



Evaluation of novel oxygen storage materials (OSM) for low-emission heat generation in a flow reactor

Niklas Syguda^{a,*}, Olga Ravkina^b, Robert Hoffmann^b, Lars Zigan^a

^a Institut für Thermodynamik, Professur für Energiewandlung, Fakultät für Luft- und Raumfahrttechnik, Universität der Bundeswehr München (UniBw M), Neubiberg, D-85579, Germany

^b Hochtemperaturmembranen und -speicher, Institut für keramische Technologien und Systeme, Fraunhofer IKTS, Hermsdorf, D-07629, Germany

ARTICLE INFO

Keywords:

Oxygen storage materials
Oxy-fuel combustion
Packed bed reactor
Cyclic operation
Heat release dynamics

ABSTRACT

A promising approach to increase the sustainability of hydrocarbon combustion processes is carbon capturing. This requires high exhaust gas purity, which can be realized by utilizing pure oxygen, also known as oxy-fuel combustion. To reduce the complexity of handling and cost of pure oxygen, the present work investigates the alternative application of novel ceramic-based perovskite oxygen storage materials (OSM). A lab-scale model reactor was designed to investigate their oxygen storage and release characteristics. As the OSMs operate at elevated temperatures, the active part of the reactor is mounted above a McKenna type burner, which is intended to quickly preheat the packed bed. After heat-up, thermal energy release is implemented by alternating between air and fuel flow, facilitating a dynamic and recurring process of oxygen charging and discharging of the OSM. Operating behavior is investigated using an exhaust gas analysis (for measurement of oxygen and carbon dioxide) and temperature measurements within the OSM reactor bed. The tests show that, once the packed bed reaches its operating temperature, thermal energy can be generated by means of combustion (exothermal reaction) of methane during oxygen release (endothermal reaction), but also while recharging the OSM (exothermal reaction). The study examines the impact of fuel flow rates and operating temperatures and compares the performance to common oxygen carriers. The temperature increase caused by air or fuel flow through the packed bed indicates the storage and release reaction of oxygen. According to the thermal analysis, reactor performance improves at increased fuel flow rates and larger preheat temperatures. The improved performance and fuel conversion trend are confirmed by the flue gas analyses showing larger carbon dioxide concentrations and increased oxygen exchange. This is intended to achieve a high exhaust gas purity while maintaining continuous operation with the longest possible effective test duration.

Novelty and significance statement: Application of OSMs for process heat generation has previously been investigated for simple metal oxides as well as for perovskites. The present work investigates CSFM-type perovskite OSMs in a small-scale packed bed reactor operated under dynamic conditions with cycle durations below one minute. The novelty lies in the combination of cyclic packed bed operation, short charging and discharging phases, and operation without inert gas purging or fuel dilution. For the investigated operating conditions, both charging and discharging phases exhibit rapid exothermic behavior. This approach contributes to carbon capture concepts by enabling oxy-fuel combustion with high exhaust gas purity while avoiding cost- and energy-intensive oxygen supply by using oxygen from air. The impact of thermal and flow conditions on oxygen exchange and heat release is examined to support the development of continuous heat-release systems, while a high-purity exhaust gas remains a long-term objective.

1. Introduction

The generation of process heat is of crucial importance for numerous industrial applications. At present, process heat is predominantly

generated by the combustion of fossil fuels with air [1,2]. As carbon dioxide avoidance remains unattainable in many cases, carbon capture technologies provide a possibility for reducing the environmental impact of combustion processes [3].

* Corresponding author.

E-mail address: niklas.syguda@unibw.de (N. Syguda).

<https://doi.org/10.1016/j.proci.2026.106634>

Received 11 March 2026; Accepted 16 June 2026

Available online 9 October 2026

1540-7489/© 2026 The Author(s). Published by Elsevier Inc. on behalf of The Combustion Institute. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

Open access funding enabled and organized by Projekt DEAL.

To make the exhaust gas directly usable for carbon capture, a high level of carbon dioxide purity is necessary [4]. This requires that only (condensable) steam and carbon dioxide are present in the exhaust gas stream. Such conditions can be achieved by utilizing combustion processes that employ pure oxygen instead of air, also called oxy-fuel combustion. However, the production and handling of pure oxygen is complex and cost intensive [5,6], making oxy-fuel combustion economically inaccessible for many applications. This study, therefore, investigates an alternative method for oxygen supply through CSFM-based oxygen storage materials (OSM) operated in a cyclic packed bed reactor for combustion of gaseous fuels (in this study methane). These ceramic materials have the ability to reversibly adsorb oxygen from ambient air and release it, due to concentration gradients at elevated temperatures. This process enables combustion of the fuel inside a fixed and non-fluidized OSM packed bed at ambient pressure. This configuration facilitates safe and convenient handling of the materials while mitigating health and environmental hazards associated with particle abrasion that can occur during fluidization, as reported for chemical looping combustion (CLC) processes [7].

The primary aim of this work is the continuous generation of process heat through cyclic combustion of hydrocarbon-based fuels using oxygen supplied by the OSM. In contrast to other studies [7–9], no dilution with nitrogen is applied. Producing an exhaust gas stream composed solely of steam and carbon dioxide remains a long-term objective. The generated heat is intended to be utilized via the exhaust gas, for example by transferring it to the surroundings using a regenerative or recuperative (radiant) tube burner concept. For this purpose, a lab-scale packed bed reactor is designed and rapidly heated with a McKenna burner. To evaluate cyclic oxygen charging and release of the OSM, temperature and gas composition are analyzed in the reactor. Especially, the impact of preheat temperatures and the ratio of fuel to air during the respective phases on the OSM performance and heat release characteristics of the reactor are investigated. Heat release is examined during cyclic reactor operation without pressurization, preheating of gases and any other additional heating of the packed bed. However, due to the small-scale setup, heat losses may dominate, making sustained autothermal operation unlikely, while the compact design enables efficient parametric studies over a wide range of operating conditions. The objective is therefore to quantify the impact of relevant operating parameters and resulting trends, for application in larger-scale systems.

