Experimental Demonstration of Two-Stage Packed Bed Chemical-Looping Combustion Using Syngas with CuO/Al₂O₃ and NiO/CaAl₂O₄ as Oxygen Carriers

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ABSTRACT: Recently, a novel two-stage reactor configuration for packed bed chemical-looping combustion (CLC) has been proposed and studied by numerical simulations. This two-stage CLC consists of two pressurized packed bed reactors connected in series, where the first bed contains an oxygen carrier material which is reactive at relatively low temperatures (450 °C) such as CuO/Cu, while the second bed contains an oxygen carrier which is resistant to relatively high temperatures (typically 1200 °C) such as NiO/Ni. In this work, this two-stage CLC concept has been experimentally demonstrated using CuO/Al₂O₃ and NiO/CaAl₂O₄ as bed materials in a high-pressure, high-temperature packed bed reactor. The influence of the operating conditions has been examined, and a validated reactor model has been used to scale up the process to industrial scale. The two-stage CLC concept is successfully demonstrated with a maximum temperature of 839 °C in the second bed. The operating pressure, the throughput during the reduction cycle, and the fuel concentrations have been found to result in small or negligible influences on the maximum temperature rise. This means that they do not affect the TS-CLC performance as long as the cycle time is adopted such that the heat produced in the first reactor bed is exactly transferred to the second bed. It has also been demonstrated that operation at higher pressures (to reach a higher overall process efficiency) does not affect the performance of the TS-CLC reactor. However, the fuel type (H₂, syngas, CO, or CH₄) strongly influences the temperature increase in the reactor, since it influences to what extent the oxygen carriers can be reduced. The experimental results could be well described by a one-dimensional packed bed reactor model provided that the extent of heat losses and the response time of the thermocouples are properly taken into account. The validated reactor model shows that the desired gas flow rate at 1200 °C can indeed be produced after some small changes in the operating conditions and the active weight content of the oxygen carriers. Therefore, TS-CLC can be regarded as a feasible technology for power production with inherent CO₂ capture with high LHV efficiency.

1. INTRODUCTION

Chemical-looping combustion (CLC) is a combustion process that inherently integrates the capture of carbon dioxide in power production with a great potential to have relatively very high overall energy efficiencies provided that an air stream at very high temperatures (ca. 1200 °C) and pressures (ca. 20 bar) is produced. In CLC, an oxygen carrier (metal oxide) is exposed to alternating oxidizing and reducing environments. During oxidation, the oxygen carrier (metal) reacts with oxygen from air and is oxidized to a metal oxide in a strongly exothermic reaction. The metal oxide reacts with the fuel in a reduction reaction which is either endothermic or slightly exothermic, depending on the oxygen carrier and fuel. In the CLC concept, the air and the fuel are not in direct contact, which makes it possible to obtain a highly concentrated stream of CO₂ after condensation of water. In 2001 Lyngfelt et al. proposed a CLC system that consists of two interconnected fluidized beds, namely a fuel reactor and an air reactor, while the oxygen carrier is circulated between the two reactors. Hot air is continuously produced in the air reactor, and the oxygen carrier is regenerated in the fuel reactor. However, the gas-solid separation is difficult at the desired stringent operating temperatures and pressures, in particular considering the inevitable fines generation due to particle attrition. In the end, the hot air stream will be sent to a downstream gas turbine and therefore no fines can be tolerated in this stream, which is the main challenge of this configuration.

To avoid these problems, a new reactor concept was introduced by Noorma et al. in 2007, based on packed bed reactor technology. In this reactor concept, the solids are stationary, while they are exposed to alternately reducing and oxidizing gases by switching the gas feed streams. With this technology the separation of gas and particles is intrinsically avoided. A continuous stream of hot gas can be produced using several packed bed reactors in parallel. The main technical challenges exploiting this technology are related to the development of the oxygen carriers and the high-temperature valves that are needed to switch the outlet streams of the packed beds. These challenges seem to be smaller than avoiding sending fines to the gas turbine, which makes the packed bed process easier to use at high pressures and thus with high overall electrical efficiencies. Previous work has demonstrated that a high overall process efficiency can be reached with syngas as fuel in both reactor configurations, provided that it is possible to work at high pressures.
Three main process steps can be distinguished in packed bed CLC, namely (i) combined oxidation and heat generation, (ii) heat removal, and (iii) reduction. In the first step, air (generally at 450 °C after adiabatic compression) is fed to the reactor and reacts exothermally with the reduced oxygen carrier until the reaction front reaches the end of the bed. After the bed is completely oxidized, the air feed is continued and a hot air stream is produced. The hot air is transported to the highly efficient gas turbine producing electricity, which needs air generated at high temperature (1200 °C) and pressure (20 bar). When the reactor outlet temperature decreases significantly below 1200 °C, the bed is purged and the feed is switched to syngas to start the reduction of the oxygen carriers, after which a new cycle can be started.

Different materials have been proposed to act as an oxygen carrier in CLC, but it has proved to be difficult to find one material that meets all the requirements. The material should have a high reactivity and high selectivity at low temperatures (450 °C) and must be thermally and mechanically stable at high temperatures (1200 °C) and after many cycles, while also allowing a temperature rise during the oxidation of at least 750 °C, which means that it needs to have a high oxygen transport capacity. For this reason, Hamers et al. investigated a system with two packed beds in series, the so-called two-stage CLC (TS-CLC) process. The principle of the TS-CLC configuration is that the second bed is heated by the heat produced in the first bed. This makes it possible to divide the total temperature increase over two beds and reduces the demands on the oxygen carriers and reactor materials. The process has been proposed and investigated theoretically by modeling, but has not yet been experimentally demonstrated.

