Chemical Looping Combustion Using Two Different Perovskite Based Oxygen Carriers: A Pilot Study

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Two perovskite type oxygen carriers, for the application in chemical looping combustion, called C14 and C28 are investigated. The composition of C14 is CaMn₀.₃Mg₀.₇Oₓ–₀.₄ and CaMn₀.₇₇Mg₀.₃₋₀.₃₋₀.₃ for C28, respectively. Both oxygen carriers allow chemical looping with oxygen uncoupling (CLOU), they release oxygen under conditions with low oxygen partial pressure. The materials are tested in a 120 kWth pilot plant at TU Wien. Operating temperatures from 800°C to 960°C are investigated, further the influence of active inventory and air equivalence number is reviewed. In addition to the experiments in the pilot plant, particle analysis is performed. In total, the CLC operation for C14 was 29.5 h and 22.7 h for C28, resulting in 75 different operating points. Both oxygen carrier materials are able to fully convert the natural gas, used as fuel. A temperature dependency is noticeable for both, the best results are achieved at 960°C, the highest investigated temperature. Both, C14 and C28 are able to release about 10% of the total available oxygen via oxygen uncoupling. The performance of both oxygen carriers is strongly linked to the air equivalence number and the resulting amount of excess oxygen in the air reactor. Low oxygen partial pressures lead to incomplete fuel conversion.

Introduction

The reduction of CO₂ emission is one of the biggest challenges of humankind to slow down global warming. The International Panel on Climate Change (IPCC) identified the energy production in the industrial sector as the major CO₂ emitter.[1] Luckily, energy production sites are geographically focused, so they have a great potential for Carbon Capture and Storage (CCS).[2] By separating CO₂ from a flue gas stream, a process with CCS avoids emission of CO₂ to the atmosphere. The separated gas is compressed and stored consecutively. The CCS value chain involves the following consecutive steps: separation, compression, transport and storage of the CO₂.[3] The task of separation can be done by post-process capture, syngas/hydrogen capture, oxy-fuel combustion or inherent separation. The present work concerns investigation of a very energy efficient carbon capture process called chemical looping combustion (CLC). CLC uses the principle of unmixed combustion to separate CO₂ inherently and generate a pure CO₂ stream.

Chemical Looping Combustion

In the CLC process combustion air and fuel are never mixed. The highly irreversible combustion reaction is divided into two reactions. Two reactors are necessary, the air reactor (AR) and the fuel reactor (FR). The needed transport of oxygen from the combustion air to the fuel is realized with a so called oxygen carrier (OC). The OC is oxidized in the AR (compare Eq. 1) and reduced in the FR by the fuel (compare Eq. 2). With this arrangement unmixed combustion is possible, after condensation of water a pure CO₂ stream is generated. A scheme of the process is presented in Figure 1.

\[
\text{MeO}_x + \frac{1}{2} \text{O}_2 \rightarrow \text{MeO}_x
\]  

Since the separation of CO₂ is inherent, CLC is highly suitable for CCS applications. In conventional carbon capture
processes, the CO₂ capture from the flue gas goes along with high energy losses caused by gas separation.

However, the technology of CLC has the advantage that the net released heat is the same as in a regular combustion process and the CO₂ is never mixed with the combustion air[9]. The CLC process consisting of AR and FR can be designed as a fluidized bed process.[5,6] The fluidized bed reactors are interconnected with loop seals. These seals guarantee gas tightness between the reactors and transport the solids from one reactor to the other. They are fluidized with inert gas or steam.

**Oxygen Carriers**

Next to the reactor system, the oxygen carrier is a crucial component of the CLC process. Sufficient oxygen and heat transport from the AR to the FR are the main requirements the OC has to fulfill. Furthermore the OC has to be highly reactive in the FR, oxidation in the AR must not be limited and the OC has to withstand the harsh conditions in the CLC system (mechanical, chemical and thermal stress). Along with these properties the OC also has to be cost efficient over lifetime, no danger for the human health, and environmentally friendly.[7] Common oxygen carrier materials are iron oxide, cobalt oxide, copper oxide, ilmenite, manganese oxide, nickel oxide, and mixed oxides.

