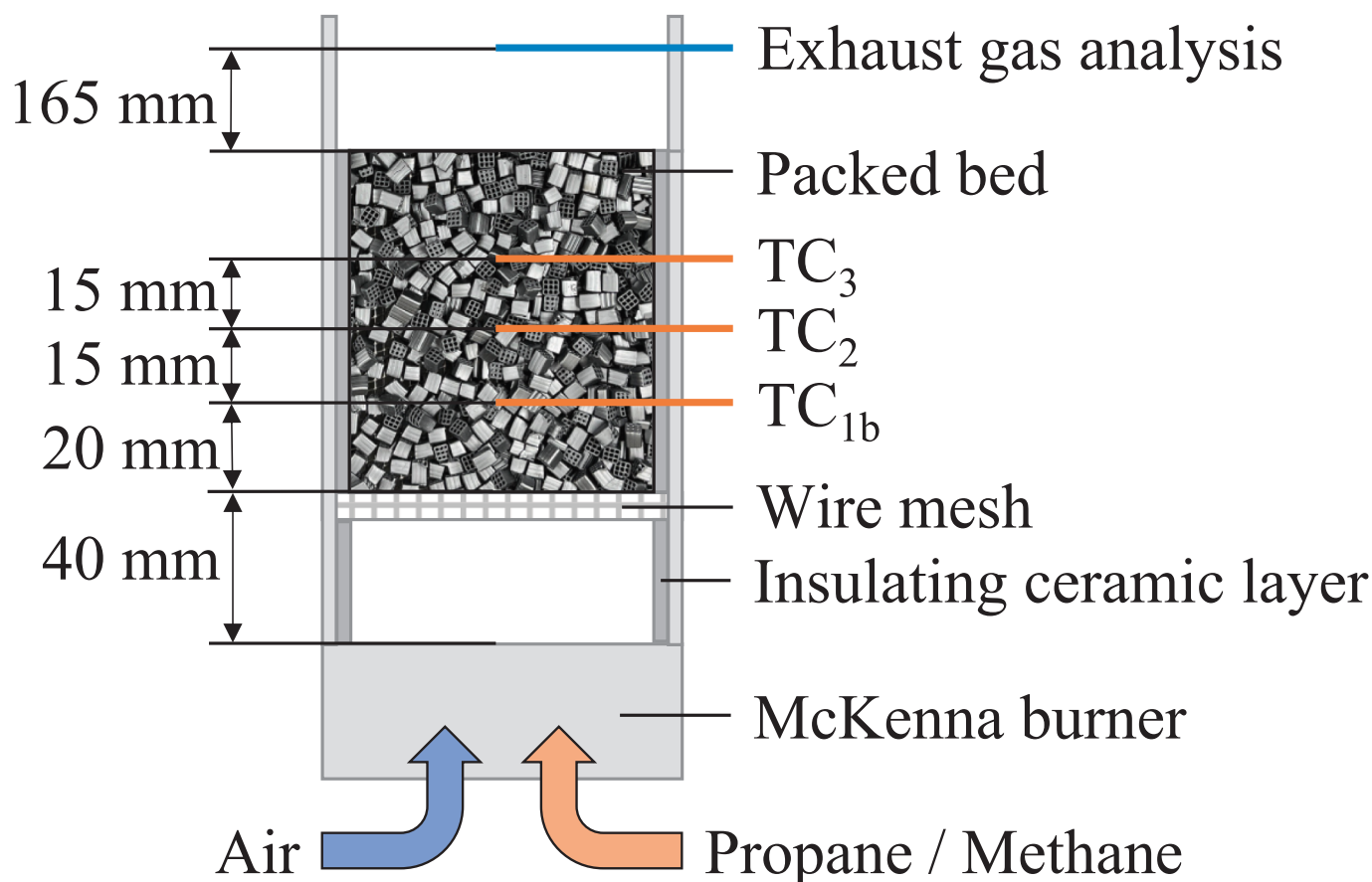


Fig. 1. Schematic of the model reactor equipped with CSFM OSMs. Three thermocouples within the packed bed and the sample point of the exhaust gas analysis are depicted. The gas supply of air and fuel for cyclic operation is introduced via the previously shut off burner.

1.2 g cm^{-3} . The mini-honeycombs were randomly introduced into the reactor; consequently, their channel axes had no preferential alignment with the reactor axis, as also illustrated in Fig. 1. The total gas-accessible void fraction (total bed voidage) of the packed bed was calculated to be approximately 78%. This value includes the open pores within the ceramic material, the honeycomb channels, and the voids between individual mini-honeycombs. The inter-unit voidage could not be quantified separately because the number and total external envelope volume of the geometrically varying mini-honeycombs were not recorded. To minimize radial heat losses, the packed bed is insulated from the outer stainless steel reactor wall by ceramic half-shells with a thickness of approximately 12.5 mm. The OSMs are supported on a temperature-resistant wire mesh. A water-cooled McKenna flat-flame burner with a maximum thermal power of 1 kW is positioned 40 mm below the packed bed. During the heat-up phase (see Section 2.3), the burner is used to preheat the OSMs to the desired operating temperature. After the heat-up phase, the burner is switched off and subsequently serves as the gas inlet for air and fuel (methane or propane) during cyclic operation. Owing to its homogeneous heat-flux density and adjustable relative air-fuel ratios ($\lambda_{\text{heat-up}}$), the burner enables controlled preheating of the packed bed prior to cyclic operation.

Mass flow controllers (MFCs, Bronkhorst, EL-Flow) regulate the gas supply to the burner and reactor. The controllers provide a premixed air-fuel stream for burner operation during the heat-up phase and supply undiluted air and fuel separately to the reactor during cyclic operation.

In contrast to many studies reported in the literature, the inlet gases are not preheated during cyclic operation but are supplied to the reactor at room temperature [11,21]. This approach reduces both system complexity and auxiliary energy demand. However, the introduction of cold gases may promote cooling of the OSM packed bed and thereby

limit the achievable temperature increase during cyclic operation.

To analyze the operating behavior of the OSM, the reactor is equipped with eight type K thermocouples (TCs, sampling rate 1 Hz) distributed along its height. While five thermocouples are located within the packed bed, the other three are positioned in the exhaust gas stream. The temperature analysis focuses on the centrally located thermocouples TC_{1b}, TC₂, and TC₃ (see Fig. 1). During cyclic operation, a temperature front propagates from bottom to top within the packed bed. Consequently, peak temperatures are reached earlier and attain higher values in the lower region of the bed (area TC_{1b}) than in the upper region (area TC₃). To account for these spatial temperature differences, the core temperature T_{core} is defined as the mean value of T_{1b} , T_2 , and T_3 (measured by TC_{1b}, TC₂, and TC₃, see also Figs. 1–3).

As shown in Fig. 1, the exhaust gas stream is sampled 165 mm above the OSM packed bed and analyzed using a Fourier-transform infrared spectrometer (FTIR, Gasmet, DX series), a flame ionization detector (FID, Mess- und Analysetechnik, ES series), and a paramagnetic oxygen sensor (M&C Tech Group, PMA series). These instruments are used to measure unburned hydrocarbons (UHC), carbon monoxide (CO), carbon dioxide (CO₂), nitrogen oxides (NO_x), and oxygen (O₂). The sampling rate of the exhaust gas analysis is 0.17 Hz. Because the time-dependent total exhaust-gas flow rate was not measured and the UHC signal was evaluated qualitatively, neither an absolute fuel conversion efficiency nor a closed carbon balance can be derived from the present measurements. The measured carbon dioxide, carbon monoxide, and UHC concentrations are therefore used to assess qualitative trends in exhaust gas composition and combustion completeness rather than absolute conversion values. The present reactor-scale measurements also do not allow the experimental determination of the oxygen-release capacity, oxygen-utilization efficiency, cycle-specific $\Delta\delta$, mass-specific oxygen-

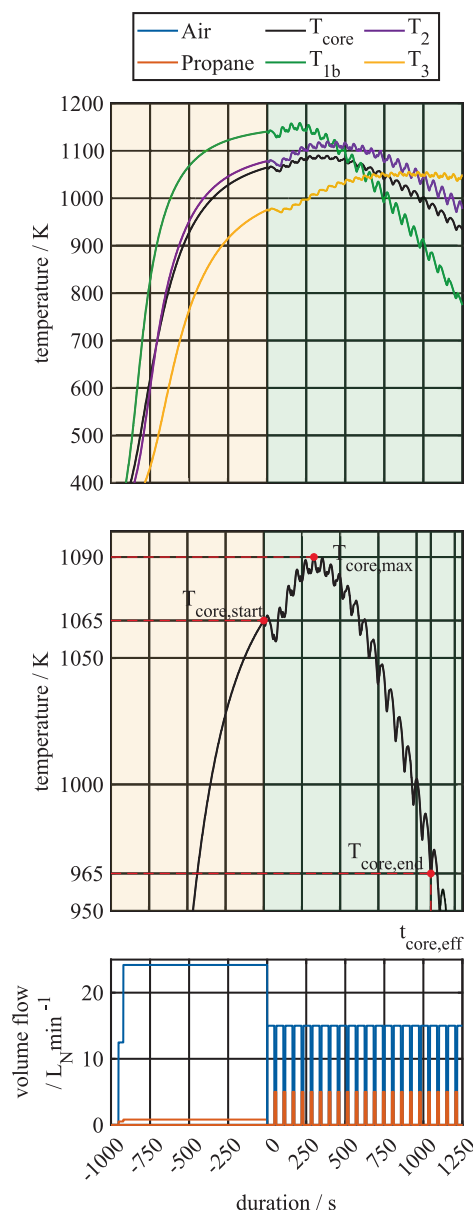


Fig. 2. Measured temperature evolution of test U1 (see Table 2) during heat-up phase (top, yellow highlighted) and cyclic operation (top, green highlighted). Detail view of temperature evolution of T_{core} with characteristic temperature points (middle). Recorded volume flows (bottom) during the heat-up phase and the cyclic operation with the charging phase (air, blue) and the discharging phase (propane, orange). Temperature measurement uncertainty is approximately ± 8 K at 1000 K. Accuracy of the MFCs is $\pm 0.5\%$ of the measured value.

uncoupling rates, or intrinsic oxygen-transport kinetics. During discharging, the measured outlet oxygen concentration represents the combined effects of oxygen release from the OSM, oxygen consumption by the fuel, and the displacement and mixing of residual gas during phase switching. Determination of the gross oxygen-release rate would additionally require the time-dependent total exhaust gas flow rate and a complete product balance. Furthermore, the sampling rate and transport delay of the exhaust gas analysis are insufficient to resolve the rapid oxygen-release dynamics during the short discharging phases. For the same reason, a phase-resolved net heat release could not be quantified. Such a calculation would require a transient energy balance including the inlet and outlet enthalpy flows, heat storage within the OSM packed bed and reactor components, and heat losses through the reactor wall and exhaust gas. Accordingly, the measured temperature

evolution, effective test duration, and outlet-gas concentrations are used as comparative indicators within the qualitative proof-of-concept framework rather than as measurements of quantitative reactor performance, fuel and oxygen conversion, or net heat release.

Measurement uncertainties were considered for all quantitatively evaluated signals in this study. For the TCs, the uncertainty results from both the TC tolerance and the data logger uncertainty, yielding a combined uncertainty of about ± 8 K at 1000 K. The resulting uncertainty of ΔT_{core} was estimated using root-sum-square (RSS) propagation, yielding an uncertainty of approximately ± 11 K. The oxygen concentration was measured with an accuracy of ± 0.1 vol.% after calibration. The uncertainty of the FTIR-based carbon dioxide measurement is estimated to be approximately ± 0.2 vol.% over the investigated concentration range. For carbon monoxide concentrations up to 1500 ppm, the uncertainty of the FTIR measurements is estimated to be approximately ± 50 ppm. UHC and NO_x measurements are evaluated qualitatively and are therefore reported without a separate uncertainty analysis.

2.3. Experimental procedure

To achieve sufficiently high oxygen exchange rates for sustained cyclic operation, temperatures above approximately 850 K are required (see Section 2.1). Therefore, a heat-up phase (see Fig. 2, top and middle, yellow highlighted area) is performed at the beginning of a test. During this phase, the McKenna burner located beneath the packed bed is operated to heat up the OSMs uniformly to the desired starting temperature.

The thermal power of the burner (set via volume flow rate $V_{\text{heat-up}}$ and $\lambda_{\text{heat-up}}$) and the duration of the heat-up phase $t_{\text{heat-up}}$ determine the starting temperature T_{start} at which the burner is shut off and cyclic operation is initiated. In the tests analyzed here (see Tables 1 and 2), the duration of the heat-up phase is 15 min or 30 min depending on the fuel in order to reach steady temperature conditions in the reactor.