The first reactor in the TS-CLC should contain a material that is reactive at low temperatures (>450 °C), while the second bed should contain a material that is stable at relatively high temperatures (1200 °C). CuO (with Al2O3 as support) has been demonstrated as an appropriate oxygen carrier for packed bed CLC using methane or syngas, because of its high reactivity. A copper based oxygen carrier cannot be used for the one-stage CLC process, because its low melting point, but this material is still applicable in the first bed of the TS-CLC. For the second bed, a manganese, nickel, or ilmenite based oxygen carrier might be used, provided that the active weight content is adjusted to a temperature rise of about 400 °C. NiO/CAI2O4 has been selected in this study for the second bed, because this material has been proven to be suitable for packed bed reactors. Ni-based materials have the disadvantages that no full gas conversion can be reached at the desired high temperatures due to thermodynamic limitations, they are toxic, and they are relatively expensive. For large scale applications a cheaper oxygen carrier should probably be selected, but with this oxygen carrier the TS-CLC concept can be demonstrated.

The goal of this work is to experimentally demonstrate the TS-CLC configuration in a lab scale pressurized reactor. The experimental data are also used to validate a reactor model to be used to predict the performance of the novel reactor configuration at industrial scales. In section 2, information about the oxygen carriers and the reactor setup is provided. Section 3 starts with the experimental demonstration of TS-CLC in a packed bed reactor containing copper and nickel based oxygen carriers fueled by syngas (section 3.1). After this demonstration, in section 3.2 the effects of different operating conditions are discussed, viz., flow rates, operating pressure, fuel concentration, and type of fuel (H2, CO, syngas, or methane). Finally, in section 3.3 the experimental results are described with a packed bed reactor model, which is also used for a prediction of the performance of the TS-CLC on an industrial scale.

### 2. MATERIALS AND METHODS

#### 2.1. Oxygen Carriers

The Cu-based particles (13 wt % CuO on Al2O3) have been obtained from Sigma-Aldrich and have an average particle size of 1.1 mm (size at which they are commercially available). The Ni-based particles (17 wt % NiO on CaAl2O4 support) were obtained from Johnson-Matthey as fluted rings with a height and diameter of 11 mm. The Ni-based particles have been crushed and sieved to particle sizes of 2 mm to facilitate a homogeneous oxygen carrier distribution over the reactor bed. Before the oxygen carrier was placed in the reactor, the particles were activated by exposing them to two redox cycles with reductions with H2 at 900 °C and oxidations with air. The main reactions that prevail in the reactor with these materials are listed in Table 1.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>ΔHf [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxidation of CuO</td>
<td>CuO + 2H2 → Cu + H2O</td>
<td>ΔHf = -394 kJ/mol O2</td>
</tr>
</tbody>
</table>

#### 2.2. Experimental Setup

A high pressure/temperature packed bed reactor (L × o.d. × i.d. = 1600 × 400 × 63 mm) is used to study the TS-CLC concept. The overall scheme of the experimental setup can be found in Figure 1. The reactor consists of a high temperature steel liner (6 mm thickness) that contains the bed material, insulation material (Isolfrax 160 kg/m3) that separates the liner and the reactor shell, and the reactor shell (made of carbon steel), which is used to maintain the pressure. The reactor shell is heated up to 300 °C to minimize heat losses. The reactor itself has no external heating source, and the temperature profiles inside the reactor are generated by the CLC process itself. The axial temperature profile in the two beds can be measured in the center of the reactor by a tube (L × o.d. = 1000 × 14 mm) that contains in total 20 thermocouples (1.5 mm K-type thermocouples, Rössel). Due to this thermocouple construction a response time is observed, which is taken into account when the experimental data are compared with the model. More information about the reactor construction and the response time delay can be found in Hamers et al.10

The reactor feed flow rate and composition are controlled by mass flow controllers (Bronkhorst) and valves. The gas feed is heated by two ovens (2.2 kW each) installed in series before
of the tube is materials stacked on top of each other. The bottom section (38 cm) of the reactor is filled with alumina as inert material). The properties of the two beds are listed in Table 2.

The reactor inlet temperature of the gas is approximately 450 °C, which corresponds to the temperature of air that is adiabatically compressed from atmospheric conditions to 20 bar. A small flow of nitrogen (2 L/min) was fed to the insulation layer to prevent accumulation of reactants in the insulation material in case of leakages. This N2 is mixed with the gases from the reactor at the reactor exit. The outlet stream of the reactor is cooled first by air and subsequently by a water cooler. Afterward, a digital back pressure regulator is used to control the system pressure (maximum 10 bar). The composition of the dry gas stream is analyzed by a mass spectrometer (MKS Cirrus 2) and a CO analyzer (Siemens Ultramat 23) in parallel. The CO analyzer is used in order to differentiate the signals from N2 and CO, since these components have the same molecular mass.

In the two-stage CLC concept, two different packed bed reactors can be used, each containing one bed material. In this work, one packed bed reactor is used containing two bed materials stacked on top of each other. The bottom section (38 cm) of the tube is filled with 13 wt % CuO supported on Al2O3, while the upper section (32.5 cm) is filled with 17 wt % NiO on CaAl2O4 as illustrated in Figure 1 (the rest of the reactor is filled with alumina as inert material). The properties of the two beds are listed in Table 2.

