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Performance of an oxy-polishing step in the 100 kW$_{th}$ chemical looping combustion prototype

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**A R T I C L E I N F O**

**Keywords:** Chemical looping combustion, Oxy-polishing, Post-oxidation chamber, Solid fuel, Manganese ore, Overall oxygen ratio

**A B S T R A C T**

Unconverted fuel gases are normally present in the gas leaving the fuel reactor of a Chemical Looping Combustion (CLC) process. Depending on several factors, including oxygen carrier and fuel volatiles content, the unconverted gases represent 5–30% of the oxygen needed for full combustion. Further conversion of these fuel components is imperative to achieve adequate combustion and to fulfill the requirements for CO$_2$ storage. An oxy-polishing step using highly concentrated O$_2$ to fully oxidize the fuel components offers a straightforward one-step way to reach complete combustion. However, systematic and detailed investigation is lacking while it is essential for design, scale up and optimization. In this work, the oxy-polishing is studied in a post-oxidation chamber (POC) of a 100 kW$_{th}$ unit using different solid fuels and manganese ores in the CLC process. With various flows of air as oxidation agent, the POC performance was evaluated under stable operations in a wide range of operating conditions. An overall oxygen ratio was defined to analyze the effect of O$_2$ excess in the POC. Experimental results show that the oxidation of fuel gas from the fuel reactor can be greatly enhanced by air entering the POC, with the gas conversion being improved from 87 to 90% before the POC to as high as 99–100% after the POC. Full oxidation in POC can be accomplished with excess of O$_2$. For the cases of incomplete oxidation, CO was normally found in higher concentrations than CH$_4$. In a few cases close to optimum, CO and O$_2$ simultaneously have normalized concentrations below 0.5–1% with a low overall oxygen ratio of around 1.01. The POC performance was further compared to the results from a simple reactor model.

1. Introduction

The mean atmospheric CO$_2$ concentration has been continuously rising after the pre-industrial decades, which is widely acknowledged as a major factor to the global warming. To limit the temperature increase within a reasonable level, elimination of CO$_2$ emission is imperative [1]. Chemical Looping Combustion (CLC) is a technology which can generate power with the feature of intrinsic CO$_2$ capture [2–6], thus avoiding the associated high energy penalty for a CO$_2$ separation step. Solid fuels, such as coal and biomass, are more extensively studied in CLC, due to their abundance and high accessibility [3,7], while gas and liquid fuels are also feasible in this process [8–12]. A simplified CLC system is basically composed of an air reactor, a fuel reactor and oxygen carrier particles circulating between the two reactors [11,13], as depicted in Fig. 1. In the fuel reactor, the solid fuel is decomposed to volatiles and char via reaction (R1), while the char is gasified to CO and H$_2$ via reaction (R2). The oxygen carrier, a metal oxide with MeO$_x$ as the oxidized form, supplies oxygen for the combustion of volatiles and gasification products in reaction (R3). The reduced oxygen carrier, in the form of MeO$_x$, is then conveyed to the air reactor to recover to the initial form via reaction (R4). The gas leaving the fuel reactor is mainly comprised of CO$_2$, H$_2$O and minor other components (e.g. S- and N-based species), where CO$_2$ can be captured by simple condensation of steam using a condenser. Thus, CLC is a combustion technology with low energy penalty for CO$_2$ capture [2,3,14]. To date, >3700 h of operation with solid fuels have been successfully demonstrated in continuous CLC units with a nominal thermal power of 0.5 kW$_{th}$ to 3 MW$_{th}$ [2–4,15–19]. Great progress has been achieved in oxygen carrier development, reaction kinetics, modeling and reactor design [3,7,20–26], while there are still some challenges to be faced and addressed [4,27].

**Fuel reactor:**

Solid fuel → Char + Volatiles

(R1)
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Better system performance as well as to have almost pure CO

Consequently, the effluent flue gas from fuel reactor needs to be further converted with methods leading to a combustion close to 100%, to get a better system performance as well as to have almost pure CO$_2$ stream for storage.

The post-oxidation step, also called oxy-polishing, uses highly concentrated gaseous O$_2$ to burn the residual fuel components from the fuel reactor. It is a straightforward one-step way to reach full combustion [46], which can address the described problems. The oxygen amount required in oxy-polishing step can be adjustable, which makes the CLC system more flexible for different fuels and operation conditions. Therefore, only a post-oxidation chamber and an ASU unit could be enough for the oxy-polishing step. In this case, full combustion with 100% CO$_2$ capture can be realized in the CLC process without the development and use of complex systems. Meanwhile, the heat released during the combustion of the unconverted fuel-reactor residual fuel components can be recovered by using a heat exchanger. The total energy penalty for gaseous O$_2$ generation in oxy-polishing step is at a comparably low level [6,7,48], because the required amount of O$_2$ is relatively quite low. Thus, in the case of a CLC system with 90% gas conversion, the added energy penalty will be only around 0.6% units [7].

$$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} ΔH^0 = -802.3 \text{kJ} \cdot \text{mol}^{-1} \quad \text{(R5)}$$

$$\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O} ΔH^0 = -241.8 \text{kJ} \cdot \text{mol}^{-1} \quad \text{(R6)}$$

$$\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2 ΔH^0 = -282.9 \text{kJ} \cdot \text{mol}^{-1} \quad \text{(R7)}$$

$$\text{C} + \text{O}_2 \rightarrow \text{CO}_2 ΔH^0 = -393.5 \text{kJ} \cdot \text{mol}^{-1} \quad \text{(R8)}$$

Although the oxy-polishing concept for CLC has been proposed in early publications [6,46], the systematic and detailed study of this technology is still lacking, while it is essential for design, scale up and optimization. Few works were performed on the oxy-polishing process [49-52] to examine the feasibility for further improving the combustion. In those works, the oxy-polishing was tested in a post-oxidation chamber (POC) using air or pure O$_2$, downstream of the fuel reactor. According to those preliminary tests, the oxygen demand after the POC was decreased to 2.5% from 18% before the POC at 860 °C for the 100 kW$_\text{th}$ system located at Chalmers University of Technology [49,50], meaning further improvement is needed. The oxy-polishing step was also tested by several cases in a 1 MW$_\text{th}$ unit erected at Technische Universität Darmstadt under partial CLC conditions, i.e., combustion in the fuel reactor was partly assisted by air flow [51], or full CLC conditions [52].