Since the equilibrium oxygen content of the OSM decreases when the oxygen partial pressure falls below that of ambient air ($p_{\text{air}} = 21$ kPa, see Section 2.1), partial discharge of the OSMs is expected to occur during the heat-up phase. This is attributed to the reduced oxygen concentration in the burner exhaust gas stream and is indicated by the temperature increase (during oxygen incorporation) observed during the first charging phase at the beginning of cyclic operation (see Figs. 2 and 3). In order to limit unintended oxygen release and reduction of the OSMs during preheating, the heat-up phase is kept as short as practicable and under lean to stoichiometric conditions with $\lambda_{\text{heat-up}}$ ranging from 1.0 to 1.25. However, the temperature increase is small compared to the increases following a discharge phase. The impact of $\lambda_{\text{heat-up}}$ on the subsequent cyclic operation was generally minor (not shown here). A longer heat-up phase, however, resulted in a higher core starting temperature $T_{\text{core,start}}$ and thereby increased the effective test duration. To achieve the required starting temperature, the total volume flow rate of the burner $V_{\text{heat-up}}$ is varied between $15 \text{ L}_N \text{ min}^{-1}$ and $30 \text{ L}_N \text{ min}^{-1}$.

The heat-up phase is followed by cyclic operation (see Fig. 2, top and middle, green highlighted area) during which the OSM packed bed is alternately exposed to an oxidizer flow (air, charging phase) and a fuel flow (propane or methane, discharging phase). The sequence may be initiated with either phase. A complete cycle consists of one charging phase followed by one discharging phase. No inert purge is applied between the phases; instead, the incoming gas directly displaces the atmosphere remaining from the preceding phase.

Cyclic operation is strongly affected by the four cyclic parameters. These include the durations of the charging and discharging phases (t_{air} and t_{fuel} , in seconds) and the corresponding volume flow rates (V_{air} and V_{fuel} , in normal liters per minute $\text{L}_N \text{ min}^{-1}$, referenced to 273.15 K and 1013.25 hPa). The gas supply is controlled automatically according to the specified volume flow rates and phase durations. The parameters of the test series considered in this study are listed in Tables 1 and 2.

The charging phase durations vary between 15 s and 175 s depending

Table 1

Operation parameters of test series A–F for investigating the impact of the starting temperature.

Test	Fuel type	Heat-up phase				Cyclic operation					
						Air charging phase		Fuel discharging phase		λ_{cycle}	
		$t_{\text{heat-up}}$ (min)	$V_{\text{heat-up}}$ (L _N min ^{−1})	$\lambda_{\text{heat-up}}$	$T_{\text{core,start}}$ (K)	t_{air} (s)	V_{air} (L _N min ^{−1})	t_{fuel} (s)	V_{fuel} (L _N min ^{−1})		
A1	Propane	15	23	1.25	1059.2	15	20	10	1.0	1.26	
A2			25		1101.9						
A3			27		1136.6						
A4			29		1174.9						
A5			31		1204.3						
B1			23		1045.5				1.3	0.97	
B2			25		1084.5						
B3			27		1116.3						
B4			29		1158.3						
B5			31		1190.6						
C1			23		1030.7				1.8		
C2			25		1071.9						
C3			27		1101.2						
C4			29		1142.3						
C5			31		1174.5						
D1			23		1042.9				2.3	0.55	
D2			25		1084.1						
D3			27		1123.6						
D4			29		1157.9						
D5			31		1197.7						
E1	Methane	30	15	1.1	909.3	15	15	10	2.0	1.18	
E2			17		961.8						
E3			19		1008.0						
E4			20		1053.2						
F1			15	1.1	898.7				2.4		
F2			17		955.0						
F3			19		1003.5						
F4			20		1050.6						

Table 2Operation parameters of test series U–Z for investigating the impact of the cyclic relative air-fuel ratio λ_{cycle} .

Test	Fuel type	Heat-up phase				Cyclic operation				
						Air charging phase		Fuel discharging phase		λ_{cycle}
		$t_{\text{heat-up}}$ (min)	$V_{\text{heat-up}}$ (L _N min ^{−1})	$\lambda_{\text{heat-up}}$	$T_{\text{core,start}}$ (K)	t_{air} (s)	V_{air} (L _N min ^{−1})	t_{fuel} (s)	V_{fuel} (L _N min ^{−1})	
U1	Propane	15	25	1.25	1064.8	45	15	12	5.0	0.47
U2					1067.9			8		0.71
U3					1066.3			6		0.95
U4					1069.5			4		1.42
V1					1074.9	60		17		0.44
V2					1083.7			10		0.76
V3					1088.8			7		1.08
V4					1087.9			6		1.26
W1	Methane				1098.7	70		30	3.0	0.49
W2					1107.5	115				0.81
W3					1090.6	145				1.02
W4					1088.4	175				1.23
X1					1094.9	15		10	2.4	0.39
X2					1080.1				2.0	0.47
X3					1099.1				2.0	0.47
X4					1073.2				1.6	0.59
X5					1075.8				1.2	0.79
X6					1086.0				1.0	0.95
X7					1069.2				0.75	1.26
X8					1082.7				0.5	1.89
Y1					1075.9	45	15	30	5.0	0.47
Y2					1065.0			20		0.71
Y3					1071.5			15		0.95
Y4					1072.3			11		1.29
Z1					1075.9	60		40		0.47
Z2					1079.3			25		0.76
Z3					1080.8			20		0.95
Z4					1077.4			15		1.26

on the fuel and the flow rates. The shorter phase durations are comparable to tests conducted with simple metal oxides (oxygen carriers) [12]. In contrast, cycle durations reported in previous packed bed studies typically range from approximately 10 min to 50 min [10,11,17]. The

discharging phases, on the other hand, have considerably shorter durations between 6 s and 40 s. This results in total cycle durations between 25 s and 205 s. The present tests therefore investigate a more dynamic operating regime, including total cycle durations below one

minute.

The relationship between the air supplied during the charging phase and the fuel supplied during the discharging phase is characterized by the cyclic relative air-fuel ratio (λ_{cycle}). Higher values of λ_{cycle} correspond to a larger relative amount of air supplied per cycle. The cycle-specific stoichiometric oxygen demand was calculated from the normalized fuel volume flow rate and discharging duration using oxygen-fuel ratios of 5 mol O₂ per mol propane and 2 mol O₂ per mol methane. The resulting molar and mass-based oxygen demands for all investigated operating conditions are reported in Table S1 in the Supplementary Material, together with an example calculation of λ_{cycle} .

The calculated stoichiometric oxygen demand must be distinguished from the oxygen actually released and consumed during cyclic operation. The demand-to-capacity ratios in Table S1 are theoretical reference values calculated from the inlet-based stoichiometric oxygen demand and the assumed changes in oxygen non-stoichiometry of $\Delta\delta = 0.2$ and $\Delta\delta = 0.7$. They do not represent experimentally determined oxygen release, oxygen-utilization efficiency, actual OSM conversion, or cycle-specific $\Delta\delta$. The parameter λ_{cycle} is likewise an inlet-based stoichiometric comparison parameter rather than an experimental measure of oxygen utilization.

For the fuel comparison, λ_{cycle} was selected as the primary normalization parameter because it relates the oxygen supplied during the charging phase to the stoichiometric oxygen demand of the fuel supplied during discharging. Complete combustion requires 5 mol O₂ per mole of propane and 2 mol O₂ per mole of methane. Consequently, when identical air and fuel volume flow rates and an identical charging duration are applied, the methane discharging phase must be 2.5 times as long as the propane discharging phase to obtain the same λ_{cycle} . The comparison at equal λ_{cycle} therefore represents an equal ratio of the cycle-integrated oxygen supplied with air to the fuel-specific stoichiometric oxygen demand, but not identical absolute phase durations, molar fuel inputs, or instantaneous nominal thermal input rates.

An example of cyclic operation together with the corresponding volume-flow profiles over time is presented in Fig. 2 (bottom). The illustrated operating condition starts with a 45 s charging phase (15 L_N min⁻¹) followed by a 12 s discharging phase (5 L_N min⁻¹).

Depending on the selected parameters, both phases may lead to a temperature increase, resulting in a maximum core temperature $T_{\text{core,max}}$. The corresponding temperature increase is defined as

$$\Delta T_{\text{core}} = T_{\text{core,max}} - T_{\text{core,start}} \quad (2)$$

For a consistent comparison of the tests, the temperature-based effective test duration t_{eff} was defined as the time from the beginning of cyclic operation until the core temperature had decreased by 100 K relative to its initial value. This relative threshold represents an empirical operational criterion rather than a material-specific physical limit. A sustained temperature decrease of this magnitude indicates that the positive thermal response during cyclic operation is no longer sufficient to compensate for heat losses and cooling by the incoming gases.

The criterion was selected based on preliminary tests in which the cyclic operating parameters were adjusted after the onset of a temperature decrease. At comparatively high packed bed temperatures, such adjustments could still produce a limited stabilizing effect. After a pronounced temperature decrease, however, the resulting thermal response was insufficient to restore the previous packed bed temperature level. A smaller threshold would have caused some tests to be terminated before a representative number of cycles had been evaluated, whereas a larger threshold would have prolonged operation after a pronounced and practically irreversible decrease in the packed bed temperature that could not be reversed by the tested parameter adjustments.

The same relative temperature criterion was applied to all tests to enable comparison between different initial temperatures and cyclic parameters. An absolute threshold based on the approximate minimum operating temperature of 850 K was not used because it would provide

different allowable temperature decreases for tests starting at different temperatures and would therefore bias the comparison. The effective test duration should consequently be interpreted as a comparative measure of the duration over which the packed bed temperature can be maintained under the investigated conditions and not as a direct measure of oxygen release, oxygen-utilization efficiency, OSM conversion, cycle-specific $\Delta\delta$, or fuel conversion.

3. Results

As shown in Fig. 2, cyclic charging and discharging of the OSMs begin once the desired starting temperature has been reached. The alternating flow of air and propane through the packed bed results in corresponding variations of the measured temperatures. To investigate the fundamental effects of cyclic operation, Fig. 3 (top) presents a detailed view of the temperature evolution observed during the initial cycles.

Consistent with the qualitative proof-of-concept scope of this study, the following discussion uses the measured temperature responses and outlet-gas concentrations as comparative indicators and distinguishes the experimental observations from mechanistic interpretations of the

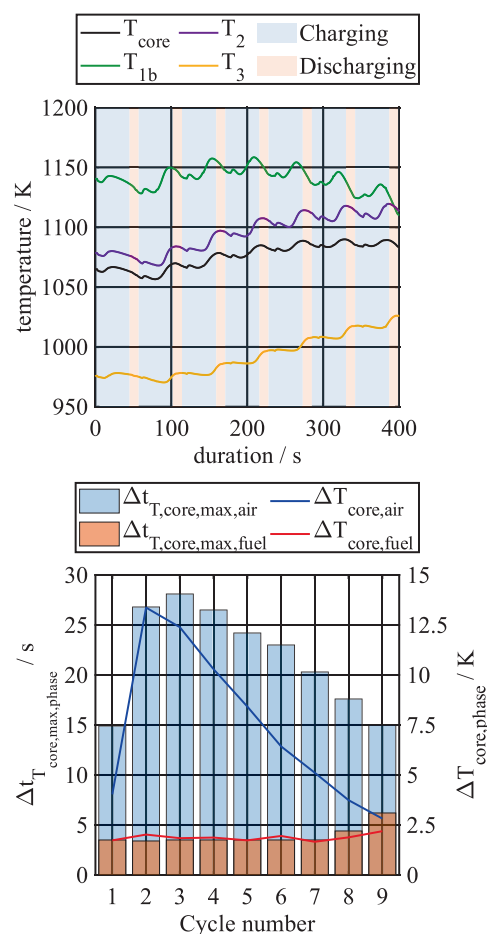


Fig. 3. Detailed view of the measured temperature evolution inside the CSFM packed bed during cyclic operation of test U1 (top view). The bars (bottom view) show the time to reach the maximum core temperature $\Delta t_{T_{\text{core,max,phase}}}$ of the charging (blue bars) and discharging (orange bars) phase during first cycles 1–9. The curves show the maximum temperature increase $\Delta T_{\text{core,phase}}$ per cycle of the charging (blue curve) and discharging (red curve) phase. The $\Delta T_{\text{core,phase}}$ and $\Delta t_{T_{\text{core,max,phase}}}$ are derived from temperature measurements with an uncertainty of approximately ± 8 K at 1000 K resulting in an estimated uncertainty of about ± 11 K. Error bars are omitted for clarity; the overall trends remain clearly identifiable.

local OSM behavior.

In general, the temperature profiles reflect the axial positions of the thermocouples. Initially, the temperature in the lower part of the packed bed is higher. Due to the rapid response of the packed bed to the alternating flow, pronounced temperature fluctuations and a rapid increase to a maximum temperature are observed in this region. In the upper part (TC₃) the temperature increases more slowly and over a longer period of time. As a result, the two phases of charging and discharging are hardly noticeable in the region of TC₃. This behavior is consistent with the propagation of a temperature front through the packed bed from the lower to the upper reactor regions. The upper OSM layers are progressively heated by the hot gas flowing through the bed, which is expected to accelerate local oxygen exchange and contribute to the delayed temperature response observed in the upper region.