### 3. RESULTS AND DISCUSSION

#### 3.1. Experimental Demonstration of TS-CLC with Syngas as Fuel

Several cycles consisting of a reduction, purge, oxidation, and another purge step have been performed for the demonstration of TS-CLC. The oxidation cycle consists of a 120 L/min air flow for 3 min. The reduction cycle consists of a 60 L/min flow with 20% syngas for 8 min. The ratio between CO, H2, and CO2 (2.3:1:0.4) is comparable to the syngas obtained from a gasifier in an integrated gasification combined cycle (IGCC) power plant. Steam was added to prevent carbon deposition and to stimulate the water gas shift reaction. The amount of steam has been adjusted such that no carbon deposition occurs above 450 °C according to thermodynamics calculations using HSC 5.1. Between the oxidation and reduction a 2 min purge with N2 was introduced. Cycles with alternating oxidation and reduction were performed at 2 bar. An overview of the operating parameters during the cycles is given in Table 3.

#### Table 3. Operating Conditions of the Base Case Used during the Packed Bed Reactor Experiments

<table>
<thead>
<tr>
<th>reaction</th>
<th>flow rate, L/min</th>
<th>press., bar</th>
<th>inlet temp, °C</th>
<th>time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>reduction with syngas</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>8.4</td>
<td>2</td>
<td>450</td>
<td>8</td>
</tr>
<tr>
<td>H2</td>
<td>3.6</td>
<td>2</td>
<td>450</td>
<td>8</td>
</tr>
<tr>
<td>CO2</td>
<td>1.4</td>
<td>2</td>
<td>450</td>
<td>8</td>
</tr>
<tr>
<td>H2O (steam)</td>
<td>12.6</td>
<td>2</td>
<td>450</td>
<td>8</td>
</tr>
<tr>
<td>purge</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N2</td>
<td>34.2</td>
<td>2</td>
<td>450</td>
<td>2</td>
</tr>
<tr>
<td>oxidation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>air</td>
<td>120</td>
<td>2</td>
<td>450</td>
<td>3</td>
</tr>
<tr>
<td>purge</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N2</td>
<td>120</td>
<td>2</td>
<td>450</td>
<td>2</td>
</tr>
</tbody>
</table>

A cycle consists of the following procedure. First, the packed bed reactor is heated by a 450 °C N2 flow. Subsequently, five cycles are performed after which the temperature profiles during the cyclic process become in cyclic steady state. In Figure 2 the outlet temperature is displayed for the first five cycles. Figure 2 shows that, when the first reduction is performed, both beds have an initial temperature of 433–485 °C and the gas is fed to the reactor at 480 °C. The heat produced during the reduction and oxidation in the first bed is transferred to the second bed and increases the temperature of the initial temperature profile of the next cycle. After five cycles the outlet temperature becomes close to its cyclic steady state, leading to a maximum outlet temperature of 839 °C (ΔT = 359 °C) during the oxidation. Mainly due to heat losses, this temperature is lower than the desired temperature of 1200 °C. In section 3.3.3, it is described how this temperature can be reached. The axial temperature profiles and outlet gas fraction during the fifth cycle are shown in Figures 3 (reduction) and 4 (oxidation and heat removal). The performance during these steps is discussed in sections 3.1.1 and 3.1.2.
3.1.1. Reduction. The axial temperature profiles and the outlet gas fractions during the reduction are shown in Figure 3. A temperature increase in the first bed is observed ($\Delta T_{\text{max}} = 87 ^\circ C$). This temperature increase is the consequence of the water gas shift (WGS) reaction and the reduction reaction of CuO, which are both exothermic. Since the reduction enthalpy of NiO is much lower compared to CuO and due to relatively high heat losses, no temperature increase is observed in the second bed. The temperature profiles show that the reduction takes places at an elevated temperature, which increases the reactivity of the second bed material.

The breakthrough profiles show that initially CO$_2$ is formed, since all the fuel is oxidized to CO$_2$ and steam, while the steam is condensed and separated before the analyzer. Breakthrough of syngas occurs after 4 min. In the breakthrough curves in Figure 5, a larger amount of H$_2$ is produced after breakthrough than fed (and less CO), which indicates that the WGS reaction occurs in the reactor as expected.

It is important to remark that, in industrial application, fuel slip should be avoided. If the reduction was stopped at this point, a lower degree of reduction would be reached with the oxygen carrier material, which makes it very difficult to compare the breakthrough curves with other experiments and the model simulations. Therefore, some fuel slip was tolerated during these experiments. For industrial application, the reactor scale is much larger and then the section with a lower degree of reduction is much smaller.

After a reduction of 8 min, the setup is purged by N$_2$ for 2 min.