**Nomenclatures**

- $a$: example of the first variable for uncertainty analysis
- $b$: example of the second variable for uncertainty analysis
- $c$: example of the third variable for uncertainty analysis
- $\text{ASU}$: air separation unit
- $\text{CLC}$: chemical looping combustion
- $\text{CSTR}$: continuous stirred-tank reactor
- $f$: target function to be calculated, with $f = f(a, b, c, \ldots)$ being $a$, $b$, and $c$ the measured parameters
- $F_{\text{AR},ij}$: volumetric flow of air entering reactor $j$ ($j = \text{AR}$ or POC), L$_\text{s}$s$^{-1}$
- $F_{\text{CO},ij}$: molar flow of CO at the inlet ($i = \text{in}$) or outlet ($i = \text{out}$) of the POC reactor, mol·s$^{-1}$
- $F_{ij}$: molar flow rate for gas $i$ ($i = \text{CH}_4$, CO, CO$_2$, H$_2$, or O$_2$) at the outlet of reactor $j$ ($j = \text{FR}$ or POC), mol·s$^{-1}$
- MeO$_x$: oxygen carrier in oxidation state
- MeO$_{x,1}$: oxygen carrier in reduced state
- $m_{\text{FR}}$: fuel reactor solids inventory per MW$_\text{th}$ thermal power, kg·MW$_\text{th}^{-1}$
- POC: post-oxidation chamber
- $t$: time, min
- $T_{\text{FR}}$: fuel reactor temperature, °C
- $T_{\text{POC},i}$: temperature at the inlet ($i = \text{in}$) or outlet ($i = \text{out}$) of the POC reactor, °C
- $x_{i,j}$: concentration of gas $i$ ($i = \text{CH}_4$, CO, CO$_2$, H$_2$, or O$_2$) in reactor $j$ ($j = \text{FR}$, AR or POC)
- $x_{i,N}$: normalized concentration of gas $i$ ($i = \text{CH}_4$, CO, CO$_2$, H$_2$, or O$_2$) at the outlet of POC
- $\Omega_{\text{OD},j}$: oxygen demand at the outlet of reactor $j$ ($j = \text{FR}$ or POC)
- $\eta_{\text{gas},ij}$: gas conversion in reactor $j$ ($j = \text{FR}$ or POC)
- $λ_{i,\text{overall}}$: overall oxygen ratio considering fuel reactor and POC
- $σ_i$: absolute standard deviation of variable $i$ ($i = a, b, c, \ldots$)

**Fig. 1.** Schematic diagram of CLC technology using a solid fuel.
Complete combustion of those residual fuel components can be accomplished using a high flow rate of air or O₂ to the POC. However, the connection and the interrelation of the POC performance and the fuel reactor behavior was not fully explored, which would be important for getting a better system efficiency and a high CO₂ capture. The flow of O₂ to oxy-polishing step should be carefully studied to help to find out the optimal ratio of O₂ injection, because it is directly linked to the cost for oxygen generation and the purity of the CO₂ stream.

The present work explores the performance of the oxy-polishing step by using a POC reactor in a 100 kWth CLC unit, which can contribute to the design and scale up of an oxy-polishing reactor in large CLC systems. Stable operations were achieved in the 100 kWth unit by using three fuels and two manganese ores under different temperatures, fuel rates and oxygen carrier circulations, which produced various fuel compositions at the inlet of POC. These different cases, in combination with the change of air flow to the POC, resulted in a wide range of influencing factors for the behavior of POC. By comparing the gas composition at the inlet and outlet of the POC, an improved combustion was always reached, whereas a dependence on fuel reactor gas types was also found. Under conditions close to optimum, simultaneous low concentration of different combustibles was detected at the outlet of POC, which is encouraging for the scale up of oxy-polishing technology.

2. Experiments and simulation

2.1. Oxygen carriers

Two manganese ores were involved in the experimentation, which were denoted as SC and Sinaus, respectively, according to their as-received forms and origin/suppliers. The SC was a calcined (identified by “C”) manganese ore supplied by Sibelco (identified by letter “S”) company. The Sinaus was an Australian (identified by “aus”) manganese ore, where the term “Sin” indicated its sintered state in supply. These manganese ores were extensively used in the 10 and 100 kWth pilot CLC units in previous works [2,17,49], which showed good reactivity and physical properties. The ore particles received were mainly composed of Mn, Fe, Si and Al elements with a Fe/Mn molar ratio of 0.1 and 0.2 for SC and Sinaus, respectively [17,49]. Minor fractions of alkali, e.g. around 1 wt% K element, were also present in the fresh material, which could act as a catalyst favoring the gasification of char, thus, to reach a better combustion [43,53]. The manganese ores were crushed and sieved to smaller than 355 μm, ready for use in the 100 kWth unit. Some of the physical properties of these oxygen carrier particles are summarized in Table 1. The bulk density was determined following an ISO standard funnel method [54] by pouring an amount of particles to a cylinder container with a determined volume, which is important for the estimation of a suitable velocity of fluidization gas in the reactors of the CLC unit. The sieved oxygen carrier materials have an average particle size of d50 = 185 μm for SC and 175 μm for Sinaus, respectively, which was determined by sieving a weighted amount of particles through a series of stainless-steel standard sieves. The crushing strength of the particles was the average value for fracturing the 30 randomly selected particles, which was determined by a digital apparatus (FGN-5, Shimpo) and took a value of 3.2 and 3.5 N for SC and Sinaus, respectively. Attrition index of the manganese ore particles was determined at room temperature using a customized jet cup rig [55,56]. The attrition indexes of SC and Sinaus are 1.37 and 1.21 wt%h⁻¹, respectively, which in combination with the high crushing strength suggest their suitability for applying in fluidization systems [55,57].

2.2. Solid fuels

Steam cured biomass “black pellets” provided by Arbaflame from Norway, a type of wood char from Schütte in Germany, and a type of Colombian coal from Calenturitas mine, which were designated as BP, GWC and CAL, respectively, were used as fuels for the tests performed in the 100 kWth unit. These solid fuels were crushed and sieved to a median size of d50 = 1800, 250 and 130 μm for BP, GWC and CAL, respectively, before the experiments. Here, the median size of the fuel particles was determined with the same method for the oxygen carriers, as stated in the previous section. The proximate and ultimate analysis of the solid fuels were determined following an ISO and an ASTM standard method [58,59], respectively. As seen in Table 2, the BP pellets are a high-volatile biomass fuel, while the GWC wood char and CAL coal have significantly lower volatiles. The heating value of BP is lower than that of the other two fuels, which can be related to its lower carbon content and higher oxygen fraction. Thus, a higher flow rate of fuel would be expected for BP than GWC and CAL to reach the same thermal power.