In Fig. 3, cyclic operation starts with a charging phase of 45 s, followed by a discharging phase of 12 s (see Table 2, test U1). During both phases (especially in the lower part of the packed bed, e.g. at TC_{1b}), the temperature increase occurs only after a time delay (up to 5 s). In addition to the finite switching time between charging and discharging phases, this behavior is interpreted as resulting from the different timescales of gas displacement, chemical reactions, and heat transfer within the packed bed. Following a local change in gas composition, oxygen exchange and fuel combustion during discharging may begin before the associated temperature response becomes detectable because heat must first be transferred within the bed. The observed delay therefore reflects coupled transport, reaction, and thermal processes and cannot be used to determine the intrinsic oxygen storage and release kinetics. Such a delayed temperature response is consistent with existing observations in the literature [14].

To assess the extent to which gas remaining in the voids of the packed bed after a phase change affects the subsequent cyclic behavior, an additional reference test was performed using BaTiO₃ mini-honeycombs without relevant reversible oxygen-storage functionality under the investigated conditions. The reference honeycombs had the same 3 × 3 channel geometry as the CSFM mini-honeycombs and were packed to the same bed height in the reactor. The test was conducted using alternating air and methane phases corresponding to the charging and discharging phases of the OSM test. The air phase lasted 15 s at a volume flow rate of 15 L_N min⁻¹, while the methane phase lasted 10 s at 5 L_N min⁻¹. The resulting temperature profiles and exhaust gas concentrations are shown in Fig. 4.

Throughout cyclic operation, both measured packed bed temperatures showed an overall decrease, indicating that the thermal response was insufficient to compensate for heat losses and cooling by the incoming gases in the BaTiO₃ reference bed. Only minor temperature fluctuations were observed during the first three cycles. These fluctuations were comparable to the measurement uncertainty and substantially smaller than the temperature increases observed in the CSFM tests. They therefore cannot be assigned unambiguously but may be associated with transient reactions caused by the direct contact between gas remaining in the voids and the gas introduced during the subsequent phase.

The initially elevated carbon dioxide concentration decreased rapidly as residual exhaust gas from the preceding heat-up phase was displaced from the reactor and sampling system. During the subsequent cycles, the carbon dioxide and carbon monoxide concentrations remained low and exhibited only minor fluctuations, without progressively increasing or consistently recurring carbon dioxide peaks. These observations indicate that gas displacement and short-term mixing between residual and incoming gases occur during phase switching. Under the investigated reference conditions, these effects had only a minor influence on the overall temperature evolution and exhaust gas composition compared with the cyclic behavior observed for the CSFM packed bed. The reference test therefore provides a qualitative estimate of the impact of the void gas volume during direct switching between the air and fuel phases. Because methane and a specific set of cyclic

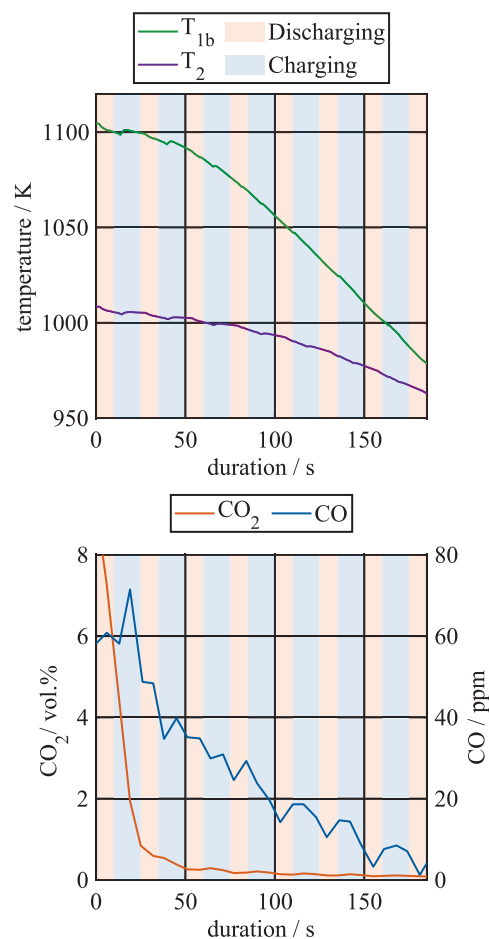


Fig. 4. Local packed bed temperatures T_{1b} and T_2 (top) and corresponding carbon dioxide and carbon monoxide concentrations measured at the reactor outlet (bottom) during cyclic operation of the BaTiO₃ reference bed. The BaTiO₃ honeycombs had the same 3 × 3 channel geometry and packed bed height as the CSFM honeycombs but no reversible oxygen-storage functionality under the investigated conditions. Charging phases were operated for 15 s at 15 L_N min⁻¹, and discharging (methane) phases for 10 s at 5 L_N min⁻¹. Measurement uncertainties are approximately ±8 K at 1000 K, ±0.2 vol.% for CO₂, and ±50 ppm for CO. Error bars are omitted for clarity; the overall trends remain clearly identifiable.

parameters were used in the reference test, a transient contribution from direct air–fuel overlap under propane operating conditions cannot be fully excluded. Nevertheless, the reference test suggests that residual-gas displacement and direct gas-phase reactions alone are unlikely to explain the recurring carbon dioxide peaks and pronounced temperature responses observed for the CSFM packed bed.

For a future application involving carbon capture, the exhaust streams from the charging and discharging phases would have to be collected separately, while gas mixing during phase switching and within the reactor void volume should be minimized.

Since partial discharge of the OSMs is expected to occur during the heat-up phase (see Section 2.3), a temperature increase is observed during the first charging phase. This behavior is consistent with the exothermic storage of oxygen and has also been reported for several oxygen carriers, including CuO, NiO, and FeTiO₃ [10,17,22,23]. A positive temperature response is also observed during the subsequent discharge phase and is attributed primarily to oxy-fuel combustion. As with the OCs studied in the literature, oxygen release from the CSFM OSM is endothermic. However, the observed temperature increase indicates that combustion was sufficient to produce a positive thermal response despite the endothermic oxygen release and other heat losses.

Although the temperature increase during discharge is smaller than during charging, it still contributes to the overall thermal response. This behavior differs from several previous packed bed studies employing conventional oxygen carriers, where the reduction phase was often associated with a temperature decrease [17,21]. The larger temperature increases during charging after the first cycle are consistent with a greater extent of oxygen release during the preceding discharging phase than during the heat-up phase (see also Fig. 3, bottom). However, these temperature profiles do not allow the degree of OSM discharge to be quantified because neither the local values of δ nor a phase-resolved energy balance were determined.

After initially increasing to a maximum, the measured temperatures decrease in all parts of the packed bed. This decrease is partly attributed to the supply of gases at room temperature. Especially at higher volume flow rates, convective cooling of the OSM mini-honeycombs by inflowing cold gas occurs in the lower part of the packed bed. Heat losses to the reactor surroundings and thermal energy carried away by the exhaust gas flow also contribute to this. In addition, the selected cyclic operating parameters may contribute to the temperature decrease. As discussed below, excessively long charging or discharging phases can weaken the positive temperature response and thereby accelerate cooling of the packed bed.

Fig. 3 (bottom) shows that the charging phase is longer than required to reach the maximum core temperature under the investigated operating conditions. The phase duration t_{air} set for this test was 45 s. However, the maximum core temperature $T_{\text{core,max}}$ is already reached between 15 s and 30 s in the first nine cycles. The cessation of the temperature increase is consistent with a decreasing rate of exothermic oxygen storage as the OSM approaches a more highly charged state. However, the temperature profiles alone do not demonstrate complete charging or the absence of further oxygen storage during the remaining charging period. During this period, the decreasing exothermic contribution may no longer compensate for cooling by the incoming air and other heat losses, resulting in a temperature decrease. The resulting temperature decrease may slow the oxygen exchange rate and consequently weaken the positive thermal response in subsequent cycles. This feedback may contribute to a gradual cooling of the packed bed and promote unstable cyclic operation.

During the discharging phase, the time required to reach the maximum temperature is approximately 3.5 s, which is considerably shorter than the specified phase duration of 12 s. However, during the first nine cycles, both the time required to reach the maximum temperature ($\Delta t_{T,\text{core,max,phase}}$) and the corresponding temperature increase ($\Delta T_{\text{core,phase}}$) remain relatively consistent. This suggests that the selected discharge duration t_{fuel} is better matched to the observed temperature response than the charging duration discussed above. Nevertheless, oxygen release may continue after the maximum temperature has been reached. In contrast to the charging phase, the temperature response during discharge is influenced by both the endothermic oxygen release and the exothermic combustion process. Consequently, the point of maximum temperature does not necessarily coincide with the end of oxygen release.

The cyclic operation with alternating air and propane flows results in corresponding fluctuations of the measured oxygen and carbon dioxide concentrations (see Fig. 5). During the first charging phase, the oxygen concentration at the reactor outlet increases toward the air inlet value of approximately 20.9 vol.%. Together with the temperature increase during this phase, this behavior is consistent with partial discharge during the preceding heat-up phase and subsequent oxygen storage during charging.

The oxygen concentration at the reactor outlet qualitatively reflects the combined effects of gas displacement, oxygen storage and release, and fuel combustion. Following the gas switch, the remaining exhaust gas from the preceding discharge phase is rapidly displaced from the reactor by the comparatively high air flow rate, resulting in a steep increase in oxygen concentration. After this initial displacement, oxygen

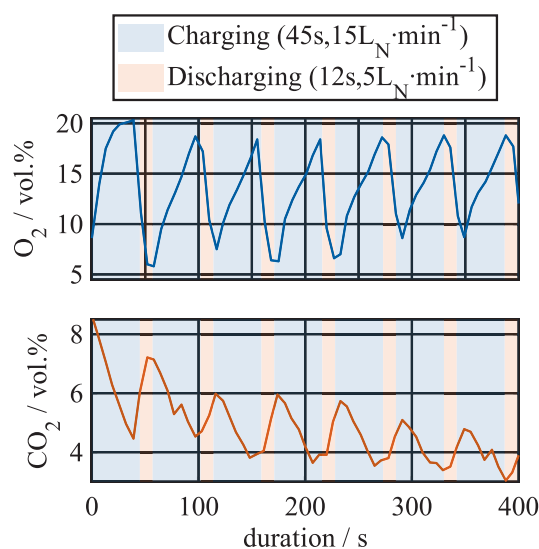


Fig. 5. Detailed view of the measured oxygen (top view) and carbon dioxide (bottom view) concentrations at the outlet of the reactor bed during cyclic operation of test U1 (propane). The estimated measurement uncertainties (± 0.1 vol.% O₂ and ± 0.2 vol.% CO₂) are small compared to the observed trends; error bars are omitted for clarity.

storage within the packed bed reduces the outlet concentration relative to the inlet concentration. As the net oxygen storage rate decreases, the outlet concentration gradually approaches the inlet value. The progressively higher oxygen concentrations observed at the end of successive charging phases are consistent with the decreasing packed bed temperature (see Fig. 3), which may slow the oxygen exchange rate and consequently reduce the extent of oxygen release and subsequent storage during each cycle. A low oxygen concentration at the end of the charging phase indicates that net oxygen removal from the gas stream is still occurring and suggests that the charging duration may be insufficient for the OSM to approach a highly charged state. Conversely, elevated oxygen concentrations persisting beyond the initial gas-displacement transient during the discharge phase indicate that the available oxygen is not fully consumed by combustion. Because this signal may include both released lattice oxygen and residual air and may also be affected by gas mixing and reaction kinetics, it does not by itself demonstrate an insufficient fuel flow rate.

The carbon dioxide concentration (Fig. 5, bottom) generally exhibits a trend opposite to that of oxygen concentration and increases primarily during the discharge phase as a result of oxy-fuel combustion. The measured profiles further illustrate the limited temporal resolution of the exhaust gas analysis system. Due to an approximately 2 m sampling line and the associated gas residence time, the concentration signals are delayed and appear smoother than the corresponding temperature profiles. Additional mixing of gases within the sampling system during phase switching further contributes to the comparatively gradual transitions between charging and discharging phases.

Despite the delay and smoothing introduced by the exhaust gas analysis system, distinct increases in the carbon dioxide concentration are observed after switching from propane discharge to the subsequent air-charging phase (Fig. 5, bottom). As discussed above, the BaTiO₃ reference test shows only minor signals attributable to gas remaining in the voids under the investigated reference conditions and suggests that residual gas alone is unlikely to explain the recurring carbon dioxide increases (Fig. 4). The observed carbon dioxide increases are therefore consistent with the temporary formation of carbonaceous deposits during propane discharge and their subsequent oxidation during air charging. This interpretation is further supported by an additional propane test with different cyclic parameters, which exhibits comparable carbon dioxide increases during the charging phases (Fig. S1). In

contrast, no corresponding effect is evident during methane operation shown in the same figure. Taken together, these observations support temporary carbon deposition as a plausible interpretation during propane operation but do not provide direct proof of solid carbon formation. The amount of potentially deposited carbon cannot be quantified from the available measurements.