3.1.2. Oxidation and Heat Removal. After the purge, the oxygen carriers are oxidized with air. The axial temperature profiles and O$_2$ fraction at the outlet during oxidation are shown in Figure 4. Outlet temperature profile during the first five cycles of the TS-CLC experiment with syngas (base case, operating conditions listed in Table 3).
reported in Figure 4. A temperature increase can be observed in both beds due to the strongly exothermic reactions. The maximum temperature in the Cu/CuO bed is 651 °C ($\Delta T_{\text{max}} = 72$ °C), while the maximum temperature in the Ni/NiO bed is 839 °C ($\Delta T_{\text{max}} = 173$ °C). The temperature rise in both beds is lower than theoretically possible with these materials, because the reactor experiences heat losses and in this case the oxygen carriers are not fully reduced. An apparent active weight content is expected of 10 wt % CuO and 11.5 wt % NiO based on thermal gravimetric analysis (TGA) experiments at these conditions. Without heat losses higher temperature rises would be observed: $\Delta T_{\text{max}}^{\text{Cu}} = 199$ °C and $\Delta T_{\text{max}}^{\text{Ni}} = 384$ °C. Hence, a maximum temperature could be reached of 1033 °C. These numbers are based on the energy balance solved for the exothermic reactions that occur with these gas/solid compositions, which is explained in more detail elsewhere.4

However, during these experiments some heat that is released during the oxidation is taken up by the liner that surrounds the reactor bed and has a relatively high heat capacity. As a consequence of the heat transport from the reactor bed to the liner and the response delay of the thermocouple, the theoretical maximum temperature is never measured and a lower temperature rise is reached. More information about the effect of the liner, the heat losses to the environment, and the residence time delay can be found in ref 10.

In the second bed a higher temperature rise is measured at the exit than in the rest of the bed, because during the previous reduction the temperature was higher and thus a higher degree of reduction was reached.

In the $O_2$ breakthrough profile in Figure 4, an oxygen fraction of 1% is initially measured. This is related not to the experiment itself, but to a small leakage in the analyzer (that is operating below atmospheric pressure). This has been taken into account when analyzing the results. After 1 min, both beds are fully oxidized and oxygen starts to break through.

The heat removal that is required for heat transfer inside the reactor (from the first to the second bed) and to the reactor exit is integrated with the oxidation (after 1 min) and also carried out during the subsequent purge. The temperature profile during the heat removal is illustrated in Figure 5. These profiles are obviously also influenced by the heat losses occurring in the reactor. It is important to remark that the heat from the first bed is not fully transferred to the second bed, because the heat transfer continues during the subsequent reduction and purge step. The time needed to transfer the heat from the first bed to the second bed should equal the total cycle time (the duration of a complete cycle, containing reductions, oxidations, and purges). If the total cycle time exceeds the time that is required to transfer the heat from the first bed to the second bed, the process becomes rather a one-stage CLC process.

3.2. Effects of Operating Conditions. The influence of the operating conditions has been investigated with respect to the operability of the TS-CLC process. The studied operation conditions are pressure, reduction flow rate, fuel concentration, and fuel type. In the base case, the oxygen carriers have been reduced with $H_2$ (20% $H_2$ balanced with $N_2$) so that no competitive reactions (like WGS reaction) can be observed during reduction. An overview of the operating conditions for the base case is given in Table 4. Two variables are used in order to express the performance of the process: maximum temperature increase ($\Delta T_{\text{max}}$) in the beds and the maximum temperature ($T_{\text{max}}$) during the oxidation. For all the experiments, the data of the fifth cycle have been used, since the cyclic procedure became steady state after five cycles.

### Table 4. Operating Conditions of the Base Case Used during the Experiments To Investigate Effects of Pressure, Reduction Flow Rate, Fuel Concentration, and Fuel Type

<table>
<thead>
<tr>
<th>reaction</th>
<th>flow rate, $L_\text{H}_2/\text{min}$</th>
<th>press., bar</th>
<th>inlet temp, °C</th>
<th>time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>reduction with $H_2$</td>
<td>$H_2$: 12</td>
<td>2</td>
<td>450</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>$N_2$: 48</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>purge</td>
<td>$N_2$: 120</td>
<td>2</td>
<td>450</td>
<td>2</td>
</tr>
<tr>
<td>oxidation</td>
<td>air: 120</td>
<td>2</td>
<td>450</td>
<td>3</td>
</tr>
<tr>
<td>purge</td>
<td>$N_2$: 120</td>
<td>2</td>
<td>450</td>
<td>2</td>
</tr>
</tbody>
</table>

When the operating pressure is increased from 2 to 7 bar, the temperature increase during oxidation becomes slightly higher in the Cu/CuO bed and slightly lower in the Ni/NiO bed. These effects cancel each other out, but the maximum temperature reached at the end of the second bed is about 25 °C lower. This is related to very small differences in the initial axial temperature profile at the start of the oxidation cycle shown in Figure 6. The reason for this small difference is not clear, but it cannot be attributed to a difference in the extent of reduction, because the temperature rise and the oxygen consumption do not change significantly. The oxygen consumption is thus hardly influenced by the operating pressure, which is in line with a kinetic study about the pressure effect.13 This demonstrates that increasing the operating pressure does not affect the TS-CLC performance. Hence, TS-CLC can also be carried out at 20 bar, at which the highest possible process efficiency can be reached.5,14
3.2.2. Fuel Concentration. The effect of the fuel concentration has been investigated by comparing cycles in which the H₂ fraction during the reduction cycle is varied. The reduction time has been adjusted to partly compensate for the amount of H₂ that is fed. The reduction is performed with a concentration of 20% H₂ (for 8 min) and 40% H₂ (for 5 min) with a 60 L/min reduction flow rate at 2 bar.

The results are given in Table 6, showing the temperature rise during oxidation and the maximum temperature at the thermocouple. The maximum temperature rise during the oxidation is similar for reductions with different concentrations and also the oxygen consumption is the same. Despite similar temperature rises, the maximum temperature in the case of 40% H₂ is substantially higher. A higher temperature is reached, because the temperature is initially higher as shown in Figure 7.