2.3. Operation conditions in the 100 kWth system

In previous publications, details about the 100 kWth prototype were well documented [50,60], where more information can be found. The system is featured by a circulating fluidized-bed fuel reactor and a high efficiency 4-chamber carbon stripper located between the fuel and air reactor. These designs allow a long residence time of char inside the fuel reactor and an efficient separation of carbon and oxygen carrier in the carbon stripper, thus the loss of char to air reactor was minimized [18,60]. Experimental tests were conducted with two manganese ores, i.e. SC and Sinaus, and three solid fuels, i.e. BP, GWC and CAL, under various operation conditions, as seen in Table 3. The main variables during steady operations are the air flow rate to air reactor, F_air,AB, and the thermal power input, Pth, which were changed in the range of 28–42 Nm³h⁻¹ and 42–85 kWth, respectively, depending on the types of fuel and oxygen carrier, see Table 3. The variation of air flow to the air reactor is made to reach different solids circulation, since the latter is controlled by the air flow [61]. With the change of air flow, the solids circulation was varied, which resulted in the change of fuel reactor temperature, TFR, in a small interval of 960–970 °C. Except for that, the other operation parameters, such as air reactor temperature and fluidization gas flow, were kept roughly constant under stable operations. The fuel reactor, loop seals and carbon stripper were all fluidized with steam, while the fuel tank and pressure measuring ports along the reactor were usually swept with known flow rates of N₂. Gas from the outlet of the fuel reactor was first led to a condenser to remove the moisture and then to a gas analysis unit to determine the composition at room temperature. The concentration of CH₄, CO, CO₂, H₂ and O₂ were measured by an online gas analyzer (NGA2000, Rosemount ™) and registered with a data logger at a rate of one point per second. This gas analyzer can determine the concentration of CH₄, CO, CO₂ and O₂ in the range of 0–100 vol% and the concentration of H₂ within 0-20 vol%. The air-reactor gas was cooled down and analyzed by another analyzer (Sick Malhak, SIDOR) to determine the fractions of CO, CO₂ and O₂ within a range of 0–20 vol%, 0–5 vol% and 0–25 vol%, respectively. These determined gas concentrations in combination with the known amounts of N₂ entering the reactors were later used to calculate the molar flow rate of the measured gas component.

2.4. Post-oxidation chamber (POC)

Downstream of the cyclone of the fuel reactor, the gas was led to the POC for further combustion of fuel gases and/or char particles from the fuel reactor, see Fig. 2. The POC was a vertically situated cylindrical tube
manufactured with high-temperature-resistant steel and insulated by Table 3.

to facilitate the evaluation under different operation conditions, see

and outlet of POC were continuously monitored by a K-type thermal

with an inner diameter of 0.30 m and a length of 1.50 m, which was

was used as a zero-dimensional model composed of a series of continuous stirred-tank

theoretical ratio of O

in the effluent gas stream, the total gas molar flow rate can be
determined for each reactor.

where the

Fuel reactor (CSTR) to simulate the oxy-polishing process. Three inter

considered for comparisons with the POC results. This model, after a

validation with experiments, could be useful for guiding future scale-up

design of the POC subsystem in a CLC unit.

3. Data evaluation

3.1. Calculations

The molar flow rate, \( F_j \), with a unit of mol s\(^{-1}\), of the gas leaving the fuel reactor (\( j = \text{FR} \)) or the POC (\( j = \text{POC} \)) was calculated in Eq. (1) based on N\(_2\) flow, \( F_{N2,j} \), entering these reactors. Using a known molar flow of N\(_2\) and the concentration, \( x_{ij} \) (vol\%), of component \( i \) (i.e. CH\(_4\), CO, CO\(_2\), H\(_2\) or O\(_2\)) in the effluent gas stream, the total gas molar flow rate can be determined for each reactor.

\[
F_j = \frac{F_{N2,j}}{1 - \sum x_{ij}}
\]  

(1)

Then, the molar flow rate of gas component \( i \) in reactor \( j \) can be obtained in Eq. (2) using the total molar flow \( F_j \) calculated from Eq. (1) and the gas concentration \( x_{ij} \).

\[
F_{ij} = x_{ij} \cdot F_j
\]  

(2)

With the concentration, \( x_{ij} \) (i.e. CO, CH\(_4\), H\(_2\) or CO\(_2\)), at the outlet of reactor \( j \), a dimensionless oxygen demand, \( \Omega_{O2,j} \), representing the theoretical ratio of O\(_2\) required for complete oxidation of residual combustibles [18] can be calculated by Eq. (3).

\[
\Omega_{O2,j} = \frac{0.5x_{CO2,j} + 2x_{CO,j} + 0.5x_{H2,j}}{\Phi_0(x_{CO} + x_{CH4} + x_{CO2})}
\]  

(3)

where the \( \Phi_0 \) represents the stoichiometric moles of O\(_2\) per mole carbon for fully burning the fuel, being calculated as \( \Phi_0 = 1.05, 1.05 \) and 1.19 for BP, GWC and CAL fuels, respectively.

According to the values of oxygen demand, the gas conversion in reactor \( j \), \( \eta_{gas,j} \), which reflects how far or close from complete conversion of gaseous combustibles [49] to CO\(_2\) and H\(_2\)O, can be easily obtained as Eq. (4).

\[
\eta_{gas,j} = 1 - \Omega_{O2,j}
\]  

(4)

Specific solids inventory, \( m_{Bc} \), in the fuel reactor, with the unit of

<Table 2>

<table>
<thead>
<tr>
<th>Oxygen carrier</th>
<th>Fuel</th>
<th>( F_{th} ) (kW(_{th}))</th>
<th>( F_{gas,FR} ) (L(_s)(^{-1}))</th>
<th>( F_{gas,POC} ) (L(_s)(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>BP</td>
<td>67</td>
<td>28-42</td>
<td>0-6.7</td>
<td>[17]</td>
</tr>
<tr>
<td>SC</td>
<td>GWC</td>
<td>80</td>
<td>28-42</td>
<td>0.8-6.7</td>
<td>[17]</td>
</tr>
<tr>
<td>SC</td>
<td>GWC</td>
<td>42</td>
<td>38-42</td>
<td>1.7-3.3</td>
<td>[17]</td>
</tr>
<tr>
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<td>GWC</td>
<td>67</td>
<td>42</td>
<td>0.8-1.7</td>
<td>[17]</td>
</tr>
<tr>
<td>SC</td>
<td>CAL</td>
<td>85</td>
<td>28-42</td>
<td>0.5</td>
<td>[17]</td>
</tr>
<tr>
<td>Sinaus</td>
<td>BP</td>
<td>67</td>
<td>28-38</td>
<td>0-5</td>
<td>–</td>
</tr>
<tr>
<td>Sinaus</td>
<td>BP</td>
<td>51</td>
<td>38</td>
<td>0-3.3</td>
<td>–</td>
</tr>
<tr>
<td>Sinaus</td>
<td>GWC</td>
<td>55</td>
<td>33-42</td>
<td>0-5</td>
<td>[49]</td>
</tr>
<tr>
<td>Sinaus</td>
<td>CAL</td>
<td>65</td>
<td>28-42</td>
<td>0-6.7</td>
<td>[49]</td>
</tr>
</tbody>
</table>