As a specialty of the CLC process, chemical looping with oxygen uncoupling (CLOU),[8,9] has been developed. The difference between conventional CLC and CLOU lies in the properties of the OC. Conventional oxygen carriers have to react with the fuel in the FR in a heterogeneous reaction. In contrast, CLOU oxygen carriers release oxygen under the conditions in the FR and a homogeneous reaction with a gaseous fuel is possible. The release of oxygen is due to an instability of the oxidized OC under conditions with low oxygen partial pressure. The equilibrium oxygen partial pressure is also a drawback of the CLOU process, though. The amount of oxygen in the AR has to be above the equilibrium oxygen partial pressure to allow full oxidation of the OC.

**Perovskite Type Oxygen Carriers**

The common composition of a perovskite type mineral is CaTiO₃. The perovskite structure can be reduced to a generalized form, ABO₃. The cation on the A site is larger than the one on the B site. Many metals show stable perovskite structures. It is possible to replace parts of the A and B site cations to synthesize new multicomponent perovskites with a generalized form of Aₓ₋ₓ'Bₓ'Bₚ'Oₙ₋ₙ'[10].

Perovskites have been investigated as oxidation and reduction catalysts.[11,12] These materials are used in solid oxide fuel cell applications because they show a high mobility of O²⁻. Perovskites are able to release oxygen in atmospheres with low oxygen partial pressure.

This makes them suitable as OC in a CLOU process.[13] A promising perovskite for CLOU is CaMnO₃₋₋. The influence of the oxygen partial pressure on CaMnO₃₋₋ has been investigated by Bakken et al.[14] They report a correlation of 3 – δ and oxygen partial pressure, the material is higher oxidized at higher oxygen concentrations. A decomposition of the perovskite under conditions forcing deep reduction has been observed. This behavior and structural changes during oxidation and reduction have been investigated by Bakken et al.[15] and Leonidova et al.[16] This Perovskite, CaMnO₃₋₋, is the starting basis for the materials investigated in this study, CaMnₓ₋ₓMgₓ'Oₙ₋ₙ₋ and CaMnₓ₋ₓ₋₋₋Mgₓ₋₋₋₋Oₙ₋ₙ₋₋₋.

Jing et al.[17] investigated the effect of adding MgO to CaMnO₃₋₋ by replacing some manganese. A wider range of B site replacements has been investigated by Hallberg et al.[18] Continuous operation in a 300W₀ unit using a perovskite containing titanium in parallel with manganese at the B site has been carried out by Ryden et al.[19] All these tests showed that perovskite type OC materials have a great potential in CLC applications. Jing et al.[20] investigated the influence of production conditions on the suitability of CaMn₋ₓ₋₋₋Mgₓ'Oₙ₋ₙ₋₋₋ for CLC operation. This work has been performed within the FP7 project INNOCUOUS. The materials tested in this work have been developed consecutively in the same project.

**Experimental**

**Analysis of OC Particles**

**Particle Size Distribution**

A laser diffraction analyzer (Mastersizer 2000) is used to measure the particle size distribution (PSD) of the OC. The dry-dispersion unit (Scirocco 2000 B), attached to the analyzer, is used for the measurements. An OC sample of 10 g is dispersed with air for the measurement. Each series of sizing implies 5 single measurements. The particle size spectrum of the detector is 0.02 m to 2000 m. In this study the parameters d₁₀,3, d₅₀,3 and d₉₀,3 are used. They are derived from the cumulative size distribution, the d₁₀,3 stands for the diameter that cuts off 10.3 % of the particles that are smaller, the d₅₀,3 cuts off 50.3 % and the d₉₀,3 90.3 %.

**Degree of Oxidation, R_OC and CLOU Potential**

To determine the degree of oxidation (X₀, compare Eq. 4), the oxygen transport capacity (R_OC, compare Eq. 3) has to be determined first. R_OC is measured with fresh particles in a thermogravimetric analyzer (TGA, NETSCH STA 409). An amount of 50 mg oxygen carrier is placed in the ceramic crucible of the TGA. The sample is heated to 950 °C in air to fully oxidize the material (m₀₀). Afterwards the sample is reduced with a mixture of 30 vol.% hydrogen in nitrogen until no change in the weight of the sample is observed (m_red). The oxygen transport capacity is calculated as shown in Eq. 3.
Since C14 and C28 are CLOU materials, the share of the CLOU effect ($R_{OC\text{,CLOU}}$) to the $R_{OC}$ is also determined. The procedure is similar to the determination of the $R_{OC}$, the only difference is the use of nitrogen, instead of hydrogen, during the reduction phase.