This is the consequence of two effects: due to the longer reduction time for the 20% H₂ reduction, the heat front moves further into the reactor bed and also more time is available for heat losses. Hence, the difference in maximum temperature is not an effect related to the operating parameter, but to the cycle time and this can be adjusted. This implies that the TS-CLC process can be operated with a wide range of fuel concentrations as long as the heat removal time is properly adjusted, so that the heat produced in the first reactor bed is exactly transferred to the second reactor bed.

3.2.3. Flow Rate during Reduction. The effect of the reduction flow rate is studied by performing the reduction with 60 L/min (8 min) and 120 L/min (5 min). The reduction time is increased in order to make sure that similar amounts of H₂ are fed to the packed bed reactor. In both cases, the reduction is performed with 20% H₂ at 2 bar.

The temperature increase in both reactor beds and the maximum temperature are shown in Table 7, which shows that the influence of the flow rate on the maximum temperature and maximum temperature increase is negligible. Therefore, apparently the axial temperature profiles and the degree of reduction are not influenced by the flow rate (which is also to be expected) and the heat front has moved similarly in both cases, because when the flow rate is reduced also the velocity of the heat front decreases proportionally. In this case, the reduction time was also increased to compensate for this effect. Hence, the temperature profiles obtained from both cases can hardly be distinguished (and are not reported here).

3.2.4. Fuel Type. The influence of the fuel type is investigated for four fuel types: H₂, CO, syngas, and methane. The exact compositions of the feed stream during the reduction cycle are listed in Table 8.

![Figure 7. Initial oxidation temperature profile followed after reductions with different H₂ concentrations.](image)

![Table 6. Fuel Concentration Effect on Temperature Differences in Reactor Sections and Maximum Temperature](image)

<table>
<thead>
<tr>
<th>H₂ fraction, %</th>
<th>reduction time, min</th>
<th>ΔT_max, °C Ni, °C</th>
<th>ΔT_max, °C Cu, °C</th>
<th>T_max, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>8</td>
<td>80</td>
<td>218</td>
<td>865</td>
</tr>
<tr>
<td>40</td>
<td>5</td>
<td>74</td>
<td>220</td>
<td>931</td>
</tr>
</tbody>
</table>

*Base case from Table 4.

<table>
<thead>
<tr>
<th>Table 7. Flow Rate Effect on Temperature Differences in Reactor Sections and Maximum Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>flow rate during reduction, L/min</td>
</tr>
<tr>
<td>-----------------------------------</td>
</tr>
<tr>
<td>60°</td>
</tr>
<tr>
<td>120</td>
</tr>
</tbody>
</table>

*Base case from Table 4.

<table>
<thead>
<tr>
<th>Table 8. Influence of Fuel on Temperature Differences in Reactor Sections and Maximum Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>fuel composition</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>H₂</td>
</tr>
<tr>
<td>syngas</td>
</tr>
<tr>
<td>CO</td>
</tr>
<tr>
<td>CH₄</td>
</tr>
</tbody>
</table>

*Balanced with N₂. *Base case from Table 4. *Operating conditions listed in Table 3.

![Image](image)
oxidation is lower at the exit of the reactor than in the middle of the Ni/NiO bed. From this, it can be deduced that the end of the NiO/Ni bed is less reduced compared to the rest of the bed. It is expected that this is related to the slower kinetics for NiO reduction with CO. If the reduction time was increased, a higher solid conversion would have been reached at the end of the NiO bed and then a higher temperature rise would have been observed in the subsequent oxidation cycle. In that case, more fuel slip would have occurred and the heat front would have moved further into the bed, which makes it more difficult to compare the cases with the different fuels. For that reason, the reduction time was not increased in the experiment. Thus, the concept is able to deal with only CO as fuel, after fine-tuning of the flow rate during reduction in order to avoid fuel slip, while the reactor bed is used as much as possible.

The reactivity with respect to CH₄ is very low. The temperature increase and subsequent maximum temperature are substantially lower compared to those for the other fuels. Two different mechanisms for the reduction of the bed materials by CH₄ are proposed. CH₄ could directly reduce the oxygen carrier forming H₂O and CO₂. Another possibility is that CH₄ is combusted indirectly by first the steam methane reforming reaction (CH₄ with steam is converted into syngas). Afterward, the oxygen carrier is reduced by the produced syngas, resulting in H₂O and CO₂. A condition for the second mechanism is that a catalyst is available for the steam methane reforming, like metallic nickel.

However, a very low temperature rise is observed during the oxidation after the reduction with CH₄ as illustrated in Figure 10. This means that quite a low solid conversion is obtained during the previous reduction. In the second bed, the temperature even drops, which indicates that the material was hardly reduced by CH₄. If some CH₄ was converted into syngas, the syngas would have reacted with the oxygen carriers as happened during the syngas experiments. Due to the low solid conversion in the first bed, little heat is produced there during oxidation. As a consequence, not much heat can be transferred to the second bed and therefore this bed is also at low temperature, at around 500 °C. At this temperature the NiO/CaAl₂O₄ is not reactive for the direct reduction with CH₄ nor for the steam methane reforming, because the nickel is not available in metallic form. Because of the low reactivity of CuO/Al₂O₃ with CH₄ at 450 °C, TS-CLC cannot be demonstrated with methane in this case. Due to the large extent of heat losses between the gas oven and the reactor, it was not possible to perform this experiment at higher temperatures.

If an oxygen carrier is found that is reactive with methane at these operating conditions, or when mixing the oxygen carrier with a catalyst active at this low temperature, this concept would also become very interesting for methane as fuel.