<Table 3>

<p>| Main operation conditions of the 100 kW(_{th}) reactor. |
|-----------------|-------------------------------------------------|</p>
<table>
<thead>
<tr>
<th>Oxygen carrier</th>
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<td>0-6.7</td>
<td>[49]</td>
</tr>
</tbody>
</table>

<Fig. 2>

Sketch of the POC connecting the 100 kW\(_{th}\) fuel reactor cyclone.
kg·MW/kgfuel, which represents the mass of oxygen carrier particles per MW/kgfuel fuel [49], can be estimated by Eq. (5) using the measured pressure drop of the fuel reactor, \( \Delta \rho_{FR} \) (Pa), and the thermal power input, \( P_{in} \) (kWth).

\[
m_{FR} = \frac{A_p}{g} \cdot \frac{\Delta \rho_{FR}}{P_{in}} \cdot 10^3
\]  

where \( A_p \) (m²) is the geometric inner cross-section area of the fuel reactor tube and \( g \) (m·s⁻²) refers to the gravitational acceleration.

To make a comparison for the results from different operation conditions, the concentration of component \( i (= \text{CH}_4, \text{CO}, \text{H}_2 \text{ or O}_2) \) at POC outlet was normalized by the total gaseous carbon fraction using Eq. (6).

\[
x_i = \frac{x_i}{x_{\text{CH}_4} + x_{\text{CO}} + x_{\text{CO}_2}} \quad (\text{POC})
\]  

A new parameter, namely overall oxygen ratio (\( \lambda_{O,\text{overall}} \)), was defined to evaluate the relation of full combustion and excess of \( \text{O}_2 \) in the POC. As seen in Eq. (7), the total oxygen provided by the oxygen carrier in the fuel reactor and the air to the POC was calculated by the two numerators with the concentration of \( \text{O}_2, \text{CO}_2, \text{CO} \) and \( \text{H}_2 \) from the POC and the theoretic oxygen ratio \( \Phi_o \) for the fuel. Thus, the value of \( \lambda_{O,\text{overall}} \) can be calculated as the ratio of the above obtained total oxygen and the stoichiometric oxygen for full fuel combustion determined by the denominators.

\[
\lambda_{O,\text{overall}} = \frac{x_i}{\Phi_o(x_i + x_{\text{CO}} + x_{\text{CO}_2})_{\text{POC}} + \Phi_o - 1}
\]  

where the \( \Phi_o \) and \( x_i \) represent the stoichiometric moles of \( m \) for mole carbon for fully burning the fuel and the measured concentration of component \( i (= \text{CH}_4, \text{CO}, \text{CO}_2, \text{H}_2 \text{ or O}_2) \) at the outlet of POC, as explained in Eq. (3) and Eq. (6), respectively.

3.2. Uncertainty analysis

Gas concentration in the stream from reactors is the basis for calculating the above-mentioned parameters. The uncertainty associated with the measuring apparatus can propagate to the calculation results and lead to some errors in the values. For different gas analyzers used in this work, the accuracy of each gas component is summarized in Table 4, according to the technical data provided by the manufacturer. Except for that, these analyzers can have some significant drifts as a function of week, even under normal use. To minimize this, the gas analyzers were calibrated every day before the experiments.

With the uncertainty shown in Table 4, the relative errors of calculation results from above equations can be estimated through the formula for uncertainty propagation in Eq. (8), assuming \( f \) as the target to be calculated, which has a known relation of \( f = f(a, b, c, \ldots) \) with the measured variables, e.g. \( a, b, c \), etc. Here, these measured variables can be the gas concentration obtained from the 100 kWth unit operation, while the \( f \) can be the terms on the left side of the above equations.

\[
error = \left[ \sigma_a^2 \cdot \left( \frac{df}{da} \right)^2 + \sigma_b^2 \cdot \left( \frac{df}{db} \right)^2 + \sigma_c^2 \cdot \left( \frac{df}{dc} \right)^2 + \cdots \right]^{0.5} \cdot 100\%
\]  

where the symbol \( \sigma_i \) (e.g. \( a, b, c \)) represents the absolute standard deviation of variable \( i \), which, in the case of gas component, was calculated by multiplying the full-scale measuring range of the component, as seen in Section 2.3 and Section 2.4, with the uncertainty in Table 4, e.g. \( \sigma_{\text{CO}} \leq \pm 1\% \), \( \sigma_{\text{CO}_2} \leq \pm 1\% \) and \( \sigma_{\text{H}_2} \leq \pm 0.2\% \), for the \( \text{CO}, \text{CO}_2 \) and \( \text{H}_2 \) respectively, from the fuel reactor.

For instance, to estimate the uncertainty of \( F_i \) in Eq. (1), the differential equation for each \( x_i \) must be derived first. Using the measured \( X_{i,j} \) and \( \frac{\partial F_i}{\partial x_{i,j}} \) can be calculated, which together with the uncertainty of the measurement for \( x_{i,j} \) in Table 4 were used to get the relative error of \( F_i \) by Eq. (8). For the parameters involved in this work, typical uncertainties are summarized in Table 5. In most of the cases, the errors are low in the range of \( \pm 2\% - 7.5\% \), which suggests a good reliability of these calculations. However, some relevant uncertainty, e.g. \( \sigma_{\text{POC}} \leq \pm 17.5\% \) for gas conversion in the POC, was also obtained, mainly due to the relatively lower concentrations of fuel components.