$$R_{OC} = \frac{m_{\text{ox}} - m_{\text{red}}}{m_{\text{ox}}}$$ (3)

The oxygen carrier samples taken from the pilot plant during the experiments are cooled immediately in an inert gas atmosphere (Argon). Afterwards they are weighed and oxidized in a muffle furnace. According to Eq. 4 the degree of oxidation is accessible, where $m$ is the initial weight of the dried sample. A detailed description of this procedure can be found elsewhere.\(^[21]\) $\Delta X_s$ is the difference between the $X_s$ of a sample taken from ULS and the $X_s$ of a sample taken from the LLS for the same operating point.

$$X_s = 1 - \frac{m_{\text{ox}} - m}{m_{\text{ox}} \cdot R_{OC}}$$ (4)

**Elemental Composition of OC**

X-ray fluorescence spectroscopic analysis (XRF - analysis) is used to determine the elemental composition of the oxygen carrier material. Samples of the fresh material and of used material after the experiments are taken. All samples are treated in the same way. The samples are heated with a flux material (Li – per-borate) until they dissolve melting. Afterwards the samples are cooled down and a transparent glass bead is gained from each sample. These glass beads are used for the XRF – analysis.

**Reactor System Used in this Study**

All CLC experiments in this study are carried out in a dual circulating fluidized bed reactor system (DCFB).\(^[22]\) The pilot plant consists of the two fluidized bed reactors, AR and FR. The reactors are interconnected by the upper and the lower loop seal. They avoid gas mixing between the reactors while transporting the solids from the AR to the FR and vice versa. The AR operates as a riser, it is responsible for solids circulation from the AR to the FR. The solids transport of the OC from the FR back to the AR is realized with the lower loop seal.

Air is the fluidizing agent in the AR, while the gaseous fuel is the only gas for fluidization in the FR. Steam is used to fluidize the loop seals. The FR has an internal loop seal (ILS) to close the internal solids circulation loop of the FR. Due to the DCFB arrangement of the reactors, two solids circulation loops can be identified; the global solids circulation between AR and FR and internal solids circulation in the FR. A big benefit of the DCFB system is the direct hydraulic communication to the AR and the FR via the lower loop seal (LLS). This allows high rates of global solids circulation with a stable solids distribution in the system. The DCFB system is described in more detail by Kolbitsch et al.\(^[23]\) Figure 2 shows a sketch of the DCFB pilot plant, the main dimensions of the reactor system are presented in Table 1.

![Figure 2. Scheme of the DCFB pilot plant.](image)
OC samples are taken regularly during the test runs under hot conditions from the DCFB plant. For each operating point at least one sample is taken from the upper loop seal (ULS) and the LLS. The sample taken from the ULS represents the conditions of the particles leaving the AR and the LLS sample represents the particles leaving the FR via the LLS to the AR. A special device is used for the sampling, its function is described in detail in.[21,22] The gas streams leaving the reactors of the DCFB pilot plant are mixed in a post combustion chamber, dust in the flue gas is separated in a baghouse filter. The fines are collected in the so called filter box.

Data Evaluation

During stable operating conditions for one parameter set, mean values of the measured data are calculated. The time frame is in the range of 5 min to 15 min, the recording interval for the data collection is 10s. The data containing the mean values is evaluated with the process simulation software IPSEpro. An overdetermined system of equations is generated with the help of mass and energy balances (from the process model) and the measured data. The measured data, fed to the process model, include a tolerance assigned to each measurement value reflecting its quality and deviations during the observed time interval. This system is solved with a least square approach, giving a balanced solution. This solution represents an operating condition with a probability of 95% to be the most accurate possibility, with the given data. For each solution, mass and energy balance is strictly fulfilled by the process model. A detailed explanation of this method can be found in.[23] Process parameters like global solids circulation rate or oxygen carrier to fuel ratio, which cannot be directly measured, are accessible via the evaluation with the process simulation.