Overall, this test shows that the selected phase durations have a strong impact on the ability to maintain the packed-bed temperature during cyclic operation. In this case, the charging and discharging phase durations are comparatively short, particularly when compared with values reported in the literature. These comparatively short charging and discharging phases may be partly related to the small packed bed volume and OSM inventory, which enable rapid displacement of the gas atmosphere and result in high gas flow rates relative to the OSM mass. However, the short phase durations do not provide direct evidence that the CSFM material exhibits faster intrinsic oxygen storage or release kinetics than the materials used in larger systems.

Consequently, the following sections examine the impact of the starting temperature $T_{\text{core,start}}$ and variations in the cyclic relative air-fuel ratio (λ_{cycle}). In addition, the influence of fuel type is assessed through a comparison of propane and methane operation.

Independent of the chosen parameters, elevated UHC concentrations were observed during cyclic operation, indicating incomplete fuel conversion. Because the UHC measurements were evaluated qualitatively, no quantitative fuel conversion value can be reported. A major limitation of the present reactor configuration is the packed bed height of approximately 90 mm, which provides only a short reaction zone and gas residence time. In addition, the inhomogeneous initial temperature distribution means that only part of the OSM may be sufficiently hot to release oxygen at practically relevant rates. Cooling by the unheated inlet gases, heat losses through the reactor wall, and thermal energy carried away by the exhaust gas further reduce the bed temperature and progressively slow oxygen exchange. These limitations are particularly relevant for propane: at an identical molar fuel flow, its complete combustion requires 2.5 times as much oxygen as methane. Rapid consumption of the released oxygen in the lower bed regions may therefore produce locally oxygen-deficient conditions and allow unconverted fuel and partially oxidized intermediates to leave the short packed bed. Temporary formation of carbonaceous deposits under such conditions may additionally divert part of the supplied carbon from the exhaust gas during the discharging phase. In contrast, NO_x concentrations remained low throughout all tests.

The results were reproducible across repeated tests (see [Supplementary Material, Figs. S2, S3, and S4](#)), exhibiting highly consistent temperature profiles ($\sigma_{T,\text{RMS,rel}} = 0.5\%$) and repeatable exhaust gas measurements ($\sigma_{\text{O}_2,\text{RMS,rel}} = 3.0\%$ and $\sigma_{\text{CO}_2,\text{RMS,rel}} = 23.6\%$) under identical operating conditions. The comparatively larger relative deviation of the carbon dioxide concentration is likely related to the low sampling rate relative to the short cycle duration, because small temporal shifts between the delayed and smoothed carbon dioxide profiles strongly affect the calculated RMS deviation. The repeatability of the measurements supports the robustness of the reported comparative trends but does not enable the concentration signals to be converted into quantitative species flows, conversion efficiencies, or oxygen-release metrics.

3.1. Impact of starting temperature

This section examines the impact of the starting temperature on the coupled oxygen-exchange, combustion, and thermal behavior of the packed bed. Although increasing temperature is expected to accelerate oxygen storage and release, this does not necessarily result in a longer effective test duration because oxygen release, fuel oxidation, heat transfer, and possible carbon deposition occur simultaneously and may be distributed non-uniformly within the packed bed. For this purpose, the heat-up phase was varied to achieve the highest possible starting

temperatures. The maximum attainable starting temperature was constrained by the flame length of the McKenna burner. The burner volume flow rate $V_{\text{heat-up}}$ could only be increased until the flame length approached the burner-to-bed distance of approximately 40 mm. Further increases could cause the flame to extend into the packed bed and potentially damage the lower OSM layers. Because the premixed laminar methane flames in the present setup were longer than comparable propane flames, the maximum achievable starting temperatures were lower in the methane tests. The burner-to-bed distance was kept constant to maintain the same geometric configuration across all tests.

A total of four test series were carried out for propane (see [Table 1, A–D](#)) and two test series for methane (E–F). Each test series comprised five (propane) or four (methane) tests in which the starting temperature was gradually increased. Within each test series, the cyclic parameters were kept constant while the starting temperature was varied. The test series differ in the cyclic relative air-fuel ratio (λ_{cycle}), allowing the impact of temperature to be investigated at different fuel volume flow rates (V_{fuel}).

3.1.1. Propane

In general, based solely on the temperature dependence of oxygen exchange, a higher starting temperature would be expected to promote oxygen release and combustion. However, whether this results in a longer effective test duration also depends on the spatial and temporal overlap between fuel, released oxygen, and sufficiently hot OSM regions. The local oxygen partial pressure and oxygen non-stoichiometry δ were not measured within the packed bed. The mechanisms discussed below are therefore interpretations derived from the temperature profiles, outlet-gas concentrations, and reference tests rather than direct measurements of local OSM reduction.

However, contrary to the hypothesis outlined above, the effective test duration observed in the propane test series A–D ([Fig. 6, top](#)) decreases approximately linearly with increasing starting temperature, across the selected cyclic relative air-fuel ratio values.

This behavior may reflect the combined effects of temperature-accelerated, spatially non-uniform oxygen release and the possible formation of temporary carbonaceous deposits under potentially oxygen-deficient local conditions.

Carbonaceous deposits may contribute to the decreasing effective test duration as well. As discussed above, recurring charging-phase carbon dioxide increases during propane operation ([Figs. 5 and S1](#)) are consistent with the oxidation of carbon-containing species formed during the preceding propane phase. The absence of a corresponding effect during methane operation ([Fig. S1](#)) and the minor cyclic carbon dioxide response of the BaTiO_3 reference bed ([Fig. 4](#)) suggest that residual-gas displacement and direct gas-phase reactions alone are unlikely to explain these signals.

These observations support temporary carbon deposition as a plausible interpretation but do not provide direct proof of solid carbon formation. The absence of visible soot or fuel residues after the tests does not exclude this mechanism because temporarily deposited carbon may be oxidized during each subsequent air phase. Conversely, the available data do not allow the amount of deposited carbon or its contribution to the decreasing effective test duration to be quantified.

A possible complementary explanation is temperature-accelerated and spatially non-uniform oxygen release within the packed bed. The lower bed regions are initially hotter than the upper regions and are exposed to the fuel first. Consumption of the available oxygen by propane combustion is expected to decrease the local oxygen partial pressure and thereby promote further oxygen release from the CSFM. This effect may be more pronounced for propane than for methane (see [Section 3.1.2](#)), which may contribute to the different temperature trends observed for the two fuels. Because complete propane combustion requires 5 moles of O_2 per mole of fuel, compared with 2 moles of O_2 for methane, propane imposes 2.5 times the stoichiometric oxygen demand at an identical molar fuel flow rate. Rapid oxygen consumption in the

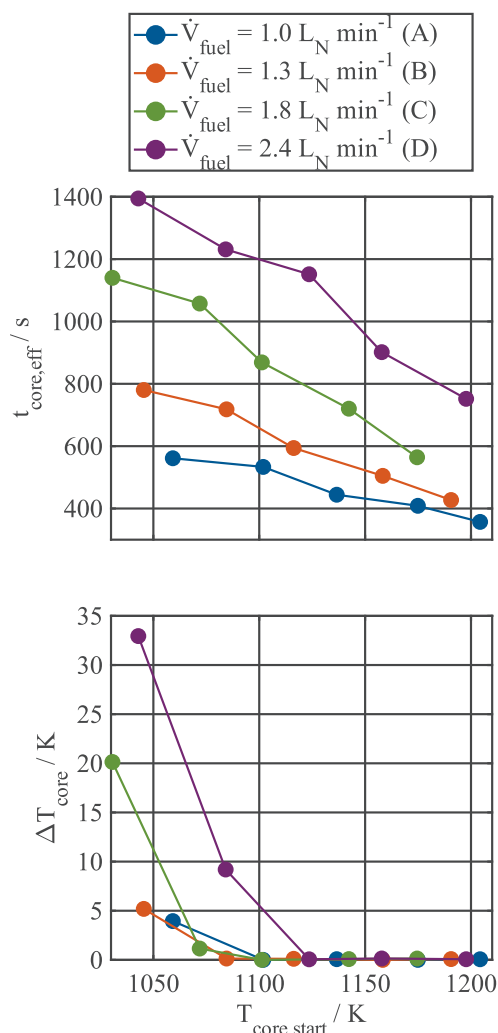


Fig. 6. Impact of starting temperature on the effective test duration (top) and the temperature increase during cyclic operation (bottom). Shown are the test series A–D (propane) as specified in Table 1. The ΔT_{core} is derived from temperature measurements with an uncertainty of approx. $\pm 8 \text{ K}$, at 1000 K (applicable to $t_{\text{core,eff}}$ and $T_{\text{core,start}}$) resulting in an estimated uncertainty of about $\pm 11 \text{ K}$. Error bars are omitted for clarity; the overall trends remain clearly identifiable.

hotter lower bed regions may therefore maintain a strong driving force for further oxygen release and lead to a greater local extent of OSM reduction in these regions.

The hot combustion products subsequently enter the upper bed regions, transfer heat to these regions, and reduce the local oxygen partial pressure through dilution, potentially promoting oxygen release even where little fuel is initially available for direct combustion. As the local oxygen availability in the lower regions decreases, local combustion and the associated heat release may decline, while a larger fraction of the unconverted fuel reaches the upper regions. However, these upper regions may already have released part of their available oxygen and remain cooler than the lower bed region. Increasing the starting temperature is expected to accelerate these coupled processes and may therefore cause the spatial and temporal overlap between fuel, released oxygen, and sufficiently hot OSM regions to deteriorate earlier, resulting in a shorter effective test duration.

This mechanistic interpretation is consistent with the measured axial temperature differences and exhaust gas trends but cannot be verified directly because neither local oxygen partial-pressure profiles nor spatially resolved values of δ were measured. It should therefore not be

interpreted as evidence that a specific degree of discharge or δ value was reached.

Accordingly, operation at higher starting temperatures may require shorter discharge durations because oxygen exchange is expected to accelerate with temperature. Such an adjustment may help to limit spatially non-uniform oxygen depletion and locally oxygen-deficient propane conditions. At the same time, the fuel volume flow rate may be increased within a suitable range to promote fuel penetration into the upper regions of the packed bed. This may promote fuel oxidation and a positive temperature response in the upper OSM layers, where the released oxygen can react directly with the fuel. Consequently, a larger fraction of the packed bed may contribute to the overall thermal response. A more spatially distributed combustion process may also reduce the local conditions promoting incomplete oxidation and temporary carbon deposition. Under such conditions, higher carbon dioxide concentrations and lower residual oxygen concentrations in the exhaust gas may be expected. In addition, high residual oxygen concentrations after the initial gas-displacement transient may suggest that the charging duration could be reduced. However, the outlet oxygen concentration alone does not demonstrate that sufficient oxygen storage has been achieved throughout the packed bed. The overall objective of these parameter adjustments is to reduce the oxygen concentration while increasing the carbon dioxide concentration in the discharge-phase exhaust gas. At the same time, sufficient local oxygen availability should be maintained to promote complete oxidation of intermediate species such as carbon monoxide to carbon dioxide.

The effects of the starting temperature on the exhaust gas composition for the four test series are shown in Fig. 7. Within each of the test series A to D, the burner volume flow rate $\dot{V}_{\text{heat-up}}$ is progressively increased from $23 \text{ L}_\text{N} \text{ min}^{-1}$ to $31 \text{ L}_\text{N} \text{ min}^{-1}$ (see Table 1), allowing the impact of temperature to be assessed.

The average maximum oxygen concentration $\text{O}_{2,\text{max,mean}}$ (Fig. 7, top) decreases with increasing starting temperature and fuel flow rate. Here, $\text{O}_{2,\text{max,mean}}$ represents the average of the maximum oxygen concentrations measured during the charging phases over all cycles within the effective test duration. The same averaging procedure is applied for the maximum carbon dioxide and carbon monoxide concentrations shown in Fig. 7 (middle and bottom) for the discharging phases. The averaged maximum concentrations are used exclusively as descriptive parameters for comparing trends between the investigated operating conditions. Because the time-dependent total exhaust gas flow rate was not measured, these values do not represent phase-integrated species quantities and cannot be interpreted as fuel conversion, oxygen utilization, or carbon dioxide yield.