2. Experimental set-up and materials

2.1. Materials

Previous studies in the literature have mainly investigated simple metal oxides (e.g. CuO, FeO, NiO, also referred to as “oxygen carrier materials” (OCM)), and their mixtures such as ilmenite (FeTiO_3) as OSMs [8–12]. A comparative overview of selected material properties and operating parameters is provided in the Supplementary (Table S1). The ceramic based mixed oxides of the CSFM ($\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$) type have a perovskite structure. Previous studies have investigated CSFM as an OCM for catalytic tar removal applications [13].

The CSFM OSM is a mixed ionic electronic conductor (MIEC), in which electrons and oxygen ions can be transported (stored and released) depending on temperature and oxygen partial pressure gradients. At low outer oxygen partial pressures, ions are transported (released) to the material surface, where they form molecules by releasing electrons. At higher outer oxygen partial pressures, oxygen molecules at the material surface are transformed into ions and incorporated (stored) into the lattice.

The δ -parameter indicates the oxygen stoichiometry [14]. Under the given operating conditions for CSFM, it is approx. 0.3 for fully charged OSM and increases during discharge to an average of about 0.5, reaching up to 1.0 at maximum. A completely loaded reactor containing approx. 300 g of OSM, which results in a comparatively large average releasable

oxygen mass of 5.91 g and a maximum of 20.69 g. OSM releases oxygen at decreasing oxygen partial pressure and incorporates it at increasing oxygen partial pressure [8,14–16]. In the tests conducted, the oxygen is incorporated by flushing with air, which causes the OSM to reach chemical equilibrium with the oxygen partial pressure of 21 kPa. Due to the larger ionic radius of the vacancies, this also results in a shrinkage of the crystal structure (below 1 % for CSFM [17]). As a result of this chemical equilibrium, oxygen can also be released to an ambient atmosphere up to a maximum oxygen partial pressure of 21 kPa.

Due to crystal structure expansion, excessive discharge of the OSM ($\delta > 1.0$) leads to mechanical stresses and promotes cracking. To prevent the OSMs from degrading, the operating parameters should therefore be selected to avoid excessive discharge.

Compared to OCMs, the oxygen exchange kinetics of ternary perovskite type OSMs are faster and start already at higher oxygen partial pressures of the surrounding air [10]. This oxygen exchange already happens at ambient temperature, but only at a very slow rate. Only above 850 K does oxygen storage and release occur at rates sufficient for combustion applications. Present CSFM OSMs can be used at temperatures of up to 1550 K and exhibit high thermal stability, even with rapidly changing temperatures and geometric changes resulting from oxygen exchange. This temperature range is comparable to that of OCMs such as CuO (900–1150 K), FeTiO_3 (800–1450 K), and NiO (850–1550 K) [7,8,12,18]. The used OSMs have an open porosity of 41.5 % and a free gas volume of 78 %.

2.2. Experimental set-up and instrumentation

A modular cylindrical model reactor (schematic view shown in Fig. 1) is designed to investigate the characteristics of the OSM. The fixed bed reactor operates at ambient pressure and contains OSMs that have a honeycomb structure with 3×3 square channels. The overall dimensions are $5.3 \times 5.3 \times 6.5$ mm, providing a large surface area. The OSMs form a bulk compound with an approx. diameter of 60 mm and a height of approx. 90 mm. This results in a bulk density of approx. 1.2 g cm^{-3} . To minimize heat losses and provide high temperature resistance, the inner walls of the steel reactor are lined with an insulating layer of ceramic half-shells. The OSM packed bed is placed on a temperature resistant steel mesh.

To heat up the OSM, a McKenna-type flat flame burner (with a thermal power of max. 1 kW) is positioned 40 mm below this mesh, representing an unusual heating approach. This type of burner enables a homogenous heat-flux density until the desired temperature of the OSM is reached and also permits heating of the packed bed at varying fuel-air ratios (Φ , FAR), thereby influencing the initial oxygen content of the OSM after the heat-up phase.

For monitoring the process, the reactor is equipped with eight type K thermocouples (TC). Five of the mentioned TCs are located within the packed bed, while three TCs are located in the exhaust gas stream. The sampling rate of the TC is 1 Hz. Due to heating by hot gas from bottom to top, a temperature front propagates through the reactor. Consequently, peak temperatures in the lower part of the packed bed (TC_{1b}) are higher

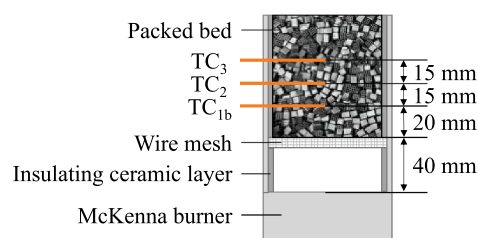


Fig. 1. Schematic of the model reactor equipped with CSFM OSMs. Three thermocouples within the packed bed are depicted. The gas supply for cyclic operation is introduced via the previously shut off burner.

and reached earlier than in the upper area (TC₃). To take these different temperature histories into account in the analysis, the core temperature T_{core} was determined as the mean of T_{1b} , T_2 , and T_3 (measured by TC_{1b}, TC₂, and TC₃, see also Figs. 1–3).

The exhaust gas stream is sampled at a height of 165 mm above the packed bed and consists of 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) for measurement of unburned hydrocarbons (UHC), nitrogen oxides (NO_x), carbon monoxide (CO), carbon dioxide (CO₂) and oxygen (O₂). The sampling rate of the exhaust gas analyses is 0.17 Hz.