Air Equivalence Ratio

Like the air ratio in conventional combustion processes, the air equivalence ratio (λ) compares the oxygen fed to the AR with the oxygen demand for complete combustion of the fuel fed to the FR. Reducing the amount of air fed to the AR for a given fuel power causes a lower air equivalence ratio. This leads to a reduced solids circulation rate due to the lower gas flow and decreased solid entrainment in the AR. Reducing the air in the AR and compensating the lack of gas with an inert gas results in a reduced air equivalence ratio with a constant solids circulation.

\[
\lambda = \frac{m_{O_2,AR}}{m_{O_2,FR_{in}}}
\]  (5)

Methane Conversion

The methane conversion \(X_{CH_4}\) is an indicator of the reactivity of the oxygen carrier towards methane:

\[
X_{CH_4} = 1 - \frac{X_{CH_4}}{X_{CH_4} + X_{CO_2} + X_{CO}}
\]  (6)

Carbon Dioxide Yield

The methane conversion only represents the reactivity of the oxygen carriers towards methane. With the focus on carbon capture, the carbon dioxide yield \(Y_{CO_2}\) is the more important parameter. It reflects the ability of the OC for full conversion of the hydrocarbons towards \(CO_2\):

\[
Y_{CO_2} = \frac{x_{CO_2}}{x_{CH_4} + x_{CO_2} + x_{CO}}
\]  (7)

In the case of methane as fuel and assuming that no higher hydrocarbons are formed, \(X_{CH_4}\) and \(Y_{CO_2}\) represent the carbon balance in the FR off gas. The difference between these two parameters gives the amount of carbon monoxide and the balance of \(X_{CH_4}\) to hundred gives the amount of methane.

Oxygen Carrier to Fuel Ratio

The above mentioned parameters \(X_{CH_4}\) and \(Y_{CO_2}\) are important figures to describe the performance of an OC. Comparing different materials only by the varied process parameter is not sufficient since the used materials often differ in many parameters: the oxygen transport capacity (\(R_{oc}\)), the particle density and the thermodynamic properties. As a consequence these parameters do not provide enough information to compare different OCs. The oxygen carrier to fuel ratio \(\Phi\) connects the oxygen transport capacity of the OC, the degree of oxidation of the particles leaving the AR, the global solids circulation rate and the oxygen demand of the fuel. With this parameter it is possible to compare OCs, even if their physical properties are different.

\[
\Phi = \frac{m_{O_2,OC}}{m_{O_2,FR_{in}}}
\]  (8)

The Oxygen Carriers Used in this Work

Two oxygen carriers are tested in this study, called C14 and C28. Both materials are perovskites, but with different stoichiometry. The composition of C14 is CaMn\(_{0.9}\)Mg\(_{6}\)(O\(_3\))\(_{4}\) and CaMn\(_{0.75}\)Mg\(_{8}\)(Ti\(_{0.125}\)O\(_{3}\))\(_{4}\) is the composition of C28. C14
and C28 are so called CLOU oxygen carriers. Both materials have been developed in the FP7 project INNOC-UOUS. The OCs have been produced by VITO via spray drying followed by calcination. The mean particle size, here \( d_{50.3} \), is used as measure for the mean diameter, of the unused material is 135 μm for C14 and 151 μm for C28, respectively. Further specifications of the oxygen carriers can be found in Table 4 and Table 5. C14 has been investigated by Källén et al. in a 10kWth pilot plant, first results of both materials have been published by Mayer et al.. Extensive kinetic evaluation of the C14 material has been carried out by de Diego et al.. The kinetics of C28 have been investigated by Abad et al..

Operating Conditions

A parameter variation is carried out for each OC material to be able to describe its performance. Table 3 shows the operating ranges of both experimental campaigns, one with C14 and one with C28. The oxygen carrier inventory, the air equivalence number, the reactor temperature and the fuel power are the main parameters, that are varied. Other process parameters cannot be adjusted, they are process related. The experimental campaign, covering the operating range reported in Table 3, featured 40 operating points for C14 and 35 for C28 respectively. The total active inventory \( m_{\text{total,act}} \) reported in Table 3 is the amount of OC in the reactors (AR and FR) without the material in the loop seals, cyclones and downcomers. The pressure drop over the fluidized bed and allows the calculation of the active inventory.

The fuel used for all operating conditions in this study is sweet natural gas (n.g.) from the local grid. The composition of the fuel is reported in Table 2.

Results and Discussion

Investigation of OC Particle Properties

During and after the CLC experiments, samples of both OC materials are taken on a regular basis. For the C14 material the total duration of the CLC operation is 29.5 h within four experimental runs. In total 40 different operating points are investigated. For C28, 22.7 h of CLC operation divided in three experimental runs give 35 different operating points.