The operating parameter study shows that, in all cases, the TS-CLC is feasible as long as the different process steps are tuned to each other so that the heat produced in the first reactor bed is effectively transferred to the second bed. Also, increasing the pressure (to reach a higher overall process efficiency) does not affect the performance of the TS-CLC process.

3.3. Description by Packed Bed Reactor Model. In order to investigate the effect of operating parameters and heat losses, a packed bed reactor model is used to describe the process. In this section, first the model is briefly explained (section 3.3.1), and then a comparison is made between the modeling and the experimental results using syngas as fuel (section 3.3.2). Afterward (section 3.3.3), the model is used for scaling up the reactor to study the performance of the TS-CLC on an industrial scale.

3.3.1. Packed Bed Reactor Model. A numerical one-dimensional (1D) pseudohomogeneous packed bed reactor model is used to describe the experimental results. During earlier research with the same the setup, it was demonstrated that the heat capacity of the liner was of great influence. Therefore, an energy balance over the reactor wall was also included. Heat losses to the surroundings have been accounted for assuming heat transfer coefficients and a constant temperature of the surroundings. An overview of the mass and energy balances is given in Table 10. The correlations used
to describe the heat and mass diffusion coefficients can be found in Hamers et al.\textsuperscript{9}

Table 9. Applied Kinetic Parameters for NiO/CaAl\textsubscript{2}O\textsubscript{4} Particles\textsuperscript{44}

<table>
<thead>
<tr>
<th></th>
<th>H\textsubscript{2}</th>
<th>CO</th>
<th>O\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{Cu}, mol/m\textsuperscript{3}</td>
<td>89 960</td>
<td>89 960</td>
<td>151 200</td>
</tr>
<tr>
<td>n\textsubscript{Cu} m/s</td>
<td>3.13 × 10\textsuperscript{-8}</td>
<td>3.13 × 10\textsuperscript{-8}</td>
<td>5.8 × 10\textsuperscript{-7}</td>
</tr>
<tr>
<td>k\textsubscript{Cu} m/s</td>
<td>3.6 × 10\textsuperscript{-4}</td>
<td>1.4 × 10\textsuperscript{-3}</td>
<td>1.2 × 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>E\textsubscript{Cu} kJ/mol</td>
<td>30</td>
<td>45</td>
<td>7</td>
</tr>
<tr>
<td>n\textsubscript{Ni} m/s</td>
<td>0.6</td>
<td>0.65</td>
<td>0.9</td>
</tr>
<tr>
<td>D\textsubscript{Ni} m\textsuperscript{3}/s</td>
<td>5.1 × 10\textsuperscript{-5}</td>
<td>2.2 × 10\textsuperscript{-5}</td>
<td>1</td>
</tr>
<tr>
<td>E\textsubscript{Ni} kJ/mol</td>
<td>150</td>
<td>300</td>
<td>0</td>
</tr>
<tr>
<td>k\textsubscript{Ni} m/s</td>
<td>5</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>b, mol of solid/mol of gas</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>q</td>
<td>0.75</td>
<td>0.85</td>
<td>1.05</td>
</tr>
</tbody>
</table>

\textsuperscript{44}Most of the kinetics are the same as published by Medrano et al.\textsuperscript{15} but an adjustment was made for the high temperature reached during oxidation.

Table 10. Mass and Energy Balances Used in the Model

component mass balances for the gas phase
\[ \frac{\partial n_g}{\partial t} - \rho_g \frac{\partial v_g}{\partial x} + \frac{\partial}{\partial x} (\rho_g D_g \frac{\partial n_g}{\partial x}) + \epsilon_g M_g = 0 \]

description of kinetics copper:
\[ \frac{d}{dt} \frac{\partial n_{Cu}}{\partial t} = \frac{\partial}{\partial x} \left( \frac{n_{Cu}}{k_{Cu}} \frac{\partial n_{Cu}}{\partial x} \right) = \frac{n_{Cu}}{k_{Cu}} \frac{\partial n_{Cu}}{\partial x} \]

nickel:
\[ \frac{d}{dt} \frac{\partial n_{Ni}}{\partial t} = \frac{\partial}{\partial x} \left( \frac{n_{Ni}}{k_{Ni}} \frac{\partial n_{Ni}}{\partial x} \right) = \frac{n_{Ni}}{k_{Ni}} \frac{\partial n_{Ni}}{\partial x} \]

energy balance over reactor bed\textsuperscript{a}
\[ (\epsilon_g \rho_g C_{p,g} + \epsilon_{Cu} \rho_{Cu} C_{p,Cu} + \epsilon_{Ni} \rho_{Ni} C_{p,Ni}) \frac{\partial T}{\partial t} = -\rho_g v_g \frac{\partial T}{\partial x} + \frac{\partial}{\partial x} \left( \frac{k_{Cu}}{\rho_{Cu} C_{p,Cu}} \frac{\partial T}{\partial x} \right) + \epsilon_{Cu} \rho_{Cu} C_{p,nid} \left( T - T_{in} \right) \]

energy balance over reactor liner\textsuperscript{b}
\[ (\epsilon_{Cu} \rho_{Cu} C_{p,nid}) \frac{\partial T}{\partial t} = -\rho_{Cu} v_{Cu} \frac{\partial T}{\partial x} + \frac{\partial}{\partial x} \left( k_{Cu} \frac{\partial T}{\partial x} \right) + \epsilon_{Cu} \rho_{Cu} C_{p,nid} \left( T - T_{in} \right) \]

momentum balance (Ergun equation\textsuperscript{c})
\[ \frac{\partial p}{\partial x} = 150 \frac{\eta_g}{d_p} \left( 1 - \frac{e_k}{e_g} \right)^2 + 1.75 \rho_g \frac{e_k}{d_p} \left( 1 - \frac{e_k}{e_g} \right) \]

\textsuperscript{a} $e_{TC} = 0.03$; $e_{liner} = 0.417$.