Measurement uncertainties were considered for all sensors used in this study. For the TCs, the uncertainty results from the TC tolerance and the logger uncertainty, yielding a combined uncertainty of about ± 8 K at 1000 K. The resulting uncertainty of ΔT_{core} was estimated by root-sum-square propagation, yielding approx. ± 11 K. The O₂ concentration was measured with an accuracy of ± 0.1 vol.% for the digital readout after calibration. The FTIR CO₂ measurement uncertainty is estimated to be on the order of ± 0.2 vol.% for the concentration range investigated. CO and UHC measurements are evaluated qualitatively; therefore, no separate uncertainty is reported.

The gas volume flows are adjusted by mass flow controllers (MFC; Bronkhorst; EL-Flow). The MFCs supply fuel (methane) and oxidizer

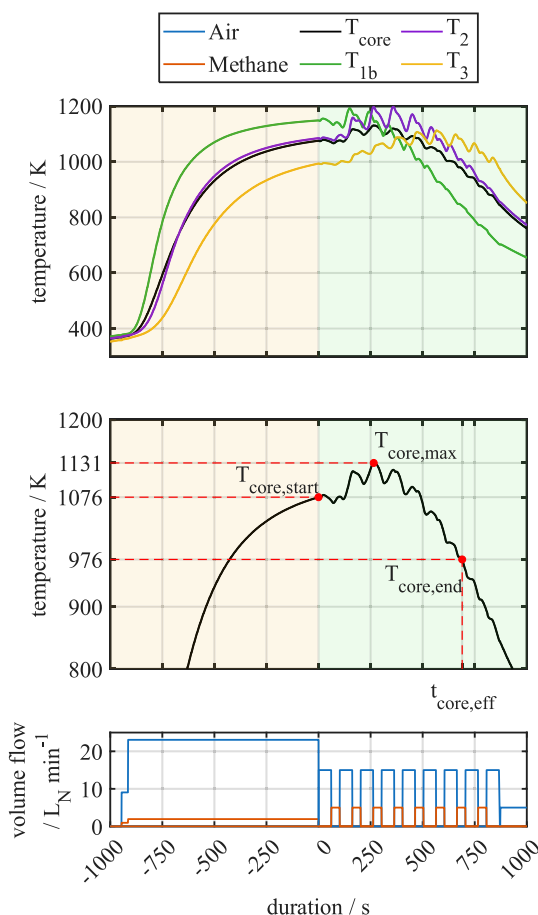


Fig. 2. Measured temperature progression of test A (see Table 1) during heat-up phase (top, yellow highlighted) and cyclic operation (top, green highlighted). Detailed view of temperature progression of T_{core} with characteristic operation points (middle). Recorded volume flows (bottom) during the heat-up phase and the cyclic operation with air (charging, blue) and methane (discharging, orange). Temperature measurement uncertainty is approx. ± 8 K at 1000 K. Accuracy of the MFCs is ± 0.5 % of the measured value.

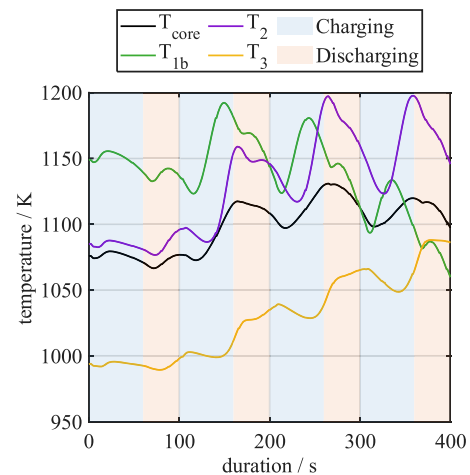


Fig. 3. Detailed view of the measured temperature progression inside the packed bed during cyclic operation of test A. Measurement uncertainty is approx. ± 8 K at 1000 K.

(air) to the reactor during the heat-up phase and during cyclic operation.

Unlike the most reactors described in the literature [18,19], the incoming gases are not electrically preheated but enter the packed bed at ambient temperature. In addition, no electrical external heating of the packed bed is applied. Although this results in cooling effects and limits the temperature increase during cyclic operation, it substantially lowers the system's complexity and additional energy demand while enabling a self-sustaining (autothermal) cyclic operation.

2.3. Experimental procedure

To reach a sufficiently high material temperature, the packed bed is heated to the predetermined temperature in a prior heat-up phase (see top view of Fig. 2, yellow highlighted area). The burner is active during this phase. The preheat duration ($t_{\text{heat-up}}$) varies depending on the test but is usually set between 15 and 30 minutes. As the partial pressure of O₂ in the burner's exhaust gas stream is lower than in the ambient air, obviously, the OSMs are continuously discharged during the heating process. To avoid excessive discharge of the OSM, the burner is operated in a lean range with a relative FAR of $\Phi = 0.8$ to $\Phi = 1.0$.

After the packed bed has been preheated to operating temperature, the burner is shut off and operation is switched to cyclic alternation between O₂ charging phase (air flow) and discharge phase (methane flow), see Fig. 2 (bottom). These two phases form one cycle. To prevent a temperature drop between phases, no inert gas purging is applied. The automated control of the cyclic operation is shown in Fig. 2 (bottom). Operation starts with a charging phase followed by a discharge phase and continues until the test is completed (when t_{eff} is reached, see its definition below). Cyclic operation can be initiated with either air or methane flow. The four variable parameters of each phase are the two volume flows (in standard liters per minute) and the duration in seconds as listed in Table 1.

The amount of methane per cycle in relation to the amount of air is described by the cycle's volume ratio (VR_{cycle}), which is defined as:

$$VR_{\text{cycle}} = VF_{\text{fuel}} \cdot t_{\text{fuel}} / VF_{\text{air}} \cdot t_{\text{air}} \quad (1)$$

VF : volume flow [$L_N s^{-1}$], t : phase duration [s]

The phase durations for charging (t_{air}) or release (t_{fuel}) were found optimal in the range of 10–30 s, which showed largest fuel conversion and longest effective test duration compared to much shorter or longer periods. This is comparable to a charging duration of 10 s for OCMs [8], but represents a significantly shorter duration than previous studies,

Table 1

Operation parameters of test series A and B for investigating the impact of the starting temperature.