The particle size distribution of fresh material and used material is determined and reported in Table 4. The C14 sample after Exp3 represents the material initially filled into the pilot plant for Exp2. After Exp2 the unit has not been emptied and taking a sample, suitable for particle size determination, was not possible. The procedure used for sampling during operation is expected to be selective for certain diameters, as a consequence only samples taken from the OC container are used for particle size analysis. The bulk density \( \rho_b \) is determined of fresh material and of material after the last experiment, for C14 and C28. The results of the bulk density measurements are also shown in Table 4. Fresh C14 has a mean particle diameter of 135.2 μm and a bulk density of 1565 kg/m³. After the whole experimental campaign the mean particle diameter of C14 does not significantly change. The \( d_{50.3} \) lowers from 198.3 μm to 181.4 μm, so the amount of larger particles decreases with time and the \( d_{50.3} \) increases slightly. This gives an overall narrower particle size distribution. Additionally the bulk density increases from 1565 kg/m³ to 1983 kg/m³ in this time. For the C28 a similar behavior is observed. The biggest difference is the decrease of the \( d_{50.3} \), which is significant, compared to the C14 results. Also for the C28 the bulk density increases with operational time. The decrease of particle size and the narrowing of the PSD can be explained with the separation efficiency of the cyclones used for particle separation. They have a critical particle diameter for a given particle density that can be separated. This is valid for too small particles and for light large particles. For a better understanding of this, scanning electron microscope (SEM) pictures of the C28 material are used to identify potential changes in the morphology of the particles.

Figure 3 shows a fresh, unused C28 particle with a heavily jointed surface. In contrast, Figure 4, shows a particle after the experimental campaign corresponding to 22.7 h of CLC operation. This particle has a dense and smooth surface. This result shows that the surface area of fresh particles is definitely different to the one of used particles. Optimizations during the production process should not focus only on fresh particles, the changes in the particle morphology during continuous CLC operation have to be taken into account. This effect does not explain the above mentioned increase of the bulk density of the material, though.

| Table 3. Operating conditions (natural gas is described in Table 2). |
|------------------|------------------|------------------|------------------|------------------|
| \( m_{\text{total,act}} \) [kg] | \( \lambda \) | \( P_{\text{add,n}} \) [kWth] | \( T_{\text{in}} \) [°C] | fuel |
| C14 18–32 | 1.2–2.0 | 50–120 | 900–960 | n.g. |
| C28 12–30 | 1.1–1.9 | 50–100 | 950–960 | n.g. |

| Table 4. Particle size and bulk density of fresh and used C14 and C28 particles. |
|------------------|------------------|------------------|------------------|------------------|
| unit | \( d_{10.3} \) [μm] | \( d_{50.3} \) [μm] | \( d_{90.3} \) [μm] | \( \rho_b \) [kg/m³] |
| C14 fresh | 91.3 | 135.2 | 198.3 | 1565 |
| after Exp1 | 96.6 | 130.0 | 180.1 | – |
| after Exp3 | 99.1 | 136.3 | 187.3 | – |
| after Exp4 | 95.6 | 131.7 | 181.4 | 1983 |
| C28 fresh | 106.6 | 151.5 | 215.3 | 1232 |
| after Exp1 | 96.6 | 141.0 | 206.4 | – |
| after Exp2 | 97.3 | 139.4 | 199.5 | – |
| after Exp3 | 96.4 | 137.8 | 196.8 | 1643 |
Figure 5 shows a SEM picture of a C28 sample with less magnification. Fragments of broken spheres can be identified in the bulk, they are highlighted in the figure. These fragments could potentially explain the increase in bulk density, without significant changes of the particle size distribution. During the production process hollow spheres are generated. The separation of fines and too large particles is done by sieving, so spheres are not separated, because they have the correct particle size. The density of the particles is lower, though. The conditions during CLC operation do not only apply thermal stress, but also chemical and physical stress is applied to the particles. This leads to a destruction of the spheres, fragments are elutriated from the reactor system and the bulk density increases.