4. Results

4.1. Gas composition after the fuel and air reactors

Stable operation was easily achieved using the two manganese ores and the three solid fuels during the experiment. As an example, Fig. 3 depicts the gas concentration from fuel reactor, air reactor and the air flow entering the air reactor as a function of fuel feed time, using the SC and CAL coal. Rapid increase of CO2 concentration to around 45 vol % for the fuel reactor was seen after the fuel started. At the same time, a continuous decrease of \( \text{O}_2 \) concentration in the air reactor was noticed until around \( t = 30 \) min, as the reduced oxygen carrier from fuel reactor was being oxidized in the air reactor. It is also noticed that there was a small CO2 peak in air reactor in the initial minutes, which could be explained by that the initial temperature was insufficient for fast char gasification in the fuel reactor and carbon stripper, i.e. \( T_{in} \) less than 845 °C. In this case, a loss of a small amount of char to air reactor occurred. After that, the temperature was always high enough for fast char conversion in the fuel reactor and carbon stripper, i.e. \( T_{in} > 925 \) °C, thus no \( \text{CO}_2 \) or \( \text{CO} \) was observed at the air reactor exit after around \( t = 50 \) min. The concentration of \( \text{CO}_2 \) from the fuel reactor was increased from 45 to 57 vol% as the air reactor air flow was changed from 34 to 42 \( L\text{s}^{-1} \), which was accompanied by a slight drop of \( \text{CO}, \text{H}_2 \) and \( \text{CH}_4 \) concentration. An increase of air flow improves the fuel reactor performance because of a higher circulation rate of oxygen carrier between the air and fuel reactors [61], which also raises the solids inventory in the fuel reactor. Thus, more oxygen carrier particles were transported into the fuel reactor at higher air flows, which led to a better contact of fuel gases and the oxygen carrier. Despite this, the \( \text{O}_2 \) concentration of the air reactor was not greatly changed in the interval of 10-15 vol%, indicating that the reduction extent of the SC ore was relatively stable.

When the fuel feed was stopped at around \( t = 135 \) min, the concentration of \( \text{CO}_2, \text{CO}, \text{H}_2 \) and \( \text{CH}_4 \) fell gradually to zero, while the \( \text{O}_2 \) in air reactor was recovered to its initial concentration. For the other fuels, i.e. BP and GWC, and manganese ores, i.e. SC and Sinaus, similar results were also obtained for the fuel and air reactors of the 100 kWth unit.

4.2. Gas composition after the POC

As the air was injected, the oxidation of the fuel-reactor gas was started in the POC, which is illustrated by the switching of air flow from \( F_{\text{air,POC}} = 0 \) to 5 \( L\text{s}^{-1} \) at around \( t = 6.6 \) min in Fig. 4. As displayed in Fig. 4, the concentration of \( \text{CO} \) and \( \text{CO}_2 \) began to decrease from 3.8 to 0 vol% and from 53 to 26 vol%, respectively, as the air flowed into the POC. There was a delay of approximately 0.5 min for gas concentration after switching the air flow from 0 to 5 \( L\text{s}^{-1} \), which was caused by the distance between the sampling port and the gas analyzers. An \( \text{O}_2 \) concentration of around 3.8 vol% was detected after the POC, which in indicated the air injected to the POC was excessive. Although more moles of \( \text{CO}_2 \) were expected by the oxidation of \( \text{CO}, \text{CH}_4 \) and char, a lower \( \text{CO}_2 \) concentration was actually detected after the injection of air, which was a result of the dilution by the 4 \( L\text{s}^{-1} \) in the air.

### Table 4

<table>
<thead>
<tr>
<th>Component</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_4 )</td>
<td>( \pm 1% )</td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>( \pm 1% )</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>( \pm 1% )</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>( \pm 1% )</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>( \pm 0.2% )</td>
</tr>
</tbody>
</table>
Typical relative errors of different parameters in this work.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$\eta_{FR}$</th>
<th>$\eta_{POC}$</th>
<th>$\eta_{FR}$</th>
<th>$\eta_{POC}$</th>
<th>$x_{N}$</th>
<th>$\lambda_{overall}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\leq \pm 7.0%$</td>
<td>$\leq \pm 5.3%$</td>
<td>$\leq \pm 7.5%$</td>
<td>$\leq \pm 6.3%$</td>
<td>$\leq \pm 17.5%$</td>
<td>$\leq \pm 2.3%$</td>
</tr>
</tbody>
</table>

Fig. 3. Concentration $x$ of CO$_2$, CO, H$_2$, and CH$_4$ for the fuel reactor (FR) as well as CO$_2$ and O$_2$ for the air reactor (AR), and the flow rate of air entering AR, $F_{air,AR}$, as a function of fuel feed time, using the SC ore as oxygen carrier and 85 kW$_{in}$ CAL coal as fuel; $t = 0$ corresponds to fuel start.

As aforementioned, the POC chamber has no external heating elements, which means that it was heated by the hot gas stream from the fuel reactor and the heat released by the exothermic oxidation reactions. As seen in Fig. 4, the temperature at the inlet, $T_{POC,in}$, was rather stable, whereas the outlet temperature was lower due to heat loss from the wall and the cooling effect by air injection. After starting air addition at around $t = 6.6$ min, the temperature at the POC outlet was gradually increased from 825 to 875 $^\circ$C, mainly attributable to the exothermic oxidation of the combustibles, see reactions (R5)-(R8).

4.3. Gas flow after the fuel reactor and POC

Molar flow rates of gas components calculated for the fuel reactor (CO$_2$, CO, H$_2$ and CH$_4$) and the POC (CO$_2$, CO, O$_2$ and CH$_4$ in some cases) are plotted as a function of time for comparison purposes, as seen in the example in Fig. 5. For the use of BP pellets, stepwise declines of gas flows for the fuel reactor are noticed in the first 27 min in Fig. 5(a). This phenomenon was a result of malfunction of a 3-way valve connecting the fuel reactor exit, purge N$_2$ and gas analyzers. In that period, unquantifiable flows of N$_2$ were directed to the analyzers, thereby incorrect gas flows for fuel reactor were obtained for the first 27 min. However, the POC measurement worked well, thus the gas flow from POC can be correctly calculated, as seen in Fig. 5(a). In the initial minutes, the POC temperature was gradually increased from 700 to 850 $^\circ$C, which resulted in a faster kinetics for CO oxidation and thus lowering the CO flow. After $t = 27$ min, stable concentrations were achieved both for the fuel reactor and the POC under various flows of air to POC and air reactor. The concentration of CH$_4$ for POC was measured after around $t = 80$ min, which can reflect the oxidation degree of volatiles [64,65]. As seen in Fig. 5(a), a flow of CH$_4$ and CO close to zero was calculated between $t = 80$ and 125 min, indicating a full oxidation of CO and CH$_4$ in POC. The unmeasured H$_2$ can also be assumed to reach a full conversion in this case, considering its higher reactivity than CO and CH$_4$. Decreasing the POC air flow to less than 6.8 L$_{\text{s}^{-1}}$ resulted in an insufficient oxidation of fuel components, therefore, increases in CO and CH$_4$ flows were seen when the air flow was reduced.