The kinetics for the gas/solid reactions with copper (oxidation and reduction with H\textsubscript{2} and CO) have been taken from Garcia-Labiano\textsuperscript{10} with the pressure factor as published by Hamers et al.\textsuperscript{13} During TGA tests with CuO/Al\textsubscript{2}O\textsubscript{3} it has been observed that only about 75% of the material reacts at 450 °C and therefore the apparent active weight content has been adjusted to 10 wt %.

For the reactions with NiO/CaAl\textsubscript{2}O\textsubscript{4}, the reduction kinetics depend on the maximum temperature reached during the oxidation in the previous cycle.\textsuperscript{10} For that reason, different parameters have been formulated for the kinetics, as shown in Table 9. The kinetics for the water gas shift reaction have been taken from Grenoble et al.\textsuperscript{17} Carbon deposition was not included in the model, because it was not observed during the experiments: in fact, no CO\textsubscript{2} was produced during oxidation in any of the experiments.

3.3.2. Model Description of the Experiments. As discussed in section 2.2, the thermocouple has a certain response time. Previous work demonstrated that a fair comparison between the model and the experimental data could be achieved, if the temperatures obtained from the model are corrected by eq 1 for the thermocouple response delay of 45 s.

\[ T_{TC} = \exp \left[ -\frac{\Delta t}{\tau} \right] T_{TC}^* + \left( 1 - \exp \left[ -\frac{\Delta t}{\tau} \right] \right) T \]  

(1)

The experiment with syngas discussed in section 3.1 has been described by the model. The axial temperature profiles during reduction with syngas are shown in Figure 11. The experimental data are represented by symbols and the modeling data by lines.

Figure 11. Axial temperature profile and outlet fraction during the reduction cycle. The operating conditions are listed in Table 3. The experimental data are represented by symbols and the simulation output is shown by the lines. The model describes the temperature during the experiment quite reasonably, except in the copper bed during the first minutes of the reduction. The time required to switch gases and the residence time between the mass flow controllers and the reactor (oven) leads to a short delay, which is not included in the model.
The outlet dry gas fraction is compared with the results from the model and reported in Figure 11. At the beginning of the reduction cycle, CO and \( \text{H}_2 \) are fully converted into \( \text{CO}_2 \) and steam. The expected dry gas \( \text{CO}_2 \) fraction is 22%. This is in accordance with the model, but the \( \text{CO}_2 \) fraction in the experiment is slightly lower, which can be related to the accuracy of the mass spectrometer calibration. After 4 min, \( \text{H}_2 \) and \( \text{CO} \) start to break through in both the model and the experiment. A similar breakthrough slope points at a sufficiently accurate description of the kinetics in the model.

The axial temperature profiles during the oxidation are shown in Figure 12. The initial temperature profile in the copper bed is described well, but the temperature at the exit of the reactor is somewhat overpredicted. As also observed during the reduction cycle, the temperature is overpredicted in the first minute, probably due to the residence time of the gas in the oven (that is upstream of the reactor), which is not accounted for in the model. After 2 min, the temperature profile inside the reactor is described well. The \( \text{O}_2 \) breakthrough profile (shown in Figure 12) is also described well by the model (the difference at the beginning is again due to the small leakage in the analyzer that was not included in the model).

3.3.3. TS-CLC for Industrial Applications. During the experiments it was shown that the heat produced in the first reactor bed was transferred to the second bed so that a higher exit temperature was obtained. Therefore, by these experiments it was proven that the TS-CLC concept works. However, the temperature of the exit stream was not constant and not sufficiently high so that the stream could be fed to a gas turbine for power production. Due to the small diameter and length of the lab scale reactor, the effect of heat losses and axial dispersion is quite significant. Hence, it is not possible to directly describe how the process would work at the industrial scale. This is studied by scaling up the reactor using the model that has been validated in section 3.3.2.

For this scaling up, the following parameters were changed. The heat losses were excluded in the model (which correspond to the situation when the reactor has a diameter of at least 1 m\(^3\)) and the length of the reactor was increased by a factor of 5 (to 3.53 m) to reduce the effect of axial heat dispersion. Furthermore, the mass flow rate was increased by a factor of 5, so that the same cycle times can be used.

Figure 13 shows the outlet temperature profiles during a cycle for the prediction on the lab scale and on the industrial scale. The maximum temperature is reached just after the oxidation (\( t = 11.5 \) min), but afterward the temperature decreases due to axial heat dispersion inside the reactor. The simulation on a larger scale shows that a higher temperature can be reached, due to the absence of heat losses. On the industrial scale, a temperature peak is observed when the bed is fully oxidized, but after the peak a hot gas stream is produced at constant temperature. Analysis of the axial temperature profiles has shown that the initial temperature peak can be avoided by increasing the heat removal time. The maximum temperature can be increased by modification of the oxygen carriers (weight content of the active species).