Test	Heat-up phase			$T_{\text{core,start}}$ (K)	$T_{\text{core,end}}$ (K)	Cyclic operation				
	$t_{\text{heat-up}}$ (min)	$VF_{\text{heat-up}}$ ($L_N \text{ min}^{-1}$)	Φ			Air charge phase		Fuel discharge phase		VR_{cycle}
						t_{air} (s)	VF_{air} ($L_N \text{ min}^{-1}$)	t_{fuel} (s)	VF_{fuel} ($L_N \text{ min}^{-1}$)	
A	15	25	0.8	1075.8	975.8	60	15	40	5.0	0.22
B1	30	15	0.9	898.7	798.7	15	15	10	2.4	0.09
B2		17		955.0	855.0					
B3		19		1003.5	903.5					
B4		20		1050.5	950.5					
B5		15	909.3	809.3	2.0					
B6		17	961.8	861.8						
B7		19	1008.0	908.0						
B8		20	1053.2	953.2						

with reported durations of 10–50 minutes [12,18,20].

In order to quantify the test duration in a standardized manner, the effective test duration t_{eff} is defined. A test is considered complete when T_{core} has fallen by 100 K relative to T_{core} at the start of the cyclic operation ($T_{\text{core,start}}$). Due to the temperature dependence of OSM activity from this point onwards, it was shown that heat release decreases rapidly.

In addition to $t_{\text{core,eff}}$, two other variables related to the temperature of the packed bed are used below. The starting temperature T_{start} refers to the temperature at the respective position of the TC in the packed bed after the previously defined heat-up phase at the beginning of cyclic operation. The temperature increase ΔT_{core} then describes the increase in temperature during cyclic operation from $T_{\text{core,start}}$ up to the maximum temperature $T_{\text{core,max}}$ reached in the test.

3. Results

First, the basic concept of heat release through the cyclic alternation of charging and discharging the OSM is demonstrated. Fig. 3 shows the detailed temperature curves inside the packed bed during the cyclic operation of test A (see Table 1) following the heat-up phase (as shown in Fig. 2, top). The test duration begins at 0 s with the start of cyclic operation. The subsequent temperature fluctuations caused by the switching between charging and discharging phases are clearly visible. Independent of the chosen volume flow rates, phase durations, or other influencing parameters, these characteristic temperature profiles appear consistently across all tests.

The results were reproducible across repeated tests (see Supplementary Figs. S1,S3), with consistent temperature profiles ($\sigma_{T,\text{RMS,rel}} = 0.5\%$) and exhaust gas measurements ($\sigma_{\text{O}_2,\text{RMS,rel}} = 3.0\%$ and $\sigma_{\text{CO}_2,\text{RMS,rel}} = 23.6\%$) under identical conditions.

A slight increase in temperature can already be observed during the initial charging phase. It depends on $t_{\text{heat-up}}$ and results from the reduced O_2 content during this phase. However, this increase is minor compared to the increases following a discharge phase. The duration $t_{\text{heat-up}}$ and the FAR of the burner have negligible effects in overall operation. Their impact is limited to the start of cyclic operation. The positive effect of a longer heat-up phase on $t_{\text{core,eff}}$, due to higher $T_{\text{core,start}}$, is more significant. However, to avoid excessive and potentially damaging discharge of the OSMs, the duration should not be set too long. Likewise, operating the burner as lean as possible is preferable to prevent fuel deposits on the OSMs.

The effect of charging and discharging is visible in the temperature profiles (Fig. 3). A temperature increase is observed in both phases. During discharging, this is a result of the exothermic combustion. The release of stored O_2 in the presence of inflowing methane forms an ignitable mixture. Reaction occurs near the hot surfaces of the OSM, where sufficient O_2 is available and where the temperature is above the autoignition temperature of methane (810 K [21]). The temperature increase during charging results from the fact that the storage of O_2 in

the OSM is an exothermic process [22,23].

As O_2 release is endothermic and counteracts the heat release of the combustion, the charging phase causes a higher ΔT_{core} than the discharging phase. During discharging, two competing effects occur: the endothermic release of O_2 from the OSM and the exothermic combustion of the fuel. In the present case, the heat released by combustion exceeds the energy required for O_2 release, resulting in an overall exothermic discharge phase. In contrast to several packed bed CLC studies employing conventional OCMs, where the discharge phase is often associated with a net temperature decrease due to the endothermic O_2 release and reduction reactions, the present tests showed an overall temperature increase during the discharge phase [12,19,23,24].

In addition to the temperature increase during both phases, local temperature reductions are observed before the end of each phase due to heat loss of the reactor, resulting in an overall global reduction of temperature in the entire packed bed.

Reasons for this overall falling temperature of the packed bed (and thus also a decrease in heat release) include the respective duration of charging and discharging. If t_{air} is excessive (e.g. > 30 s), OSMs are already fully charged before the phase has ended. Without the exothermic charging taking place, the heat release ends and the temperature drops further until the end of the phase. The same applies in the discharge phase when the combustion stops because the OSMs are presumably almost discharged. Similarly, if charging and discharging durations are too short (e.g. $t_{\text{phase}} < 10$ s), the O_2 capacity is not completely used or the OSMs are likely only partially recharged.

The following subsections examine the influence of T_{start} and VR_{cycle} on the packed bed's temperature development and the resulting CO_2 and O_2 concentrations in the exhaust gas. Independent of the chosen parameters, elevated UHC concentrations were observed during cyclic operation, indicating incomplete methane conversion (estimated below approx. 10 %). In contrast, NO_x concentrations remained low and CO concentrations were negligible.