In the combustion of GWC wood char, extremely low CH$_4$ flow was observed from fuel reactor during the entire period of fuel feed, because of the low volatiles content in this fuel, see Table 2. As seen in the first 150 min of Fig. 5(b), both CO and CH$_4$ were absent after POC, while the CO$_2$ flow was higher for the POC than fuel reactor. This means full oxidation was reached at POC during the first 150 min. Additionally, in the period of $t = 118-134$ min, there was an abrupt increase of O$_2$ flow and a decrease of CO$_2$ flow leaving the POC due to a temporary air ingress to the gas analyzing system. After around $t = 150$ min, the fuel thermal power was increased from 42 to 67 kW$_{\text{th}}$, thus higher gas flows for CO$_2$, CO and H$_2$ components were calculated at the fuel reactor and POC exit.

In the case of CAL coal combustion, there was no air flowing to the POC during the first 54 min in Fig. 5(c), meaning no oxidation of the fuel components occurred in the POC. Therefore, similar flows of CO and CO$_2$ were found for the fuel reactor and the POC in this period, while the H$_2$ and CH$_4$ from POC were not measured. The gradual increases of CO and CO$_2$ flows for both reactors as well as H$_2$ flows for the fuel reactor during the first 54 min are related to a faster char gasification, as the fuel reactor temperature was increased from 845 to 925 $^\circ$C (not shown in the figure). Despite this, the CH$_4$ flow from the fuel reactor was quite stable, which could be attributed to a roughly constant devolatilization rate of the CAL coal in this temperature interval. After around $t = 54$ min, a 1.8 L$_{\text{s}^{-1}}$ air was injected into the POC, which led to drastic increases of CO$_2$ and CO flows at POC exit. The sum of CO$_2$ and CO flow from POC was notably higher than the total flow of CO$_2$, CO and CH$_4$ from the fuel reactor, i.e. 0.13 versus 0.09 mol $\text{s}^{-1}$. Furthermore, since the complete oxidation was not achieved, it can be said that the O$_2$ supplied with the 1.8 L$_{\text{s}^{-1}}$ air was inadequate for full oxidation. Under a higher POC air flow of 3.3 L$_{\text{s}^{-1}}$, some decreases of CO flow were seen, however, the complete oxidation was still not reached albeit some excess O$_2$ were observed. This behavior might be caused by several factors, such as not enough reaction time, low temperature and inadequate mixing of char and O$_2$, however, it is not clear which is the dominant reason. At around $t = 140$ min, the fuel flow was effectively cut off, thus the molar flows of CH$_4$, CO, CO$_2$ and H$_2$ were gradually

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reduced to zero. The continuous increase of O\textsubscript{2} flow after the fuel stop was a result of switching to fluidization with air.

Consequently, further oxidation of combustibles can be realized in the POC of the 100 kW\textsubscript{th} unit, resulting in more CO\textsubscript{2} in the effluent gas stream. Some of the combustibles contain a significant fraction of char elutriated from the fuel reactor, which can be oxidized to CO and/or CO\textsubscript{2} in the POC. The char elutriated from fuel reactor was caused by the low riser height, the low efficiency of the cyclone in this small-scale CLC unit as well as by the type and particle size of fuel [49].

4.4. Improvement on gas conversion

The gas conversion - \( \eta_{\text{gas,FR}} \) and \( \eta_{\text{gas,POC}} \) for fuel reactor and POC, respectively- are plotted as a function of air flow rate to the air reactor in Fig. 6 for GWC wood char and Sinaus manganese ore. As mentioned before, a better contact between oxygen carrier and fuel gases can be realized at higher air reactor flows, thus higher gas conversions in fuel reactor are expected under higher air flows to the air reactor [61]. This principle is also applicable to the POC with a constant air injection rate, hence positive effect of air reactor flow on the gas conversion in POC is also seen in Fig. 6. The improvement on gas conversion with the use of POC is shown for the pair of “Sinaus + GWC” using a constant air flow to the POC. In this case, most of the combustibles from the fuel reactor were converted when the POC was in use, leading to a gas conversion of 0.993–0.997 compared to 0.887–0.894 after the fuel reactor, thus a great improvement on combustion was attained. By using the Sinaus + GWC pair, the oxygen demand after the POC can be decreased to 0.3–0.7% in comparison to 10.6–11.3% after the fuel reactor.

4.5. Effect of POC air flow

Increasing the POC air flow can result in more available O\textsubscript{2} in the POC as well as a higher temperature at the outlet of POC, due to the exothermic nature for the oxidation of combustibles, see reactions (R5)-(R8). In this case, more CO\textsubscript{2} and less CO were obtained at the POC outlet as shown in Fig. 7 (a), in the light of faster reaction kinetics at higher temperatures from 830 to 980 °C and higher O\textsubscript{2} availability. Complete oxidation of CO was reached with \( F_{\text{air,POC}} > 5 \text{ L N}^{-1} \text{ s}^{-1} \), while an O\textsubscript{2} flow of 0.008 mol s\textsuperscript{-1} was found at POC exit. The quite stable inlet temperature, \( T_{\text{POC,in}} \) in Fig. 7 (a) was a result of steady fuel reactor operation. For the combustion of CAL coal, the cases became a bit different in Fig. 7 (b), where the values of the parameters shown are increasing as a function of POC air flow. The continuous increase of \( T_{\text{POC,in}} \) in Fig. 7 (b) can be considered as a result of the stabilization for fuel reactor operation, which was also a function of time. This parameter would affect the temperature of POC and thus the reaction between O\textsubscript{2} and combustibles.

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Fig. 5. Comparison of gas molar flow \( F_i \) (\( i = \text{CO}_2, \text{CO}, \text{H}_2, \text{CH}_4 \) or \( \text{O}_2 \)) at the outlet of fuel reactor (\( j = \text{FR} \)) and POC (\( j = \text{POC} \)) for (a) BP pellets, (b) GWC wood char with the change of thermal power from 42 to 67 kW\textsubscript{th} at around \( t = 150 \text{ min} \) and (c) CAL coal, using SC manganese ore as oxygen carrier; Solid lines for POC exit (\( j = \text{POC} \)) and dot lines for fuel reactor exit (\( j = \text{FR} \)), under various \( F_{\text{air,AR}} \) and air flow rate \( F_{\text{air,POC}} \); No measurements of \( \text{H}_2 \) for all the cases, \( \text{CH}_4 \) was measured after around \( t = 80 \text{ min} \) for BP and during the entire period for GWC; Data from three examples of tests in Table 3.