XRF is used to identify potential decomposition of the OC on elemental basis. Table 5 shows the results of the analysis for the C14 and C28 material.

| Element | Ca [wt.%) | Mn [wt.%) | Mg [wt.%) | Ti [wt.%) |
|---------|-----------|-----------|-----------|-----------|
| C14     |           |           |           |           |
| fresh   | 50.8      | 46.0      | 3.2       | –         |
| after Exp1 | 47.5   | 48.2      | 4.3       | –         |
| after Exp2 | 48.4   | 48.2      | 3.4       | –         |
| after Exp3 | 50.0   | 46.8      | 3.2       | –         |
| after Exp4 | 48.1   | 48.6      | 3.3       | –         |
| C28     |           |           |           |           |
| fresh   | 49.0      | 39.3      | 3.4       | 8.3       |
| after Exp3 | 48.2   | 39.4      | 3.8       | 8.6       |
| Filterbox | 49.0   | 38.5      | 3.4       | 9.1       |

Table 5. Results of XRF analyses of oxygen carriers.

Fresh material is the reference to identify any potential change of the stoichiometric composition. This analysis is carried out after each experiment for C14. During the testing of C28 only fresh material and a sample after the whole experimental campaign are analyzed. Additionally the dust collected in the filterbox is also analyzed. As shown in Table 5 the composition of C14 does not change dramatically, neither for the C28 samples. The analyzed dust has nearly the same composition as the OC material taken from the reactors. These analyses show that the material does not decompose during the CLC operation, even though the morphology of the particles changes dramatically and chemical stress is applied during operation.

To be able to calculate the degree of oxidation of the solids samples during the experiments, R_OC and R_OC,CLOU are determined in a TGA (compare Experimental Section). The results are depicted in Figure 6. The total oxygen transport capacity is compared with the amount of available CLOU.
oxygen. It can be seen that the ratio of the CLOU effect to R_{OC} is only 6% for C14 and 9% for C28. R_{OC} is larger for C14, the absolute amount of available CLOU oxygen is larger for C28, though. Figure 6 also shows the smallest and biggest ΔX_{S} measured during the experiments. It can be seen that the average ΔX_{S} is in the range of available CLOU oxygen and the particles never undergo deep reduction.

Pilot Plant Parameter Variation

In the following sections the results of the parameter variation are discussed. As mentioned above the focus lies on operating temperature, inventory and solids circulation rate. During all experiments CO_{2} and CO are measured next to oxygen in the AR off gas, to identify a potential carbon formation on the OC in the FR and burn-off in the AR. During the whole experimental campaign no CO_{2} nor CO are detected in the AR off gas. As a consequence, carbon formation on the OC material in the FR can be excluded.

In the following discussion of the results X_{CH_{4}} and Y_{CO_{2}} are used to describe the fuel conversion performance. As mentioned above with this two parameters, also the amount of carbon monoxide is indicated. It is the difference between X_{CH_{4}} and Y_{CO_{2}} as a result of the carbon balance. Higher hydrocarbons (Ethane and larger) have not been observed during all operating conditions. The amount of hydrogen was in the same range as the carbon monoxide for the C14 material. In the case of C28, the amount of hydrogen was two times higher than the amount of carbon monoxide.

Temperature

The FR temperature is varied for the C14 material from 900°C to 960°C. Four operating points are investigated in this temperature range. The methane conversion rises from 75% to 90% in this 60 K window. The results of the temperature variation are shown in Figure 7. For the C28 material only two temperatures are evaluated as described above, 950°C and 960°C. The total amount of C28 is limited, so the rest of the temperature variation is performed during a cool down phase of an experiment as a dynamic operating point. All parameters of the CLC process are kept constant, only the cooling system is set to allow a steady temperature decrease of 5 K/min. In this case the methane conversion is derived from the online gas analysis. The data obtained during the dynamic temperature variation should only highlight the strong temperature dependency of the material. The results of the steady state operating points and the dynamic temperature variation are both depicted in Figure 7. The fuel conversion performance of the C28 decreases from 98% methane conversion at 960°C to 50% at 800°C. The results for C14 indicate that the increase of fuel conversion with temperature starts to lower at 950°C. Since the equilibrium oxygen partial pressure is lower for higher temperatures, oxidation of C14 in the AR seems to limit above 950°C for the given operating conditions, but further investigations are necessary to clarify this in more detail. In the investigated temperature range, the impact of the process temperature on the fuel conversion is high for both materials.