A reduced maximum oxygen concentration in the exhaust gas during OSM charging suggests that oxygen is removed from the air flowing through the packed bed. This results in an oxygen concentration in the outlet gas below the inlet value of $20.9 \text{ vol.}\%$. The increasing oxygen depletion in the charging gas is qualitatively consistent with more extensive oxygen release during the preceding discharge phase and subsequent storage at higher temperatures. However, oxygen consumption through the oxidation of residual gas or temporarily deposited carbon-containing species may also contribute during charging. Consequently, the outlet concentration alone does not provide the exchanged oxygen amount, the oxygen exchange rate, or the corresponding change in δ . Since the phase durations were kept constant across all tests in the test series A–D, a lower oxygen concentration in the exhaust gas during charging provides a descriptive indication of stronger net oxygen removal at higher temperatures. In addition, the progressively increasing fuel volume flow rate from test series A to D leads to higher packed bed temperatures, which may further enhance oxygen storage by the OSM during the charging phase.

The carbon dioxide concentrations observed during the discharging phase are qualitatively consistent with this interpretation, as they exhibit trends opposite to those observed for the oxygen concentrations during the charging phase. Higher temperatures are expected to

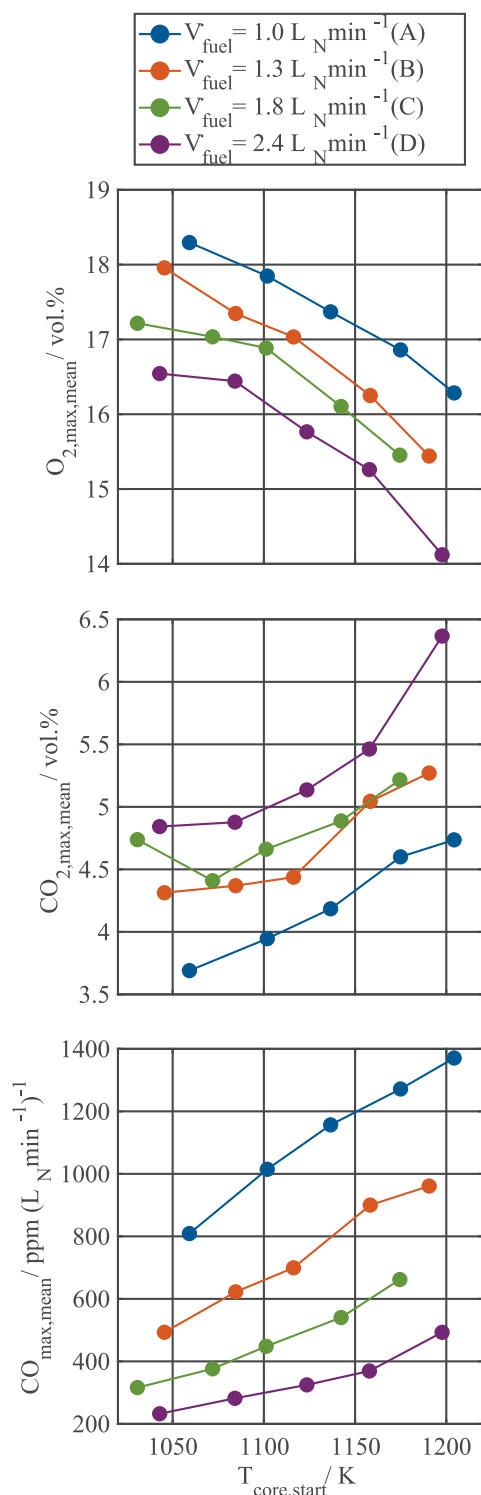


Fig. 7. Effects of the starting temperature: Mean of maxima oxygen concentration in the exhaust gas during charging phase (top), carbon dioxide (middle), and carbon monoxide (bottom) concentrations in the exhaust gas. Analyzed are the test series A–D (propane) as specified in Table 1. The estimated measurement uncertainties (± 0.1 vol.% O_2 , ± 0.2 vol.% CO_2 , and ± 50 ppm CO) are small compared to the observed trends; error bars are omitted for clarity.

accelerate oxygen exchange and may thereby increase the availability of released oxygen for fuel oxidation. The accompanying increase in the measured carbon dioxide concentration is consistent with enhanced fuel oxidation but does not quantify the oxygen release rate or the amount of carbon dioxide formed. Higher carbon dioxide concentrations at

increased fuel volume flow rates may also partly reflect the greater carbon input. Without the total exhaust gas flow rate, they do not provide quantitative measures of carbon dioxide formation or fuel conversion. The simultaneously increasing carbon monoxide concentrations are consistent with increasing limitations in complete oxidation under some of these conditions.

For comparisons involving different fuel volume flow rates, the averaged maximum carbon monoxide concentration was divided by the corresponding fuel volume flow rate. This normalization is used exclusively for descriptive comparison and does not represent a molar carbon monoxide yield or an emission factor because the time-dependent total exhaust gas flow rate was not measured.

The increasing carbon monoxide concentrations observed at higher temperatures suggest that the conditions for complete fuel oxidation become less favorable over the selected discharging duration. This may result from limited local oxygen availability, insufficient gas residence time, or a combination of both effects. Under these conditions, partial oxidation may contribute more strongly, and the subsequent oxidation of carbon monoxide to carbon dioxide becomes increasingly limited. In contrast, higher fuel volume flow rates are associated with lower measured carbon monoxide concentrations. Without the time-dependent outlet flow rate, however, this trend cannot be interpreted as a reduction in the total amount of carbon monoxide formed. A possible explanation is that a larger fraction of the unburned fuel reaches the upper packed bed regions, where additional oxygen may be released and participate in oxidation reactions. This may promote a more spatially distributed thermal response within the packed bed, which in turn may support oxygen exchange throughout a larger fraction of the bed and promote the further oxidation of carbon monoxide to carbon dioxide.

The simultaneous increases in the measured carbon dioxide and carbon monoxide concentrations during discharging and the occurrence of additional carbon dioxide signals during subsequent charging are consistent with a combination of increased propane oxidation, incomplete oxidation under locally oxygen-deficient conditions, and oxidation of temporarily deposited carbon-containing species. The available measurements do not allow the relative contributions of these processes to be quantified. Therefore, neither temporary carbon deposition nor spatially non-uniform OSM reduction can be identified as the sole or dominant cause of the decreasing effective test duration.

3.1.2. Comparison of propane and methane

To compare qualitative fuel-dependent trends in the cyclic operation of the OSM packed bed, tests were also carried out with methane. This subsection examines the impact of the starting temperature during methane operation and compares the observed behavior with the propane results discussed in the previous subsection. The starting temperature study employed identical charging and discharging durations for both fuels, whereas the air and fuel volume flow rates and, consequently, some values of λ_{cycle} differed. Test series B and F provide a comparison at nearly identical values of λ_{cycle} of 0.97 and 0.98, respectively, while test series A and E were conducted at $\lambda_{\text{cycle}} = 1.26$ and 1.18. This comparison therefore illustrates fuel-dependent temperature trends under selected operating conditions but does not isolate the fuel effect from all other operating parameters. Because the starting-temperature test series were not matched in terms of cycle-integrated fuel energy input based on the lower heating value, the observed differences may additionally reflect differences in the nominal thermal input. These test series should therefore not be interpreted as a direct comparison at equivalent fuel-energy input.

There are pronounced differences when using methane instead of propane. Propane has a lower autoignition temperature than methane [28]. In addition, propane exhibits a shorter ignition delay and higher reactivity, even at lower temperatures. These properties may promote earlier propane oxidation and more rapid consumption of released oxygen during the discharge phase, potentially maintaining a lower local

oxygen partial pressure and promoting further oxygen release. However, this does not necessarily imply a larger total oxygen inventory available from the OSM. Consequently, cyclic operating parameters that are suitable for methane operation are not necessarily equally suitable for maintaining the observed thermal response during propane operation, requiring fuel-specific adjustment of the charging and discharging conditions (see also Tables 1 and 2).

Fig. 8 shows (analogous to Fig. 6) the effective test duration (top) and the temperature increase (bottom) as functions of the starting temperature for two different fuel volume flow rates for each fuel.

For each fuel, the starting temperature was varied over the widest attainable range to include higher-temperature conditions under which oxygen exchange is expected to proceed more rapidly. As described in Section 3.1, the flame length during the heat-up phase is longer when methane is used and therefore limits the maximum burner volume flow rate that can be applied without the flame extending into the packed bed. Consequently, the maximum starting temperatures that could be investigated with methane were lower than those achievable with propane.

For methane operation, the effective test duration $t_{\text{core,eff}}$ increases with increasing starting temperature. This behavior may be related to

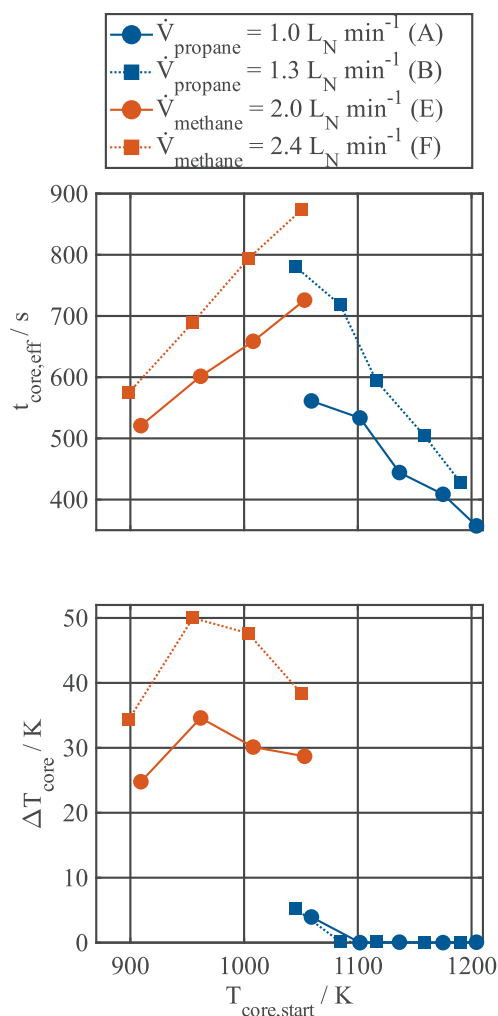


Fig. 8. Impact of starting temperature on the effective test duration (top) and the temperature increase during cyclic operation (bottom). Compared are propane test series A and B (blue lines) and methane test series E and F (orange lines) as specified in Table 1. The ΔT_{core} is derived from temperature measurements with an uncertainty of approx. $\pm 8 \text{ K}$, at 1000 K (applicable to $t_{\text{core,eff}}$ and $T_{\text{core,start}}$) resulting in an estimated uncertainty of about $\pm 11 \text{ K}$. Error bars are omitted for clarity; the overall trends remain clearly identifiable.

the lower reactivity of methane compared with propane. As listed in Table 1, the tests were carried out with identical discharge durations t_{fuel} , regardless of the fuel used. Under these conditions, methane may consume the released oxygen more slowly during the discharge phase. At higher starting temperatures, both methane oxidation and oxygen exchange are expected to be promoted, which may improve the spatial and temporal overlap between methane, released oxygen, and sufficiently hot OSM regions. This may strengthen the positive temperature response in the upper packed bed regions and contribute to the longer effective test durations observed during methane operation. Within the investigated temperature range, methane operation does not exhibit the charging-phase carbon dioxide signals observed for propane or a comparable decrease in effective test duration with increasing starting temperature. Nevertheless, the local oxygen mass and $\Delta \delta$ were not measured for either fuel, and the different behavior cannot be assigned quantitatively to a particular degree of OSM conversion. At sufficiently high temperatures, behavior similar to that observed for propane operation cannot be excluded, potentially resulting in a reduction of the effective test duration. The selected cyclic parameters therefore appear to be better matched to methane operation under the investigated conditions. For propane, the lower-temperature limit below which a further reduction in starting temperature would shorten the effective test duration has not yet been determined.

The observed behavior suggests that the positive temperature response persisted over a greater fraction of the discharging phase during methane operation, which may have promoted a more homogeneous temperature distribution within the packed bed over successive cycles. Consequently, the temperature increase is largely independent of the starting temperature and remains consistently higher than in the propane tests shown in Fig. 8.

Fig. 9 highlights distinct differences in the exhaust gas composition during methane and propane operation.

The averaged maximum oxygen concentrations in the exhaust gas during the charging phases decrease approximately linearly with increasing starting temperature. This behavior is qualitatively consistent with increased oxygen exchange at higher temperatures but does not allow the degree of OSM discharge or $\Delta \delta$ to be determined. The differences between propane and methane may reflect their different oxygen demands, reaction rates, and spatial combustion profiles. At approximately 1050 K , a slight increase in oxygen concentration is observed for propane operation. One possible explanation is that the lower packed bed regions reach a locally more advanced state of reduction before the end of the discharge phase. Under such conditions, the resulting reduction in local heat release may lower the temperature in the lower bed regions, thereby reducing oxygen exchange in the upper layers. Consequently, the overall oxygen storage during the subsequent charging phase may decrease, leading to higher residual oxygen concentrations in the exhaust gas. This interpretation is consistent with the spatially non-uniform oxygen-release hypothesis discussed in Section 3.1.1, but it cannot be confirmed without local oxygen-partial-pressure or δ measurements.