Fig. 6. Gas conversion in the POC (\( \eta_{\text{gas,POC}} \)) and the fuel reactor (\( \eta_{\text{gas,FR}} \)) for the “oxygen carrier + fuel” pair of “Sinaus + GWC” using \( F_{\text{air,POC}} = 5.0 \text{ L N}^{-1} \text{ s}^{-1} \).
It should also be notable that the POC air flow was rising at the same period, which provides more $O_2$ for oxidation. Therefore, the higher CO$_2$ flow in Fig. 7(b) obtained at POC outlet can be ascribed to both higher air flow and higher temperature. At the same time, it was also observed that the CO flow at POC exit was slightly increased in Fig. 7(b), which can be caused by the insufficient oxidation of coal char elutriated from the fuel reactor [49], although a surplus oxygen of 0.007 mol s$^{-1}$ was detected using a POC air flow of 3.3 L s$^{-1}$. This phenomenon was absent in Fig. 7(a), due to a much lower rate of elutriation for biomass char than coal char, i.e. 0–3% and 7–14%, respectively, according to a material balance calculation [50].

4.6. Trade-off between full oxidation and oxygen excess

Oxygen entering the POC with the air injection can contribute to the oxidation of various combustibles, of which CO$_2$ was used as an indicator to evaluate the behavior of the POC. The molar ratio ($F_{CO_{out}}/F_{CO_{in}}$)$_{POC}$ taking into account the flows of CO at the outlet, $F_{CO_{out}}$, and inlet, $F_{CO_{in}}$, of POC is plotted as a function of POC air flow in Fig. 8. In line with the previous discussions, it is generally found that a lower ($F_{CO_{out}}/F_{CO_{in}}$)$_{POC}$ was reached at a higher POC air flow. Despite this, oxygen at the POC flow in Fig. 7(b) obtained at POC outlet can be ascribed to both higher periods, which provides more $O_2$ for oxidation. Therefore, the higher CO$_2$ flow detected in Fig. 7(b) obtained at POC outlet can be ascribed to both higher air flow and higher temperature. At the same time, it was also observed that the CO flow at POC exit was slightly increased in Fig. 7(b), which can be caused by the insufficient oxidation of coal char elutriated from the fuel reactor [49], although a surplus oxygen of 0.007 mol s$^{-1}$ was detected using a POC air flow of 3.3 L s$^{-1}$. This phenomenon was absent in Fig. 7(a), due to a much lower rate of elutriation for biomass char than coal char, i.e. 0–3% and 7–14%, respectively, according to a material balance calculation [50].

4.7. Conversion of combustible gases versus oxygen concentration

In order to compare among different solid fuels and operation conditions, the measured concentration of CH$_4$, CO and H$_2$ from POC was normalized using Eq. (6), which in combination with the overall oxygen ratio $\lambda_{overall}$ calculated by Eq. (7) are shown in Fig. 9 as a function of normalized O$_2$ concentration at the POC outlet. An increase of normalized O$_2$ concentration at the outlet of POC is a result of a higher excess of air O$_2$ introduced to the POC, which contributes to a larger numerator in Eq. (7), thus an increase in the overall oxygen ratio is seen in Fig. 9. As observed, the increase of normalized O$_2$ concentration can lead to a linear-like increase of the overall oxygen ratio, which means a higher availability of O$_2$ for oxidation and more contacts of O$_2$ and combustibles in the POC. In this case, lower normalized concentration of CH$_4$, CO and H$_2$ were obtained under higher values of normalized O$_2$ concentration or overall oxygen ratio. In the case of CH$_4$ in Fig. 9(a), the normalized CH$_4$ concentration was decreased from 0.087 to 0 while the overall oxygen ratio was raised from 0.80 to 1.05 as a function of normalized O$_2$ concentration. For the CO in Fig. 9(b), the highest normalized concentration was 0.16 for BP pellets. Full or almost full oxidation of CO can be realized with $X_{CO,N} > 0.01$ and $\lambda_{overall} > 1.01$. For the case of H$_2$ in Fig. 9(c), again the higher normalized O$_2$ concentration led to an increase on the overall oxygen ratio, which resulted in more available O$_2$ and more opportunities for the contact of O$_2$ and H$_2$ in the POC, thus a lower normalized H$_2$ concentration was obtained. However, a complete oxidation of H$_2$ cannot be seen in Fig. 9(c), because few tests were done with the H$_2$ concentration in POC being measured. Generally, in any case of Fig. 9, it was found that a higher overall oxygen ratio can help to reach a higher extent of fuel combustion in the POC reactor. Nevertheless, too high overall oxygen ratio can also reduce the purity of CO$_2$ due to the excess of O$_2$, thereby, this parameter must be well optimized in a large-scale CLC system, e.g. by using pure O$_2$ and improving the POC design.

As can be seen in Fig. 9(b), there is some spread in the normalized CO concentration for a given normalized O$_2$ concentration in the outgoing stream of POC. The reason for this spread is not fully understood, but it is

\[ n_{\text{FR}} = 550 \text{ kg} \cdot \text{MW}_d \] in the fuel reactor. In this case, the ($F_{CO_{out}}/F_{CO_{in}}$)$_{POC}$ was decreased gradually from 1 to 0 as the POC air flow was increased from 0 to 6.7 L s$^{-1}$, with a surplus O$_2$ flow of 0–1.8 $10^{-2}$ mol s$^{-1}$ at the POC exit. Clearly, the air addition must be optimized to fulfill the requirement for the post treatment, e.g. transport and storage, of fuel-reactor gas stream in a scaled-up CLC system.
clear from the data that low O$_2$ and CO were attainable for all the three fuels, i.e. both $x_{O2,N}$ and $x_{CO,N}$ below around 0.01. Three such periods are presented in the following section.