Fuel Power Variation

Next to the temperature, the influence of the fuel load of the FR on the process performance is investigated. The FR is only fluidized with the gaseous fuel, so varying the fuel loading has an impact on the fluidized bed in the FR. In addition, the amount of air fed to the AR has to be adjusted to keep the air equivalence number constant. This influences the global solids circulation, but keeps the available oxygen in the AR constant. The amount of OC is not varied during this experiment, as a consequence the specific FR inventory (m_{spec,FR}) changes with fuel power. Due to these limitations the amount of comparable operating conditions is limited.
The results of the fuel power variation are reported in Figure 8 for both oxygen carrier materials. For C14 the investigated range of fuel power is 55 kW\textsubscript{th} to 120 kW\textsubscript{th}. C28 is only investigated at 60 kW\textsubscript{th} and 80 kW\textsubscript{th}. To be able to compare the different load points, the OC inventory is kept as constant as possible for each variation. For C14 \(m_{\text{total,act}}\) was 20 kg to 27 kg, for C28 \(m_{\text{total,act}}\) was 15 kg to 16 kg. The air, fed to the AR, is adjusted to keep the air equivalence number in the same range, 1.3 to 1.5 for C14 and 1.5 to 1.7 for C28.

The fuel conversion drops for both materials with increasing fuel power. As discussed above, high load points cause low specific inventories and high solids circulation rates compared to operating conditions with low fuel power. To identify the reason for the drop in fuel conversion, two parameters have to be further investigated. First, the specific FR inventory and second the solids circulation rate. Both are discussed in the following sections of this work.

**Solids Inventory Variation**

Figure 9 shows the influence of the FR inventory on the fuel conversion for similar operating conditions (FR temperature, fuel power and air equivalence number). The influence of the FR inventory is more pronounced for C28 than for C14. The trend towards higher conversion with more solids in the reactor is the same for both materials.

To be able to compare operating points with varying inventory, other operating parameters have to be constant. This limits the amount of comparable operating points. The fuel power specific FR inventory \(m_{\text{spec,FR}}\) equals the different fuel loadings and allows to compare a wider range of operating points, since the fuel loading does not have to be constant. The influence of \(m_{\text{spec,FR}}\) on the fuel conversion performance is shown in Figure 10. A much wider range of operating conditions is now comparable. The results show a significant influence of \(m_{\text{spec,FR}}\) on \(X_{\text{CH}_4}\) and \(Y_{\text{CO}_2}\). Comparison of the two oxygen carriers shows that C28 is able to convert the fuel with less specific inventory in the FR. C28 is able to fully convert the fuel with \(m_{\text{spec,FR}}\) of 320 kg/MW. Full conversion is also possible with C14, but 360 kg/MW are necessary in the FR. Another difference between the two
OCs is the mismatch between $X_{\text{CH}_4}$ and $Y_{\text{CO}_2}$, which represents the amount of carbon monoxide in the FR offgas. For C28 this value is low, even under conditions with incomplete conversion, in case of C14 more carbon monoxide is present in the flue gas.

**The Influence of $\Phi$ on the Fuel Conversion**

The introduction of the specific inventory already allows the comparison of a wide range of operating conditions with a focus on the inventory. The oxygen carrier to fuel ratio $\Phi$ allows the comparison of operating points with different solids circulation rates, fuel loadings and air equivalence numbers. Figure 11 compares the influence of $\Phi$ for both materials on the methane conversion and the carbon dioxide yield. Here, C28 performs better than C14 under same conditions. Full conversion of the methane is achieved with a $\Phi$ of 25 for C28 and 32 for C14.

**Effect of Oxygen Concentration in the Air Reactor Feed**

The achievable $X_8$ of perovskite materials and in particular of C14 and C28 is linked to oxygen concentration in the AR. Due to this behaviour, the effect of the oxygen partial pressure in the AR is investigated. The simplest way to vary the amount of oxygen in the AR is to adjust the air equivalence number. The results of this variation are depicted in Figure 12. Additionally $\Delta X_8$ and $X_8,\text{ AR}$ are shown, to highlight the change of the particle conversion.

Lowering the air equivalence number causes a drop in performance for both materials. Data suggests that the increase of fuel conversion with $\lambda$ stagnates for C14 for $\lambda$ larger than 1.8. C28 shows a more linear correlation of fuel conversion and $\lambda$ in the investigated range. Both materials are more oxidized at high air equivalence numbers, the difference is below 5%, though. With decreasing $\lambda$ the $\Delta X_8$ increases, indicating that the OC gets more reduced in the FR under these conditions. This effect is similar for both, C14 and C28. Reducing the air equivalence number by reducing the amount of air, fed to the AR, also lowers the solids circulation rate and as a consequence $\Phi$. As already shown, lowering $\Phi$ has a negative effect on fuel conversion, the drop of fuel conversion due to lowering $\lambda$ by decreasing the air in the AR can not be fully explained with this parameter variation.