3.1. Impact of start temperature t_{start}

To investigate the influence of varying T_{start} in cyclic operation, tests were conducted for four distinct temperature ranges. The corresponding operating parameters for the heat-up phase and cyclic operation are specified in Table 1. The required T_{start} were reached by varying the volume flow of the burner ($VF_{\text{heat-up}}$) during the heat-up phase.

All tests were operated with the same parameters t_{air} , VF_{air} , and t_{fuel} , except for the discharging volume flow VF_{fuel} . To analyze the impact of temperature on tests with different VR_{cycle} values, two fuel volume flows were tested as shown in Fig. 4 and Fig. 5.

Fig. 4 presents the impact of the $T_{\text{core,start}}$ at the beginning of the cyclic operation. Initially, it can be seen that a larger $T_{\text{core,start}}$ leads to an almost linear increase of $t_{\text{core,eff}}$. Due to the temperature-dependent exchange rate [8,25] of O_2 into and out of the OSM, higher temperatures result in faster O_2 exchange during the charging and discharging phases.

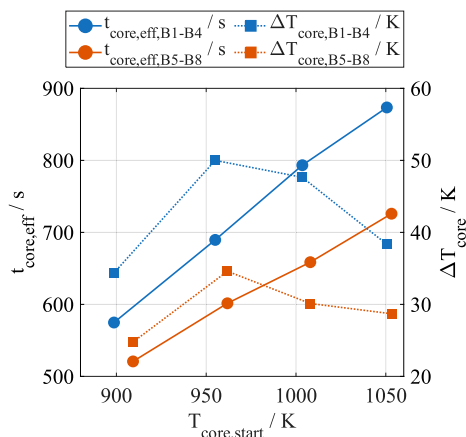


Fig. 4. Impact of $T_{\text{core,start}}$ on $t_{\text{core,eff}}$ (left axis, straight line) and ΔT_{core} during cyclic operation (right axis, dotted line). Tests with VR_{cycle} of 0.09 (orange, B5–B8) and 0.11 (blue, B1–B4) as specified in Table 1. The ΔT_{core} is derived from temperature measurements 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.

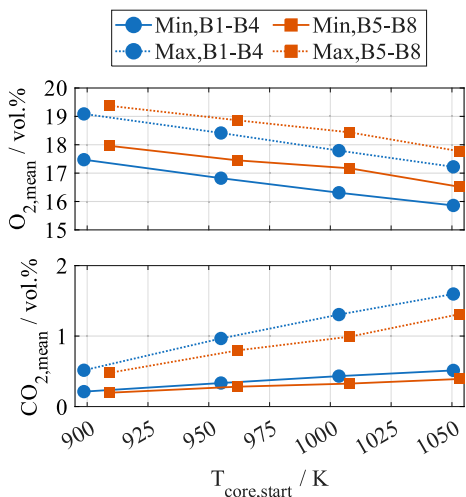


Fig. 5. Minima (left axis, straight line) and maxima (right axis, dotted line) of mean O_2 (top) and CO_2 (bottom) concentrations in the exhaust gas depending on the starting temperature. Analyzed are two different VR_{cycle} values of 0.09 (orange, B5–B8) and 0.11 (blue, B1–B4) as specified in Table 1. The estimated measurement uncertainties (± 0.1 vol.% O_2 and ± 0.2 vol.% CO_2) are small compared to the observed trends; error bars are omitted for clarity.

This leads to an increased O_2 release within the given phase duration and thus to a higher reaction rate with methane, which would otherwise leave the packed bed unreacted at lower temperatures. This is supported by the observed decrease in UHC concentrations. Enhanced combustion increases heat release, which is maintained during the subsequent charging phase as the more discharged OSM takes up larger amounts of O_2 and releases heat. The higher heat release promotes a more homogeneous temperature distribution within the packed bed and delays cooling, thereby prolonging $t_{\text{core,eff}}$.

An increase in the $T_{\text{core,start}}$ affects $t_{\text{core,eff}}$ regardless of the VR_{cycle} value. The two curves (solid lines) from tests B1–B8 in Fig. 4 indicate that an increase of VF_{fuel} generally results in a longer $t_{\text{core,eff}}$ while the slope of the trend remains unchanged. This means that $T_{\text{core,start}}$ has an impact that is independent of VR_{cycle} .

The analysis of the impact of $T_{\text{core,start}}$ on ΔT_{core} (see dotted lines in

Fig. 4) demonstrates that the two quantities are independent of each other.

The temperature increase can be interpreted as an indirect indicator of OSM discharge and reaction intensity, although transient heat transfer within the packed bed may cause thermal and reaction fronts to propagate differently during cyclic operation. A higher degree of discharge results in a larger ΔT_{core} during the subsequent charging phase. Compared to OCMs reported in the literature, the observed ΔT_{core} is relatively low [7,12,24]. However, for continuous operation and industrial applications, maintaining a stable temperature level is preferable, with minimal temperature fluctuations and consistent heat release.

Although a higher $T_{\text{core,start}}$ accelerates the O_2 exchange and increases methane conversion, the effect on ΔT_{core} remains limited compared to variations in the cyclic parameters (see Section 3.2). This is primarily due to the high O_2 concentration in the exhaust gas, indicating that complete fuel conversion is not achieved within the available residence time. While higher temperatures promote faster reaction kinetics, the residence time of the fuel within the packed bed remains insufficient for complete combustion. In contrast, increasing the t_{fuel} directly extends the reaction time between the available O_2 and the fuel. This results in a more complete utilization of the released O_2 and therefore leads to a larger ΔT_{core} .

During cyclic operation, O_2 concentrations in the exhaust gas alternate between minima (discharge phase with pure methane flow) and maxima (charge phase with pure air flow). Each operating point shown in Fig. 5 represents the average minima and maxima over all cycles within a test (B1–B8, see Table 1).