4.8. Simultaneous low CH$_4$, CO and O$_2$ after the POC

Fig. 10, as an example, shows in detail the normalized concentration of CH$_4$, CO and O$_2$ reached after the POC under different air flow rates,
using the BP, GWC and CAL fuels. These cases were obtained after the flow of air to the POC was increased or decreased under stable fuel reactor operation with different thermal powers of fuel. Similar to that shown in Fig. 5, the increase of POC air flow led to a better combustion but also a dilution on gas concentration, while the opposite happened when decrease the POC air flow, which can also be clearly seen in Fig. 10. For each case, the variation of air flow to POC resulted in rapid increases or decreases of the normalized concentration of CH₄, CO and O₂ at the POC exit, which eventually converged to the desirable cases with relatively stable low concentrations. For the BP pellets in Fig. 10(a), with the air flow increased to around 6.7 L·s⁻¹, the normalized concentration of CH₄ and CO was greatly lowered, while a gradual increase of O₂ was observed. After stabilization, low average normalized concentration of 0.5% for CO, 0.1% for CH₄ and 0.7% for O₂ was achieved with a duration of around 10 min before another test was conducted at t = 25 min. Similarly, an average normalized concentration of 0.5% CO was also reached in the cases of GWC char and CAL coal, see Fig. 10(b) and (c). For the GWC char, the low normalized CO concentration was reached with an air flow of around 5 L·s⁻¹, while an O₂ concentration of zero was calculated. Also, CH₄ was zero, which is reasonable considering the lower fraction of methane entering the POC due to the low content of volatiles in this fuel. For CAL coal, the low CO was attained under an average normalized O₂ concentration of 0.5% in Fig. 10(c) using 3.3 L·s⁻¹ air flowing to the POC. These experimental results in Fig. 10 confirm that a good conversion of combustibles from the fuel reactor can be realized in the POC unit of the 100 kWth system with low excess of O₂, which is encouraging for the further optimization.

5. Discussion

5.1. Importance of lowering the char elutriation from fuel reactor

From the gas leaving the POC, it can be identified which combustible component is more dominant. As shown in Fig. 11, the comparison of normalized concentration indicates that CO is normally present in similar or higher concentration than CH₄ and H₂. The normalized concentration of CH₄ were always lower than CO, whereas only two measurements were available for H₂. Nevertheless, H₂ is generally easier to burn than CO, thus, with sufficient air addition H₂ should be lower. For CH₄, the dependence on fuel type is also observed in Fig. 11 and clearly related to the different volatiles fractions as discussed before. As can be seen from Fig. 10(a), the oxygen addition removes CH₄ much more efficiently as compared to CO. This might be related to the partial post-oxidation of elutriated char to CO in the POC unit. As is noticed in Fig. 5 (c), air addition, if not sufficient, may substantially increase the flow of CO as a result of inadequate combustion of elutriated char. Thus, it is also possible that char may contribute to CO even under well-optimized conditions. The fuel with the highest char elutriation in this work, i.e. CAL coal, also shows somewhat higher CO + O₂ in Fig. 10. Accordingly, fuel properties and reactor system giving a much lower content of unburnt char in the fuel reactor stream are expected to facilitate high conversion in the oxy-polishing step.

5.2. Options for improving the POC performance

Using a typical average fuel-reactor gas composition (10.1 vol% CO, 5.0 vol% CH₄, 7.2 vol% H₂ and 52.9 vol% CO₂), the POC was simulated at 880 °C, under various air or pure O₂ flows, with the zero-dimensional model described in Section 2.5 and the results are presented in Fig. 12. In comparison with the POC experiments, the model shows reasonably good predictions for the best conversions, i.e. most cases for CH₄ and two cases for CO. Given the spread in the experimental results, the model cannot at the same time predict the lower conversions seen for the remaining data. The latter can be attributed to the residual fuel-reactor char, the uncertainty of measurements and the variations in experimental conditions, e.g. temperature in the POC. The unconverted char from the fuel reactor is expected to be partly oxidized to CO in the POC, and this unknown flow of char was not included in the model. There is no comparison of H₂ concentration and model because the number of measurements for this component is very limited in the experiments. Using pure O₂ stream in the model, the combustibles can be further lowered at the same normalized O₂ concentrations. The model predicts it would be possible to reach a fraction of combustibles plus O₂, i.e. CO + CH₄ + H₂ + O₂, below 0.009 with air and 0.006 with pure O₂.

In a scaled-up system, the oxy-polishing step would have an O₂ gas flow not diluted by nitrogen, which raises the POC oxidation capability and should improve the combustion (see Fig. 12), in particular, as it would also raise the temperature. With no air nitrogen present to form NOx, a high POC temperature should have no significant disadvantage. Furthermore, a considerably lower char elutriation is expected in larger systems due to the higher reactor height and a better separation by the cyclone. However, it would only be possible to reach low O₂ and low combustibles with a good mixing of the gases in the POC.

Fig. 11. Normalized concentration of CH₄ (cubic symbols: ■, ■, ■) and H₂ (circle symbols: ○) in comparison with normalized CO concentration at the POC outlet for BP pellets (■), GWC wood char (■) and CAL coal (■) using the SC and Sinaus manganese ores as oxygen carrier.

Fig. 12. Model and experimental results for the POC in terms of the normalized concentration of CH₄ (■, ■, ■), CO (○, ○, ○) and H₂ (■, ■) as a function of normalized O₂ concentration at the outlet of POC and the third CSTR; symbols ( ■, ■, ■) are for experimental data, continuous lines (—, —, —) represent the modeling data with air as oxidation agent and dash lines (—−, —−, —−) show the modeling data using a pure O₂ stream.
6. Conclusions

Oxy-polishing step for Chemical Looping Combustion (CLC) process was demonstrated with a post-oxidation chamber (POC) of the 100 kWth prototype using three different solid fuels and two manganese ores as oxygen carrier. Operational conditions in the fuel reactor and the POC were changed in a wide range to study the performance of the oxy-polishing process. The following findings were made.

(i) The oxy-polishing step is feasible and important for getting a high purity CO2 stream in the CLC process, which is advantageous for further gas conditioning before transport and storage. Using the POC, the gas conversion can be greatly improved from 0.887 to 0.894 after the fuel reactor to 0.993–0.997 at POC exit.

(ii) Fuel conversion in the POC is linked to the combustion behavior in the fuel reactor. Improving the fuel reactor combustion, the POC performance can be enhanced. Also, the conditions in POC can also be optimized by varying the addition of oxygen.

(iii) A trade-off was found in the POC between the fuel conversion and the excess of O2. By tuning the overall oxygen ratio to slightly higher than 1,1, an operation close to optimum was realized with only minor oxygen excess and simultaneous low fractions of CO and O2 below 0,5–1,0%.

(iv) Removal of CH4 by the POC is more efficient than removal of CO2, which might be caused by the slow oxidation of fuel-reactor char in the POC. Lowering the char elutriation from the fuel reactor is expected to lead to a better oxy-polishing combustion.

(v) Performance of the POC was compared to a simple reactor model, indicating the potential of using modeling to guide the future scale-up design. The model shows improved POC performance when using pure O2 stream as oxidation agent.

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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