The graph shows that the averaged maximum carbon dioxide concentrations during the discharging phases increase at a similar rate for both fuels with increasing temperature. The higher carbon dioxide concentrations measured during propane operation cannot be attributed solely to the three carbon atoms contained in each propane molecule. The measured concentration also depends on the amount of fuel supplied, its conversion, the distribution of carbon-containing products, and the total exhaust gas flow rate. However, the compared test series were conducted using different fuel volume flow rates. In addition, the total exhaust gas flow rate and the complete distribution of carbon-containing products are unknown. Therefore, the measured carbon dioxide concentrations cannot be used to quantify or directly compare carbon conversion. The simultaneous detection of CO and UHC, particularly during propane operation, indicates that the higher carbon dioxide concentrations do not represent complete fuel conversion. Accordingly,

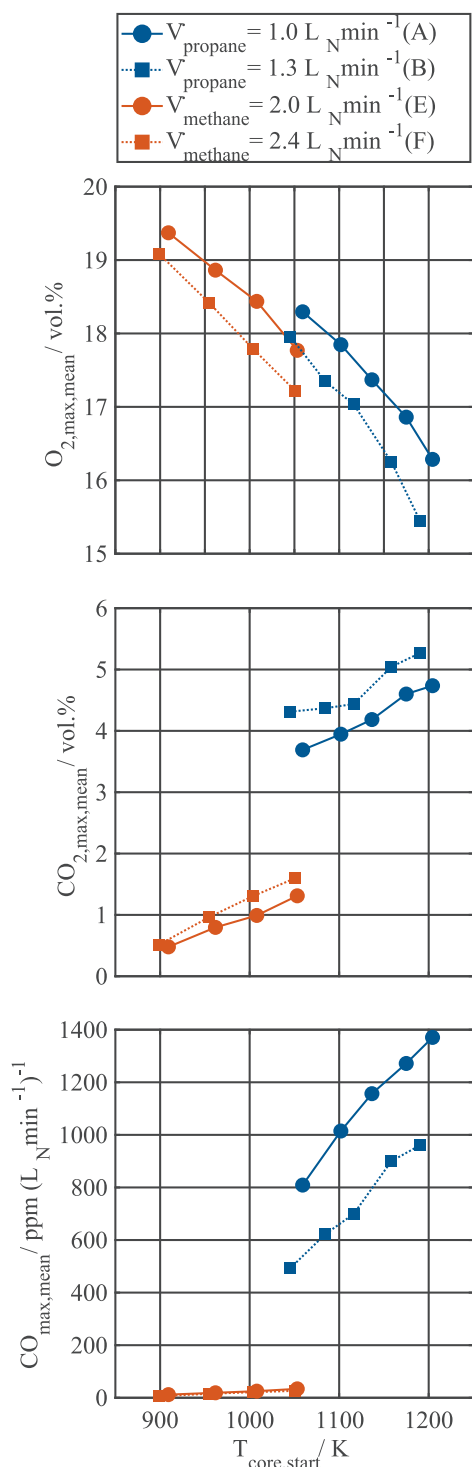


Fig. 9. Mean of maximum oxygen (top), carbon dioxide (middle), and carbon monoxide (bottom) concentrations in the exhaust gas depending on the starting temperature. Compared are propane test series A and B (blue lines) and methane test series E and F (orange lines) as specified in Table 1. The estimated measurement uncertainties (± 0.1 vol.% O_2 , ± 0.2 vol.% CO_2 , and ± 50 ppm CO) are small compared to the observed trends; error bars are omitted for clarity.

no conclusion is drawn as to whether propane operation results in a higher carbon conversion than methane operation.

Clear differences are observed in the averaged maximum carbon monoxide concentrations (Fig. 9, bottom). While almost no carbon monoxide is detected during methane operation, propane operation results in higher carbon monoxide concentrations, which increase

approximately linearly with starting temperature. This behavior is consistent with the hypothesis of spatially non-uniform oxygen release and locally limited oxygen availability discussed previously. At higher temperatures, the expected acceleration of oxygen exchange and the higher reactivity of propane may promote rapid partial oxidation of the fuel. Under these conditions, local oxygen availability may become insufficient for complete oxidation to carbon dioxide. This trend becomes more pronounced at higher fuel volume flow rates. During methane operation, the lower fuel reactivity and lower stoichiometric oxygen demand may provide a more favorable spatial and temporal overlap between methane and released oxygen, thereby supporting the further oxidation of carbon monoxide to carbon dioxide within the packed bed, resulting in the comparatively low carbon monoxide concentrations observed.

At an identical molar fuel flow rate, complete propane combustion requires 2.5 times as much oxygen as methane combustion. Rapid consumption of the released oxygen in the hotter lower bed regions may therefore produce locally oxygen-deficient conditions, allowing unconverted fuel and partially oxidized intermediates to pass through upper bed regions in which the temperature or local oxygen availability is insufficient for their complete oxidation. The possible formation of temporary carbonaceous deposits under these conditions may additionally shift part of the carbon release into the subsequent charging phase.

The presented results suggest that continuous cyclic operation of the OSM packed bed strongly depends on the selection of cyclic parameters appropriate for the prevailing temperature range. This behavior is qualitatively consistent with the temperature dependence of oxygen exchange, which is expected to influence the required duration of the individual charging and discharging phases. To further investigate the impact of the phase durations, as well as potential upper and lower operating limits, a systematic variation of these cyclic parameters is examined in the following section within a defined starting temperature range.

3.2. Impact of λ_{cycle}

As defined in Section 2.3, the cyclic relative air-fuel ratio λ_{cycle} relates the charging and discharging phases and facilitates comparison between different operating conditions. An example calculation is provided in the Supplementary Material. Within this qualitative proof-of-concept analysis, λ_{cycle} and $t_{core,eff}$ are used exclusively as comparative operating parameters and do not represent experimentally determined oxygen-utilization efficiencies or oxygen-release kinetics.

The tests considered in the following subsections are listed in Table 2. Within each test series, λ_{cycle} is varied by adjusting a single cyclic parameter, while the remaining three parameters are kept constant. All tests were conducted using identical heat-up conditions for the respective fuel, resulting in approximately constant starting temperatures.

3.2.1. Propane

Initial investigations were conducted to analyze the impact of fuel volume flow rate variations on the cyclic operation of the OSM packed bed. The phase durations used corresponded to those previously investigated in the starting temperature study and found to be associated with comparatively long effective test durations. The air volume flow rate was reduced to maintain comparable values of λ_{cycle} across the investigated test series while enabling operation at lower total volume flow rates.

Fig. 10 illustrates that an increase in fuel volume flow rate and the associated reduction of λ_{cycle} (in the range of $\lambda_{cycle} < 1$) are associated with a pronounced increase in the effective test duration. One possible explanation for the short effective test durations observed at large λ_{cycle} is an insufficient fuel volume flow rate. A low volume flow rate may limit the amount of fuel reaching and reacting within larger portions of the

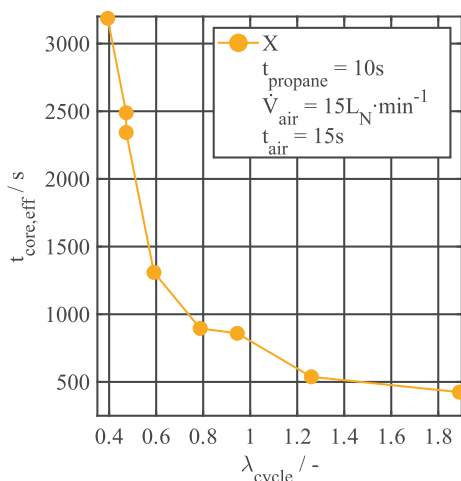


Fig. 10. Impact of λ_{cycle} on the effective test duration during cyclic operation. Shown is the test series X as specified in Table 2. The $t_{\text{core,eff}}$ is derived from temperature measurements with an uncertainty of approx. ± 8 K, at 1000 K. Error bars are omitted for clarity; the overall trend remains clearly identifiable.

packed bed. As a consequence, the positive temperature response may be reduced during the discharge phase. The resulting lower temperatures may suppress oxygen exchange and thereby impair subsequent charging of the OSM. A low fuel volume flow rate may also result in insufficient fuel reaching the upper packed bed regions. Under these conditions, oxygen can continue to be released from the OSMs because of the oxygen partial-pressure gradient. Consequently, the spatial overlap between the fuel availability, oxygen release, and sufficiently hot OSM regions may overcome unfavorable. As the discharge phase proceeds, fuel reaching the upper bed regions may therefore encounter a reduced local oxygen availability, limiting the positive temperature response. The effective test duration of over 40 min achieved with the selected parameters for tests X1–X3 therefore serves as a useful reference case for the following investigations.

In addition to varying the fuel volume flow rate, the λ_{cycle} can also be varied by adjusting the duration of the charging or discharging phase. Fig. 11 shows the effect of varying the discharging-phase duration (test series U and V) and the charging phase duration (test series W), as specified in Table 2. For test series U and V, the impact of the discharging duration was investigated at two different fixed charging durations. As in Fig. 6, the analysis focuses on the impact of λ_{cycle} on the effective test duration and the maximum temperature increase.

Considering the test series U and V (see Table 2), a reduction in λ_{cycle} is associated with an increase in the effective test duration at both fixed charging durations.

As in test series X (shown in Fig. 10), the effective test duration initially increases slightly around $\lambda_{\text{cycle}} = 1$, before the slope increases in the range of $\lambda_{\text{cycle}} < 1$. For test series U and V, the comparatively short effective test durations suggest that the selected discharge duration may be insufficient. Although oxygen storage during the charging phase appears sufficient, the discharging phase may be too short to enable sufficient oxygen release and fuel oxidation throughout larger portions of the packed bed. As a result, oxygen exchange may remain spatially limited during each cycle, thereby reducing the temperature increase during the following charging phase (Fig. 11, bottom). If oxygen release remains limited during the dis-

charging phase in tests in series V, the shorter charging duration used in test series U may help to avoid unnecessary cooling during charging with cold air, resulting in longer effective test durations. These observations suggest that short discharging phases limit performance at higher λ_{cycle} within test series U and V, while the charging duration may additionally affect the differences between the test series.

An excessively long charging duration may lead to unnecessary

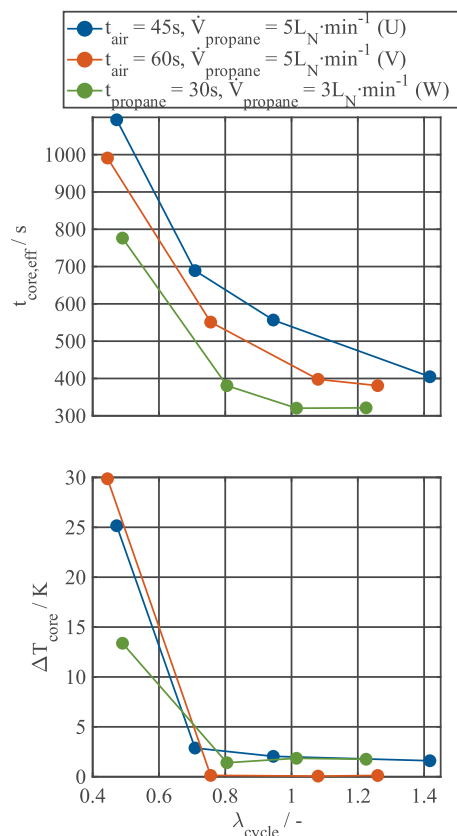


Fig. 11. Impact of λ_{cycle} on the effective test duration (top) and the temperature increase during cyclic operation (bottom). Shown are the test series U–W as specified in Table 2. The ΔT_{core} is derived from temperature measurements with an uncertainty of approx. ± 8 K, at 1000 K (applicable to $t_{\text{core,eff}}$ and $T_{\text{core,start}}$) resulting in an estimated uncertainty of about ± 11 K. Error bars are omitted for clarity; the overall trends remain clearly identifiable.

cooling of the packed bed if the positive temperature response associated with exothermic oxygen storage subsides before the end of the phase.

The variation of λ_{cycle} by varying the charging duration (with a slightly reduced fuel volume flow rate) was investigated in test series W (see Fig. 11). Compared with the previous two test series, this series employed both a longer discharge duration and a longer charging duration. The resulting behavior suggests that the selected phase durations are not among the most favorable for maintaining the packed-bed temperature under the investigated operating conditions.