In the case of the measured exhaust gas O_2 concentration as shown in the top view of Fig. 5, a higher temperature consequently results in greater discharge of the packed bed and thus lower O_2 concentration but increased concentration of CO_2 (with the same charging phase parameters). This indicates that more O_2 is extracted from the inflowing air during the charging phase. Thus, the maximum concentration during the charging phase is higher. If less O_2 is released at lower temperatures, less will be additionally stored again afterwards and the O_2 concentration in the exhaust gas reaches the initial value of 21 vol.%.

This reasoning also applies to the progression of the CO_2 concentration. The accelerated release of stored O_2 during the discharge phase leads to a more complete combustion, as fewer unburned fuel molecules pass through the packed bed. As a result, the maximum CO_2 concentration increases.

Although CO_2 concentrations increase with higher $T_{\text{core,start}}$, their absolute values remain too low to be considered capture-ready. This is primarily attributed to the limited height of the packed bed, which results in incomplete methane conversion, as indicated by the measured UHC concentrations. Increasing the bed height would improve conversion. However, larger packed bed systems may also exhibit stronger reaction front propagation and local over-reduction effects in lower bed regions. In particular, a uniformly high packed bed temperature (> 800 K) is required to ensure sufficiently fast O_2 exchange over the entire bed height, potentially supported by electrical external heating or preheated air and fuel (e.g. 650 K) as described in the literature. As shown in Fig. 5, higher $T_{\text{core,start}}$ further enhance CO_2 formation. In contrast, reducing the flow rate and extending the discharge phase do not improve conversion, as excessive discharge occurs in the lower layers of the bed.

The high O_2 concentration in the exhaust gas is inherent to the operating principle, as O_2 can be released into the gas stream even without unreacted fuel. This can be mitigated by adjusting the charging phase. Shorter charging durations (e.g. $5 \text{ s} \leq t_{\text{air}} \leq 10 \text{ s}$) promote stronger loading of the lower bed regions while limiting releasable O_2 in the upper layers, thereby reducing O_2 release into the exhaust.

3.2. Impact of cyclic volume ratio VR_{cycle}

Besides $T_{\text{core,start}}$, VR_{cycle} is a decisive parameter for increasing $t_{\text{core,eff}}$. In the two test series (C1–C4 and C5–C9, see Table 2) considered

Table 2

Operation parameters of test series C for investigating the impact of the cyclic volume ratio.

Test	Heat-up phase			$T_{\text{core,start}}$ (K)	$T_{\text{core,end}}$ (K)	Cyclic operation				
						Air charge phase		Fuel discharge phase		VR_{cycle}
						t_{air} (s)	VF_{air} ($L_N \text{ min}^{-1}$)	t_{fuel} (s)	VF_{fuel} ($L_N \text{ min}^{-1}$)	
	$t_{\text{heat-up}}$ (min)	$VF_{\text{heat-up}}$ ($L_N \text{ min}^{-1}$)	Φ							
C1	15	25	0.8	1075.9	975.9	60	15	15	5.0	0.08
C2				1079.3	979.3			20		0.11
C3				1080.8	980.8			25		0.14
C4				1077.4	977.4			40		0.22
C5				1091.3	991.3	115		30		0.09
C6				1081.2	981.2	95				0.11
C7				1095.8	995.8	70				0.14
C8				1075.9	975.9	45				0.22
C9				1085.0	985.0	30				0.33

here, VR_{cycle} was varied by increasing either t_{air} or t_{fuel} . The volume flows remain constant throughout all tests.

Fig. 6 illustrates the effect of VR_{cycle} on $t_{\text{core,eff}}$. It should be noted that, compared to previous studies in the literature [7–9], the fuel was not diluted with nitrogen. It becomes evident that an increase in fuel volume (achieved by extending t_{fuel}) leads to a longer $t_{\text{core,eff}}$. A larger number of fuel molecules passing the OSM over a longer period increases the likelihood of reactions with the released O_2 . This enhanced reaction probability results in higher temperatures, which in turn prolongs $t_{\text{core,eff}}$.

However, as VR_{cycle} increases further, the growth in $t_{\text{core,eff}}$ progressively diminishes. This behavior can be attributed to two limiting effects. On the one hand, beyond a certain fuel input, the OSM cannot release O_2 at a sufficient rate, thereby limiting the heat generation. On the other hand, an increasing discharge duration leads to excessive depletion of the lower regions of the packed bed. In these regions, the available O_2 is nearly exhausted, resulting in reduced heat release and a progressive temperature decrease. Consequently, ΔT_{core} declines. A similar effect is observed when VR_{cycle} is increased by reducing t_{air} .

An increase in VR_{cycle} leads to a rise in ΔT_{core} . This is attributable to the higher fuel content, which enhances O_2 release, intensifies combustion by reacting with the high O_2 concentration in the exhaust gas,

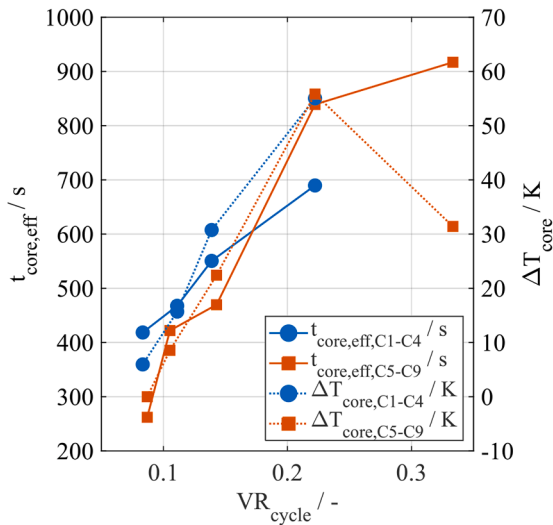


Fig. 6. Impact of VR_{cycle} on $t_{\text{core,eff}}$ (left axis, solid lines) and ΔT_{core} during cyclic operation (right axis, dotted lines). Tests with constant t_{air} (C1–C4, blue) and constant t_{fuel} (C5–C9, orange) as specified in Table 2. The ΔT_{core} is derived from temperature measurements 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.