As mentioned above, varying the air equivalence number by changing the total amount of air fed to the AR, also changes the solids circulation rate. To avoid this, a second variation is carried out where the influence of the solids circulation rate during the evaluation of the air equivalence number, is avoided. To achieve this, the missing amount of air due to lowering $\lambda$ is compensated with nitrogen. The total amount of gas fed to the AR is constant, the gas velocity remains the same and the global solids circulation rate is not influenced. The results of this experiment are shown in Figure 13.

A constant drop with a decreasing air equivalent number in fuel conversion is observed for both materials. $\Delta X_8$ remains almost constant for both materials, but the $X_8$ of the solids leaving the AR drops in both cases. This leads to a lower $\Phi$ value for low air equivalence numbers and a lower fuel conversion. The results in Figure 13 show that the low fuel conversion at low air equivalence numbers is due to the low
oxygen partial pressure and the resulting low degree of oxidation of the particles. This effect is a result of the thermodynamic properties of the OC, lowering the oxygen partial pressure in the AR would lead to less oxidized particles leaving the AR, leading to less available oxygen via CLOU in the FR and to a decrease in fuel conversion performance.

Data of the C14 testing is used to compare the two possibilities of varying the air equivalence number. First, via the total amount of air fed to the AR and second via dilution of the AR feed with nitrogen. The results are shown in Figure 14. Methane conversion is identical for both methods, even though the change of solids circulation rate, indicated as solids flux $G_{S,AR}$, is different. The other difference between the two methods is the change of $\bar{X}_S$ for the conventional method and the almost constant value for the dilution experiments. Variation of the air equivalence number and as a consequence the oxygen partial pressure in the AR has an influence on the fuel conversion in the FR. The solids circulation rate is not the sole determining factor during the variation of the air equivalence number.

**Conclusions**

The performance of two perovskite type oxygen carrier materials is evaluated in a wide range of operating conditions. Both oxygen carriers show a slight change in particle size due to elutriation of particle fragments over the course of the experiments. These fragments are broken spheres, generated during production, which are elutriated during operation. The chemical composition of the two OC materials does not change with time, even though physical, thermal and chemical stress is applied. C14 and C28 are CLOU materials, the amount of available CLOU oxygen is in the range of 10% of the total oxygen transport capacity. Analysis of OC samples during operation shows that the used oxygen transport capacity is in this range and particles do not undergo deep reduction.

Variation of the operating temperature indicates a potential upper limit for fuel conversion with increasing temperatures for C14 for C28 this effect is not observed in the investigated temperature range (800°C to 960°C). The variation of fuel power and inherently the specific inventory show that full fuel conversion is achieved with $m_{\text{spec},FR}$ of 360 kg/MW for C14 and 320 kg/MW for C28. Lower specific inventories give incomplete fuel conversion. The oxidation state of the OC is linked with oxygen partial pressure in the AR. The air equivalence number and as a consequence $X_s$, have a direct influence on fuel conversion. With increasing excess oxygen in the AR, the fuel conversion increases. Both OC materials need high air equivalence numbers for sufficient oxidation in the AR and for good fuel conversion performance in the FR.

**Nomenclature**

- $\Delta X_s$ [-] Difference in degree of oxidation between particles in AR and FR
- $\Phi$ [-] Oxygen carrier to fuel ratio
- $m_{O_2,AR}$ [kg/h] Massflow of oxygen to AR
- $m_{O_2,OC}$ [kg/h] Massflow of available oxygen to the FR
- $\lambda$ [-] Air equivalence ratio
- $\rho_b$ [kg/m³] Bulk density
Abbreviations

AR Air reactor
CCS Carbon capture and storage
CLC Chemical looping combustion
CLOU Chemical looping with oxygen uncoupling
DCFB Dual circulating fluidized bed
Exp Experiment
FR Fuel reactor
ILS Internal loop seal
LLS Lower loop seal
n.g. Natural gas
OC Oxygen Carrier
PSD Particle size distribution
SEM Scanning electron microscope
TGA Thermo gravimetric analyzer
ULS Upper loop seal
XRF X-ray fluorescence

Keywords: Mn based oxygen carrier · CLOU · chemical looping combustion · pilot study

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Conflict of interest

The authors declare no conflict of interest.

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