All three test series show that, compared with test series X, the effective test duration is substantially shorter for the selected cyclic parameters of test series U, V, and W. All three series employ longer charging durations than test series X, which may contribute to additional cooling by the incoming air. However, because other cyclic parameters also differ between the series, the shorter effective test durations cannot be attributed solely to the charging duration. Fig. 12 shows the recorded exhaust gas compositions. The top panel presents the averaged maximum oxygen concentrations for test series U, V, and W. All three test series exhibit approximately identical trends and show a pronounced decrease below $\lambda_{\text{cycle}} = 0.7$. Overall, the high oxygen concentrations, which remain close to the initial value of 20.9 vol.% indicate that little oxygen is removed from the air toward the end of the charging phases. Since the oxygen concentration decreases noticeably only at low λ_{cycle} values while remaining comparatively high overall, the results are consistent with the assumption that the charging phase duration may exceed the time over which substantial oxygen storage occurs. Once the positive temperature response associated with oxygen

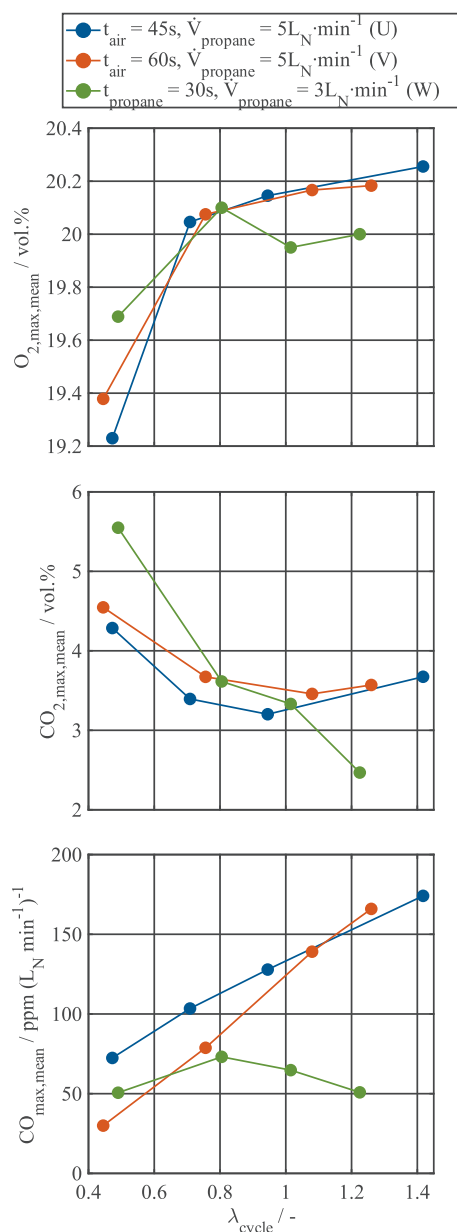


Fig. 12. Mean of maximum oxygen (top), carbon dioxide (middle), and carbon monoxide (bottom) concentrations in the exhaust gas depending on λ_{cycle} . Analyzed are the test series U – W as specified in Table 2. The estimated measurement uncertainties (± 0.1 vol.% O_2 , ± 0.2 vol.% CO_2 , and ± 50 ppm CO) are small compared to the observed trends; error bars are omitted for clarity.

storage has subsided, additional exposure to unheated air may primarily promote cooling rather than further oxygen storage. However, the outlet concentration alone cannot demonstrate that the OSM has reached a fully charged state.

The averaged maximum carbon dioxide concentration (Fig. 12, middle) increases particularly at lower values of λ_{cycle} . For test series U and V, this trend coincides with longer discharge durations and a larger amount of fuel supplied per cycle. However, this explanation does not apply to test series W, in which λ_{cycle} was varied through the charging duration. Because the total exhaust gas flow rate was not measured, the observed concentration trends cannot be interpreted as quantitative differences in carbon dioxide formation or fuel conversion.

The fuel-flow-normalized averaged maximum carbon monoxide values increase with rising λ_{cycle} . They were calculated by dividing the averaged maximum carbon monoxide concentration by the

corresponding fuel volume flow rate. This normalization is used only for a descriptive comparison and does not represent a molar carbon monoxide yield or emission factor because the total exhaust gas flow rate was not measured. The underlying cause may differ between the test series. In the test series U and V, higher values of λ_{cycle} correspond to shorter discharge durations, which may limit the spatial propagation of the reaction and temperature front through the packed bed. In test series W, higher values of λ_{cycle} result from longer charging durations, which may promote cooling by the incoming air. Both effects may reduce the spatial and temporal overlap between fuel, released oxygen, and sufficiently hot OSM regions and thereby limit the further oxidation of carbon monoxide to carbon dioxide.

In the case of test series W, the fuel-flow-normalized carbon monoxide values remain comparatively low and vary only slightly across the investigated range of λ_{cycle} . In this series, the discharge duration is kept constant at 30 s, which may contribute to the more uniform normalized values across the investigated λ_{cycle} range. The longer discharge duration may provide more time for the spatial overlap between fuel and released oxygen, thereby promoting further oxidation of carbon monoxide. The results therefore suggest that the discharge duration has a stronger influence on the observed carbon monoxide trends than the charging duration under the investigated conditions. However, the influence of the individual parameters cannot be isolated completely because the operating conditions differ between the test series.

The results suggest that favorable thermal operation under the investigated conditions requires the phase durations to be matched to the temperature-dependent oxygen exchange behavior of the OSM.

3.2.2. Comparison of propane and methane

Fig. 13 compares the dependence of the effective test duration on λ_{cycle} for propane test series U and V and methane test series Y and Z. Identical values of t_{air} , V_{air} , and V_{fuel} were applied to the corresponding test series U/Y and V/Z. Because complete combustion required 2 mol O_2 per mole of methane and 5 mol O_2 per mole of propane, the methane discharging durations were selected to be approximately 2.5 times the corresponding propane durations to obtain comparable values of λ_{cycle} .

The calculated inlet-based stoichiometric oxygen demands in Table S1 are theoretical reference values used to confirm the basis of the comparison at matched values of λ_{cycle} . For example, U1 supplies propane for 12 s and Y1 supplies methane for 30 s at an identical fuel volume flow rate of $5 \text{ L}_N \text{ min}^{-1}$. Both operating conditions correspond to a stoichiometric oxygen demand of 0.223 mol O_2 , or 7.138 g O_2 , per cycle. Thus, the different discharging durations compensate for the 2.5-fold higher molar oxygen demand of propane. Because the volumetric lower heating value of propane is also approximately 2.5 times that of methane, a methane discharging phase 2.5 times as long as the corresponding propane phase results in an approximately equivalent nominal global heat input per cycle for these matched λ_{cycle} pairs. However, the instantaneous local thermal input rate during the fuel phase and the absolute fuel-exposure time remain different. Thus, even these matched pairs do not isolate the fuel effect completely.

For both tests, the theoretical inlet-based stoichiometric demand corresponds to 120.8% of the theoretical reference capacity calculated for the $\Delta\delta = 0.2$, but only 34.5% of the theoretical maximum reference capacity calculated for the assumed $\Delta\delta = 0.7$ (see also Table S1). These percentages are theoretical demand-to-capacity reference values used to contextualize the fuel input. They do not represent experimentally determined oxygen release, oxygen-utilization efficiency, actual OSM conversion, or cycle-specific $\Delta\delta$.

Exactly matched λ_{cycle} comparisons are provided by U1/Y1 ($\lambda_{\text{cycle}} = 0.47$), U2/Y2 (0.71), U3/Y3 (0.95), V2/Z2 (0.76), and V4/Z4 (1.26). The remaining data points characterize the fuel-specific trends but are not interpreted as direct pairwise comparisons. These matched pairs compare the fuels at an equal cycle-integrated stoichiometric oxygen-to-fuel ratio while maintaining identical volume flow rates. However, because the absolute discharging durations differ, the observed

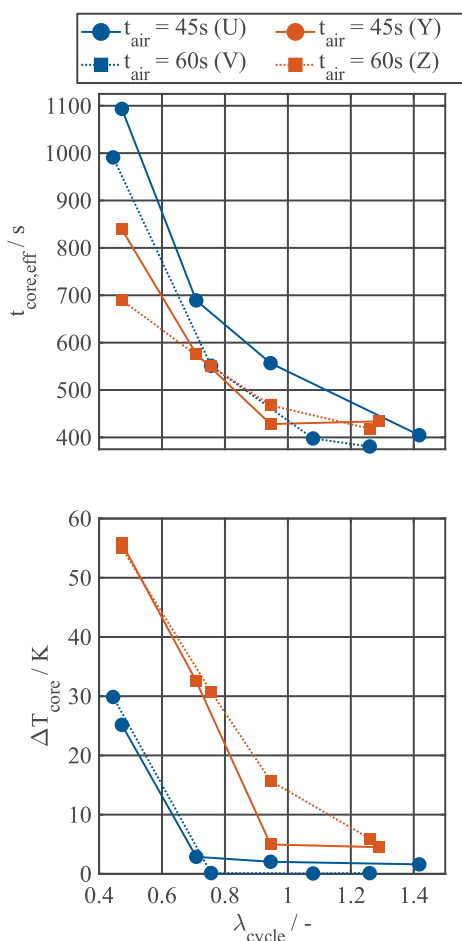


Fig. 13. Impact of λ_{cycle} on the effective test duration (top) and the temperature increase during cyclic operation (bottom). Compared are propane test series U and V (blue lines) and methane test series Y and Z (orange lines) as specified in Table 2. The ΔT_{core} is derived from temperature measurements with an uncertainty of approx. ± 8 K, at 1000 K (applicable to $t_{core,eff}$ and $T_{core,start}$) resulting in an estimated uncertainty of about ± 11 K. Error bars are omitted for clarity; the overall trends remain clearly identifiable

differences include the combined effects of fuel properties and fuel-exposure time and cannot be attributed exclusively to the fuel used.

The two comparison strategies used in this study therefore provide complementary information. The starting-temperature study compares propane and methane at identical phase durations but different inlet flow rates and values of λ_{cycle} , whereas the cyclic-parameter study includes selected test pairs at matched λ_{cycle} and approximately equal nominal lower-heating-value inputs per cycle but different discharge durations. Neither approach isolates fuel effect from all other operating parameters. However, the objective of the comparison was not to determine an intrinsic fuel effect independently of the operating conditions, but to assess how fuel-specific adjustment of the volume flow rates and phase durations affects sustained cyclic operation.

The results show that, regardless of the fuel used, the effective test duration increases as the λ_{cycle} decreases. This qualitative trend has already been discussed in subsection 3.2.1. At matched values of λ_{cycle} , propane operation generally exhibits longer effective test durations than methane operation. This difference may reflect the combined effects of the higher reactivity of propane, its higher instantaneous nominal thermal input rate, and the different fuel-exposure times. For test series V and Z, however, this difference is less pronounced. In these series, the longer charging duration may represent a larger fraction of the total cycle time, thereby reducing the relative impact of the discharge phase, where the higher reactivity of propane is most relevant.

An examination of the maximum temperature increase (see Fig. 13, bottom) shows that methane operation results in a larger temperature increase, particularly as λ_{cycle} decreases. One possible explanation is the longer discharging durations employed during methane operation. For methane operation, a substantial increase in temperature is observed for discharge durations exceeding approximately 20 s, whereas comparable temperature increases are not observed in the propane tests. Longer discharge durations may prolong the positive temperature response and improve the spatial overlap between methane, released oxygen, and sufficiently hot OSM regions. They may also promote oxygen exchange over a larger portion of the packed bed, thereby contributing to a larger overall temperature increase. These observations suggest that, although the balance between the charging and discharging phases is important for continuous operation, the absolute phase durations and volume flow rates must also fall within fuel-specific empirical ranges that support maintenance of the observed thermal response. For the investigated conditions, the comparatively small differences between the curves for a given fuel indicate that variations in the discharge duration have a stronger impact on the temperature increase than adjustments of the charging duration.

When analyzing the average maximum oxygen concentrations (see Fig. 14, top), common qualitative trends can also be observed for both fuels. Below a λ_{cycle} value of approximately 0.8, a pronounced decrease in oxygen concentration is observed, which is qualitatively consistent with more extensive oxygen release during the preceding discharge phase and subsequent oxygen storage during charging. However, the outlet concentration does not provide the corresponding oxygen quantity or change in δ . For methane operation, the increasing difference between tests at similar λ_{cycle} values may be related to larger differences in discharge duration. Compared with test series A–F (see Section 3.1), however, all tests exhibit substantially higher oxygen concentrations. This behavior may be associated with the different cyclic parameters employed in the present test series (see Tables 1 and 2). In particular, the substantially longer charging durations of 45 or 60 s (compared with 15 s in test series A–F) allow the outlet oxygen concentration to approach the inlet concentration during each cycle. This is consistent with oxygen-storage becoming less pronounced toward the end of the charging phase but does not demonstrate that the OSM reaches a particular degree of charging.