and consequently increases heat release. The simultaneous increase in discharge results in a higher degree of O_2 storage during the following charging phase and thus in greater heat release. This additional heat leads to a higher temperature of the packed bed, which in turn intensifies the O_2 exchange. The effects reinforce each other and result in a larger ΔT_{core} with increasing VR_{cycle} . However, as observed with $t_{\text{core,eff}}$, the effect diminishes beyond a certain fuel quantity because the amount of O_2 that can be released is limited. Fig. 7 shows that the maximum O_2 concentration remains approx. constant as VR_{cycle} increases. Increased durations lead to a higher percentage of O_2 charging and discharging, probably up to 100 % (saturation). An approx. constant average O_2 concentration therefore indicates that both charging and discharging during the cycle are sufficiently effective. This allows the respective phase durations to be selected according to a maximum $t_{\text{core,eff}}$.

An increase in max. CO_2 concentration with rising VR_{cycle} , together with an approx. constant min. O_2 concentration, indicates that although the OSMs are being sufficiently discharged, the released O_2 does not completely participate in a reaction. Based on the measured CO_2 concentrations and assuming complete conversion of the released O_2 to CO_2 , only approx. 4 %–12 % of the theoretically available O_2 capacity contributes to methane oxidation under the present conditions. This further indicates that fuel conversion is primarily limited by a short residence time, temperature inhomogeneities, and O_2 exchange kinetics within the reactor. Higher temperatures, increased VF_{fuel} (higher fuel penetration in upper bed regions), or reduced t_{air} (higher O_2 loading in

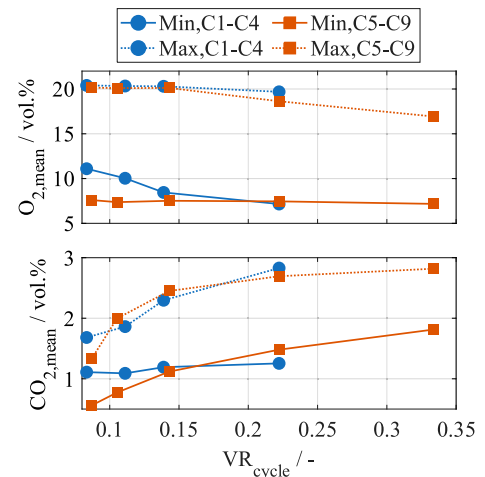


Fig. 7. Minima (solid lines) and maxima (dotted lines) of mean O_2 (top) and CO_2 (bottom) concentrations in the exhaust gas depending on VR_{cycle} . Analyzed are tests with constant t_{air} (C1–C4, blue) and constant t_{fuel} (C5–C9, orange) as specified in Table 2. The estimated measurement uncertainties (± 0.1 vol.% O_2 and ± 0.2 vol.% CO_2) are small compared to the observed trends; error bars are omitted for clarity.

lower bed regions) therefore lead to a higher CO₂ concentration. In the former case, more reactants are available to react with the released O₂. However, this trend diminishes with rising VR_{cycle} .

4. Conclusion and outlook

In the present study, CSFM OSMs operated under cyclic combustion conditions were tested in a packed bed reactor. The functional principle of heat release was demonstrated by cyclic operation of air and methane. The temperature evolution during cyclic operation can be correlated with the O₂ exchange behavior of the material and enables identification of suitable operating conditions. Due to the fast O₂ exchange kinetics of CSFM, heat release could be demonstrated even for short cycle durations and without purge gas. An increase in $T_{\text{core,start}}$ was shown to prolong $t_{\text{core,eff}}$ due to enhanced reaction kinetics, while ΔT_{core} remains largely unaffected. This is attributed to heat losses and limited residence time, which constrain the net temperature increase. At higher VR_{cycle} values, the benefit of increased fuel input saturates. This behavior is governed by two limiting mechanisms: insufficient O₂ release rates at high fuel flow and excessive O₂ depletion of the lower packed bed regions during extended discharge phases, both leading to reduced heat release and temperature in the downstream regions of the reactor. As a result, methane conversion remains limited (estimated below approx. 10 %) under the present operating conditions. This proof of concept for heat release in a continuous flow reactor is the foundation for further investigations. Future work will focus on longer or continuous cyclic operation, improving reactor performance and material utilization, and enabling more efficient fuel conversion under practical conditions. Improving fuel conversion and exhaust gas composition requires a larger OSM packed bed and improved thermal homogeneity. The continuous and dynamic operation of the reactor with exothermal charging and discharging phases serves as the basis for future industrial application e. g. in the form of a regenerative burner. In addition to optimizing cyclic parameters, varying the OSM (e.g. material, geometry, porosity) for a faster O₂ exchange and the fuel type (e.g. propane, hydrogen or hydrogen admixture respectively) offer further potential for improvement.

CRediT authorship contribution statement

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

Acknowledgements

The authors thank AIF-Forschungsvereinigung (Vorhaben-Nr. 22675 BG/3) and Federal Ministry for Economic Affairs and Energy (BMWE) for funding this project. The authors would also like to thank the project partners at Gas- und Wärmeinstitut Essen e.V. for their contributions, and the UniBw M for support.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.proci.2026.106634](https://doi.org/10.1016/j.proci.2026.106634).