In this case, the maximum temperature is below 1200 °C, but this can be increased by increasing the apparent active weight contents. The \( \text{CuO} \) content on the Cu-based OC could be increased or the support material could be replaced, so that a larger amount of oxygen reacts during reduction at low temperature. An apparent active weight content of 13 wt % \( \text{CuO} \) (instead of 10 wt %) would be sufficient to increase the final temperature by 120 °C. In the second reactor bed, a nonideal oxygen carrier has been used, because of the price and the toxicity of nickel. This oxygen carrier might have to be replaced by another material, such as a Mn-based material. To avoid interaction between the manganese and the support material (that would reduce the reactivity and stability), it could
be supported on $\text{ZrO}_2$ or $\text{MgZrO}_2$, $\text{Mn}_3\text{O}_4$ or $\text{MgZrO}_2$ (with an active weight content of 30 wt %) might be a good candidate for this reactor bed. After some optimization of the oxygen carriers, a working process configuration can be achieved, in which hot gas is produced at 1200 °C.

An LHV efficiency can be reached of 40.8% in an optimized case, which is close to the efficiency of a one-stage CLC process in packed bed reactors and the efficiency in a circulating pressurized fluidized bed system. At this moment, no oxygen carrier is available for the one-stage process and for the circulating fluidized bed process it is impossible to deliver a hot gas stream without any fines, while operating at high pressure. Hence, the TS-CLC configuration is closer to practical application than other high-pressure alternatives while able to achieve practically the same overall LHV efficiency.

4. CONCLUSIONS

Because it has proved difficult to find an oxygen carrier that fulfills all the criteria (stability, reactivity, and oxygen capacity) for successful operation of CLC in packed bed reactors, a two-stage CLC has been developed using two packed bed reactors with two different oxygen carriers placed in series. In this work, this process configuration has been experimentally demonstrated with syngas as fuel. A high pressure/high temperature packed bed reactor is used to show that it is possible to carry out CLC with this reactor configuration, which means that the heat of oxidation produced in the first bed is effectively transferred to the second bed. A final temperature of 839 °C was observed, while the gases were fed at 450 °C. The effects of the operating conditions such as the pressure, throughput, fuel concentration, and fuel type were studied in the setup. Small effects of the pressure, fuel concentration, and throughput during reduction on the maximum temperature increase have been observed as long as differences in flow rates (which are related to heat front rates) are compensated for by fine-tuning the cycle time. The fuel type has a significant effect on the performance, because the degree to which the oxygen carriers are reduced depends on the fuel type. The degree of reduction determines the temperature rise that can be reached during the subsequent oxidation. It was not possible to reduce the CuO/Al2O3 with CH4 at 450 °C, but a working process was demonstrated for syngas as fuel.

The experiments with syngas have been well described by a 1D pseudohomogeneous packed bed reactor model. A prediction of the performance on a larger scale (with higher reactor length and diameter) has been made by the same model, showing that a gas stream with a temperature between 1000 and 1070 °C could be produced in case heat losses and heat dispersion effects are diminished. This maximum temperature can further be increased to the desired level of 1200 °C after optimization of the cycle time and the oxygen carrier materials. Concluding, TS-CLC can be regarded as feasible technology for power production with integrated CO2 capture with a relatively high overall LHV efficiency. This development makes the integration of CCS to a power plant less energy intensive.

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Notes

The authors declare no competing financial interest.

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■ NOMENCLATURE

Abbreviations

- apparent active weight content = weight fraction of oxygen carrier that reacts during reduction
- CLC = chemical-looping combustion
- cycle time = duration of a complete cycle, containing reductions, oxidations, and purges
- LHV = lower heating value
- OC = oxygen carrier
- TS-CLC = two-stage chemical-looping combustion
- WGS = water gas shift

Symbols

- $b$ = stoichiometric factor in the reduction reaction of metal oxide
- $C$ = concentration, mol m$^{-3}$
- $C_H$ = heat capacity, J mol$^{-1}$ K$^{-1}$
- $D_a$ = axial dispersion coefficient, m$^2$ s$^{-1}$
- $d$ = diameter, m
- $E_A$ = activation energy, J mol$^{-1}$
- $\Delta H_R$ = enthapy of reaction, J mol$^{-1}$
- $k_0$ = pre-exponential factor, mol$^{1-n}$ m$^{3/2}$ s$^{-1}$
- $M$ = molar mass, kg/mol
- $n$ = reaction order in gas
- $P$ = pressure, Pa
- $P_{tot}$ = total pressure, bar
- $R$ = gas constant, J mol$^{-1}$ K$^{-1}$
- $T$ = temperature, K
- $t$ = time, s
- $\Delta t$ = time difference between two measurements, s
- $v$ = superficial velocity, m s$^{-1}$
- $x$ = axial position, m
- $X$ = particle conversion
- $y$ = mole fraction in gas feed

Greek Symbols

- $\varepsilon$ = volume fraction, m$^3$ m$^{-3}$
- $\zeta$ = stoichiometric factor, mol of gas/mol of solid
- $\lambda_{eff}$ = effective heat dispersion coefficient, W m$^{-1}$ K$^{-1}$
- $\eta_g$ = dynamic gas viscosity, kg m$^{-1}$ s$^{-1}$
- $\omega$ = mass fraction, kg kg$^{-1}$
- $\tau$ = time delay in the thermocouple, s

Subscripts

- act = active
- $g$ = gas component
- $i$ = gas component
- $j$ = solid component
- $p$ = particle
- $r$ = reactor
- red = reduction
- eff = effective
- $s$ = solid
- TC = thermocouple
- $w$ = reactor wall
REFERENCES


(12) HSC Chemistry software, version 5.1; Outotec: Espoo, Finland, 2013.