The carbon dioxide concentrations show an increase at lower λ_{cycle} for both fuels. However, the difference between the concentrations measured during methane and propane operation cannot be interpreted solely based on the different carbon contents of the fuel molecules. The comparatively low carbon dioxide concentrations during propane operation may be related to the short discharge durations discussed above. Under these conditions, the spatial propagation of fuel oxidation and the temperature front into the upper packed bed regions may be limited. Consequently, lower carbon dioxide concentrations may be measured at the reactor outlet, and in some cases the measured concentrations differ by less than a factor of two from those observed during methane operation. Because the total exhaust gas flow rate is unknown, this concentration difference cannot be interpreted as a quantitative difference in carbon dioxide formation or carbon conversion.

This is accompanied by an increase in the fuel-flow-normalized averaged maximum carbon monoxide values in the exhaust gas. The weaker positive temperature response and the associated lower temperature increase may suppress oxygen exchange.

Consequently, the oxidation of carbon monoxide to carbon dioxide may become increasingly limited, contributing to the lower carbon dioxide concentrations observed. In contrast, the fuel-flow-normalized carbon monoxide values remain low and nearly constant across the entire λ_{cycle} range for methane operation with the observed variations remaining within the measurement uncertainty.

Taken together, the exhaust gas measurements qualitatively indicate incomplete fuel conversion as a major limitation of the present lab-scale reactor. The comparatively short packed bed provides a limited reaction

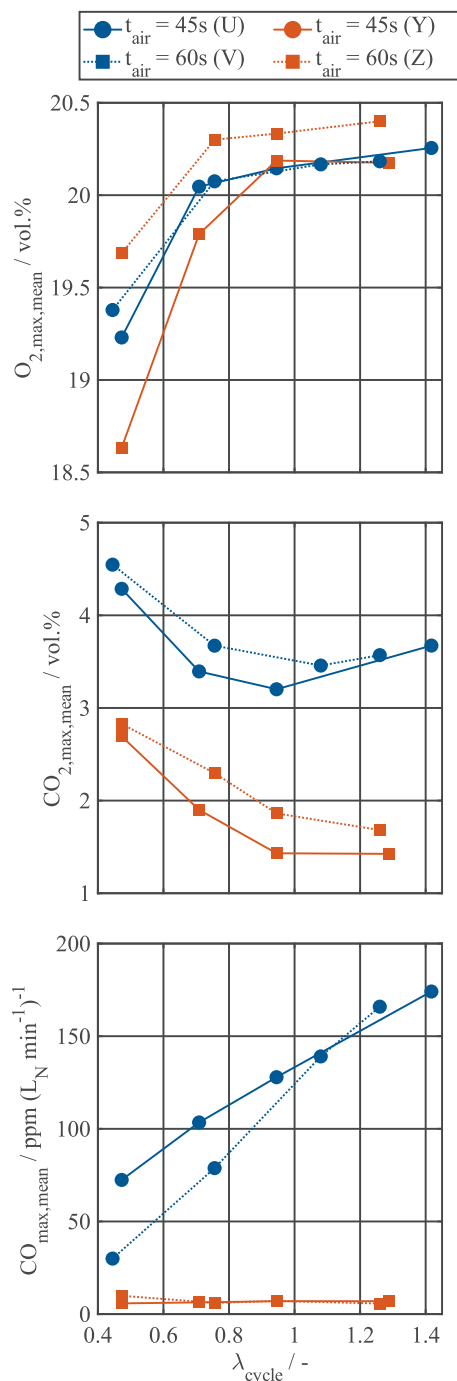


Fig. 14. Mean of maximum oxygen (top), carbon dioxide (middle), and carbon monoxide (bottom) concentrations in the exhaust gas depending on λ_{cycle} . Compared are propane test series U and V (blue lines) and methane test series Y and Z (orange lines) as specified in Table 2. The estimated measurement uncertainties (± 0.1 vol.% O_2 , ± 0.2 vol.% CO_2 , and ± 50 ppm CO) are small compared to the observed trends; error bars are omitted for clarity.

length and gas residence time for complete oxidation, particularly when oxygen release and combustion may be concentrated in the hotter lower bed regions. Under locally oxygen-deficient conditions, unconverted fuel and intermediate products may pass through upper regions in which the temperature or oxygen availability is insufficient for complete oxidation. The progressive cooling of the packed bed further intensifies this effect by slowing down oxygen exchange. Consequently, the results provide a qualitative proof of concept for sustained cyclic operation with positive temperature responses, but the investigated operating

conditions do not yet produce a carbon dioxide-rich exhaust gas suitable for direct carbon capture.

As outlined in Section 2.2, quantitative determination of phase-resolved fuel conversion, closed carbon balances, net heat release, and apparent oxygen-release rates would require time-resolved outlet-flow and species measurements together with a transient energy balance and controlled thermal conditions. Intrinsic oxygen-transport kinetics cannot be derived from the present reactor-scale tests and would require dedicated material-scale measurements.

With t_{air} , V_{air} , and V_{fuel} held constant between the corresponding fuel-specific test series, the results identify the discharge duration t_{fuel} as a key parameter for sustained cyclic operation. The higher reactivity of propane appears to provide a benefit only when the discharge duration is sufficiently long to establish a favorable spatial and temporal overlap between fuel, released oxygen, and sufficiently hot OSM regions. Under these conditions, the differences between propane and methane operation become more pronounced.

Following completion of the experimental campaign, macroscopic visual inspection of the recovered CSFM mini-honeycombs revealed no visible cracking, powder formation, or blockage of the honeycomb channels. Furthermore, no systematic deterioration of the effective test duration or thermal response that could be attributed unambiguously to progressive material aging was apparent during the tests. However, the test series were not designed as a dedicated long-term durability study, and the variation of operating conditions prevents aging effects from being isolated quantitatively from other influences on the temperature and exhaust gas profiles. No results from microscopic, structural, or mechanical post-test characterization were available for the present study. Consequently, microcracking, phase changes, sintering, or changes in porosity and oxygen-storage capacity cannot be excluded.

Accordingly, future durability studies should combine extended cycling under constant operating conditions with pre- and post-test characterization of the CSFM mini-honeycombs. Such studies should include scanning electron microscopy, phase analysis, porosity and mechanical-strength measurements, determination of changes in oxygen-storage capacity, and quantitative assessment of mass loss or powder formation. Time-resolved pressure-drop measurements could additionally help identify progressive channel blockage or changes in the packed bed flow resistance.

4. Conclusion and outlook

The present study provides a qualitative proof of concept for sustained cyclic operation with positive temperature responses during the cyclic charging and discharging of an OSM packed bed. Within this CLOU-related process, the CSFM OSM functions as a stationary non-stoichiometric perovskite oxygen carrier. Despite operating at atmospheric pressure without preheating the feed gases, sustained cyclic operation exceeding 50 min was achieved. The conclusions are based on comparative temperature and outlet-gas concentration trends. Experimentally determined oxygen-release capacity, actual $\Delta\delta$, phase-resolved fuel conversion, a closed carbon balance, oxygen-utilization efficiency, and oxygen-uncoupling kinetics were not obtained and are therefore outside the quantitative scope of this study. In addition to demonstrating the feasibility of the concept, the present study identified qualitative relationships between the selected operating parameters and the observed thermal behavior of the reactor and OSM. The observed trends are consistent with temperature-dependent oxygen storage and release, although higher temperatures do not necessarily prolong sustained cyclic operation under all operating conditions. In particular, the effective test duration during propane operation decreased at higher starting temperatures, showing that the temperature effect depends on the fuel and the selected cyclic parameters. The effective test duration and observed temperature response were highly sensitive to the selected cyclic operating parameters. For the reactor configuration investigated, fuel volume flow rates between $2 \text{ L}_N \text{ min}^{-1}$ and $5 \text{ L}_N \text{ min}^{-1}$ and air

volume flow rates between $10 \text{ L}_\text{N} \text{ min}^{-1}$ and $20 \text{ L}_\text{N} \text{ min}^{-1}$ were associated with the longest effective test durations and the most favorable observed temperature responses among the investigated conditions. Within this range, the fuel and air streams likely reached larger portions of the packed bed, promoting a more spatially distributed positive temperature response. At higher flow rates, increased convective cooling and reduced residence times likely contributed to less favorable thermal behavior. The results further suggest that charging and discharging durations should be adapted to the temperature dependent oxygen exchange behavior of the OSM. For the investigated propane operating conditions, discharge durations of approximately 5 s to 10 s and charging durations of approximately 15 s to 30 s constituted empirical phase-duration ranges associated with maintaining the observed thermal response. These flow-rate and phase-duration ranges refer exclusively to the effective test duration and observed temperature response within the qualitative proof-of-concept scope of this study. They should not be interpreted as optima for oxygen utilization, fuel conversion, carbon conversion, or overall reactor performance. These values cannot be transferred directly to methane operation. When identical air and fuel volume flow rates and comparable values of λ_cycle were applied, the methane discharging phases were selected to be approximately 2.5 times as long as the corresponding propane phases because of different stoichiometric oxygen demands. Accordingly, the comparison at matched λ_cycle represents a comparison at an equal cycle-integrated stoichiometric oxygen-to-fuel ratio rather than at identical absolute phase durations. Because the volumetric lower heating value of propane is approximately 2.5 times that of methane, these conditions also provide approximately equal nominal energy inputs per cycle. However, the instantaneous nominal thermal input rates and fuel-exposure times remain different. The observed differences therefore reflect the combined effects of fuel properties, phase duration, and instantaneous thermal input and cannot be attributed exclusively to the fuel used.

Overall, within its qualitative proof-of-concept scope, the study identifies fuel-specific empirical parameter ranges associated with maintaining the observed cyclic thermal response and provides a basis for the further development of packed bed reactor systems employing CSFM-type OSMs. While the underlying oxygen-storage and release mechanism is consistent with that of established perovskite oxygen carriers used in CLOU, the present work extends the available experimental basis by combining stationary CSFM mini-honeycombs, undiluted propane, short cycles with direct air-fuel switching, and operation without an intermediate purge phase or continuous external heating.

However, incomplete fuel conversion together with the low carbon dioxide concentrations represent major limitations of the present reactor configuration. As discussed in Section 3.1.2, these limitations were particularly evident during propane operation. The qualitative detection of UHC and the increased carbon monoxide concentrations, particularly during propane operation, indicate that complete oxidation was not achieved within the available reaction zone and gas residence time.

The packed bed height of approximately 90 mm limits both the available reaction length and the OSM inventory. In addition, cooling by the unheated inlet gases and heat losses through the reactor wall and exhaust gas progressively reduce the packed bed temperature and slow down the oxygen exchange. Increasing the packed bed height would extend the reaction zone, increase the gas residence time, and provide a larger amount of OSM for oxygen release and fuel oxidation.

Material development should focus on CSFM-type compositions providing a larger reversible change in oxygen non-stoichiometry and faster oxygen storage and release at the lower end of the investigated temperature range. Systematic variation of the perovskite composition should be combined with an assessment of redox-cycle stability, mechanical integrity, and resistance to carbon deposition under fuel-rich propane conditions. In addition, the porosity, honeycomb wall thickness, and channel geometry should be optimized to improve gas-solid mass transfer and available surface area while maintaining sufficient mechanical stability and an acceptable pressure drop.

Improved thermal management should include reduced wall and exhaust gas heat losses, preheating of the inlet gases, and a more homogeneous initial packed bed temperature. The latter could potentially be achieved using an external hot-air heating system instead of combustion-based preheating with the McKenna burner. Furthermore, introducing air and fuel from opposite ends of the packed bed during the respective phases should be investigated as a means of balancing the axial temperature and reaction profiles. Such a reverse-flow configuration could counteract the inferred tendency toward localization of oxygen release and combustion in the initially hotter lower bed regions. Alternatively, a staged reactor consisting of multiple shorter packed bed sections with intermediate gas redistribution could improve the spatial overlap between fuel and released oxygen and reduce the risk of locally oxygen-deficient conditions. Such reactor concepts would require an adapted reactor and valve configuration.

Future work should focus on extending the effective test duration, improving fuel conversion, and increasing the carbon dioxide concentration in the exhaust gas while minimizing residual oxygen and incomplete combustion products. Although a nearly pure carbon dioxide and steam exhaust gas stream was not achieved under the investigated conditions, it remains the long-term objective of this reactor concept, as such a gas composition would facilitate efficient downstream carbon capture. The present reactor therefore provides a qualitative proof of concept for sustained cyclic operation with positive temperature responses but does not yet provide an exhaust gas composition suitable for direct carbon capture. The proposed modifications provide a defined strategy for addressing this limitation. Achieving these objectives would represent an important step toward the application of packed bed OSM reactors as regenerative burners for industrial process-heat generation.

CRedit authorship contribution statement

Niklas Syguda: Writing – original draft, Visualization, Validation, Software, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Robert Hoffmann:** Writing – review & editing, Resources. **Olga Ravkina:** Resources. **Lars Zigan:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Formal analysis, Conceptualization.

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 data to this article can be found online at <https://doi.org/10.1016/j.fuel.2026.141648>.

Data availability

Data will be made available on request.

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