References

- [1] T. Fleiter, M. Rehfeldt, L. Neusel, et al., CO₂-neutral process heat using electrification and hydrogen: technologies, barriers and required action, Fraunhofer ISI, Karlsruhe, Germany, 2024. Technical Report.
- [2] M. Rehfeldt, S. Bussmann, T. Fleiter, Direct electrification of industrial process heat. An assessment of technologies, potentials and future prospects for the EU: study on behalf of Agora industry, Fraunhofer ISI, Karlsruhe, Germany, 2024. Technical Report.
- [3] T. Wilberforce, A.G. Olabi, E.T. Sayed, K. Elsaid, M.A. Abdelkareem, Progress in carbon capture technologies, *Sci. Total. Environ.* 761 (2021) 143–203.
- [4] A. Murugan, R.J.C. Brown, R. Wilmot, et al., Performing quality assurance of carbon dioxide for carbon capture and storage, *J. Carbon Res.* 6 (2020) 76.
- [5] A. Ebrahimi, M. Meratizaman, R.H. Akbarpour, O. Pourali, M. Amidpour, Energetic, exergetic and economic assessment of oxygen production from two columns cryogenic air separation unit, *Energy* 90 (2015) 1298–1316.
- [6] Y. Lee, V.M. Charitopoulos, K. Thyagarajan, I. Morris, J.M. Pinto, L. G. Papageorgiou, Integrated production and inventory routing planning of oxygen supply chains, *Chem. Eng. Res. Des.* 186 (2022) 97–111.
- [7] S. Noorman, M. van Sint Annaland, J. Kuipers, Experimental validation of packed bed chemical-looping combustion, *Chem. Eng. Sci.* 65 (2010) 92–97.
- [8] S. Noorman, F. Gallucci, M. van Sint Annaland, J.A.M. Kuipers, Experimental investigation of chemical-looping combustion in packed beds: a parametric study, *Ind. Eng. Chem. Res.* 50 (2011) 1968–1980.
- [9] H.P. Hamers, F. Gallucci, P.D. Cobden, E. Kimball, M. van Sint Annaland, CLC in packed beds using syngas and CuO/Al₂O₃: model description and experimental validation, *Appl. Energy* 119 (2014) 163–172.
- [10] L. Liu, Z. Li, Z. Li, Y. Larring, N. Cai, Heterogeneous reaction kinetics of a perovskite oxygen carrier for chemical looping combustion coupled with oxygen uncoupling, *Chem. Eng. J.* 417 (2021) 128054.
- [11] M. Arjmand, A. Hedayati, A.-M. Azad, H. Leion, M. Rydén, T. Mattisson, Ca x La 1–x Mn 1–y M y O 3–δ (M = Mg, Ti, Fe, or Cu) as oxygen carriers for chemical-looping with oxygen uncoupling (CLOU), *Energy Fuels* 27 (2013) 4097–4107.
- [12] J.R. Fernández, J.M. Alarcón, Chemical looping combustion process in fixed-bed reactors using ilmenite as oxygen carrier: conceptual design and operation strategy, *Chem. Eng. J.* 264 (2015) 797–806.
- [13] M. Ma, M. Müller, J. Richter, et al., Investigation of combined catalyst and oxygen carrier systems for the partial oxidation of naphthalene as model tar from biomass gasification, *Biomass Bioenergy* 53 (2013) 65–71.
- [14] R. Krieger, R. Kirchseisen, J. Töpfer, Oxygen stoichiometry and expansion behavior of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3–δ}, *Solid. State Ion.* 181 (2010) 64–70.
- [15] M. Takacs, J.R. Scheffe, A. Steinfeld, Oxygen nonstoichiometry and thermodynamic characterization of Zr doped ceria in the 1573–1773 K temperature range, *Phys. Chem. Chem. Phys.* 17 (2015) 7813–7822.
- [16] R. Krieger, Sauerstoff-liefernde Keramiken für Verbrennungsprozesse, *Gaswärme Int.* 4 (2017) 43–48.
- [17] A. Atkinson, T.M.G.M. Ramos, Chemically-induced stresses in ceramic oxygen ion-conducting membranes, *Solid. State Ion.* 129 (2000) 259–269.
- [18] J.R. Fernández, J.C. Abanades, Conceptual design of a Ni-based chemical looping combustion process using fixed-beds, *Appl. Energy* 135 (2014) 309–319.
- [19] H.P. Hamers, F. Gallucci, P.D. Cobden, E. Kimball, M. van Sint Annaland, A novel reactor configuration for packed bed chemical-looping combustion of syngas, *Int. J. Greenh. Gas Control* 16 (2013) 1–12.
- [20] H.P. Hamers, F. Gallucci, G. Williams, M. van Sint Annaland, Experimental demonstration of CLC and the pressure effect in packed bed reactors using NiO/CaAl₂O₄ as oxygen carrier, *Fuel* 159 (2015) 828–836.
- [21] G.M. Zabetakis, Flammability characteristics of combustible gases and vapors, *Bur. Mines Bull.* 627 (1965) 20–47.
- [22] S. Noorman, M. van Sint Annaland, J.A.M. Kuipers, Packed bed reactor technology for chemical-looping combustion, *Ind. Eng. Chem. Res.* 46 (2007) 4212–4220.
- [23] L. Han, G.M. Bollas, Chemical-looping combustion in a reverse-flow fixed bed reactor, *Energy* 102 (2016) 669–681.
- [24] R.F. Kooiman, H.P. Hamers, F. Gallucci, M. van Sint Annaland, Experimental demonstration of two-stage packed bed chemical-looping combustion using syngas with CuO/Al₂O₃ and NiO/CaAl₂O₄ as oxygen carriers, *Ind. Eng. Chem. Res.* 54 (2015) 2001–2011.
- [25] A.R. Akhmadeev, V.A. Eremin, M.V. Ananyev, Kinetics of oxygen exchange with oxides Ba_{0.5}Sr_{0.5}(Co_{0.8}Fe_{0.2})_{1–x}MexO_{3–δ} (Me = Ta, W) in non-equilibrium conditions, *J. Solid State Electrochem.* (2024) 4973–4983.