Packed Bed Reactor Technology for Chemical-Looping Combustion

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Chemical-looping combustion (CLC) has emerged as an alternative for conventional power production processes to intrinsically integrate power production and CO₂ capture. In this work a new reactor concept for CLC is proposed, based on dynamically operated packed bed reactors. With analytical expressions validated with a more detailed numerical model, it is demonstrated that a constant, very high temperature air stream can be generated efficiently using packed bed CLC reactors to drive a downstream gas turbine. The process consists of alternate oxidation and reduction cycles, intermittently alternated with short periods of mild fluidization of the bed after each cycle to level off temperature and concentration profiles. Oxygen carriers based on nickel, iron, and manganese oxide show the highest potential for use in packed bed CLC. Compared to the interconnected fluidized bed system proposed in the literature (Lyngfelt, A.; Leckner, B.; Mattisson, T. A fluidized-bed combustion process with inherent CO₂ separation; application of chemical-looping combustion. Chem. Eng. Sci. 2001, 56, 3101), the difficult separation of gas and particles is intrinsically avoided and the oxygen carrier can be utilized over the entire range of oxidation states.

I. Introduction

As a result of the ever-increasing dependency on fossil fuels for power production, the carbon dioxide concentration in the atmosphere has increased strongly over the past few decades. Serious concerns about negative effects of CO₂ on our climate (greenhouse effect) have increased, and it is now generally accepted that radical measures will be required to restrict anthropogenic CO₂ emissions. One of the possibilities to achieve this, apart from improving energy efficiency and developing power production from sustainable energy sources, is carbon capture and sequestration (CCS). In CCS, CO₂ is recovered from flue gas streams and stored in, e.g., geological formations, such as depleted gas or oil reservoirs, or in the ocean. For these processes to be performed in an economically feasible way, a concentrated CO₂ stream is required. In the past few years, much research has been focused on obtaining flue gas streams with high CO₂ concentrations (>90%), especially in the power production sector, which is responsible for approximately 30% of all anthropogenic CO₂ emissions.¹ Three general approaches in CO₂ capture can be distinguished: (i) postcombustion technologies (where nitrogen and carbon dioxide are separated), (ii) precombustion decarbonization (“hydrogen” route, where, after conversion of a fuel, typically via (autothermal) steam reforming, carbon dioxide is separated from the H₂ stream), and (iii) oxyfuel combustion (“oxygen” route, where oxygen and nitrogen are separated, typically via cryogenic distillation). In these approaches, multiple process steps are required.

One of the possibilities to inherently combine power production with the capture of pure CO₂ in a single process step is chemical-looping combustion (CLC). The main advantage of CLC over conventional power production technologies is that direct contact between air and fuel is circumvented, so that CO₂ is obtained without nitrogen dilution. In CLC, fuel and oxygen are transported via an intermediate oxygen carrier, a metal/metal oxide that can alternately be oxidized and reduced (see Figure 1). The oxidation of the oxygen carrier is strongly exothermic,

which is used to heat an air stream to very high temperatures (T = 1000–1200 °C) and subsequently drive a gas turbine. During the (often endothermic) regeneration with methane, carbon dioxide without nitrogen dilution is formed. In addition to the production of pure CO₂ (after an easy separation from steam), this process also ensures that no NOₓ will be present in the flue gas because of the absence of the very high temperatures associated with the use of a flame.

Research on CLC has so far mainly been focused on the development and selection of suitable oxygen carrier materials and the implementation of this concept in a clean-fossil power plant. Regarding the power cycle used, operation at high pressure (p ≥ 20 bar) and the use of both a gas turbine and a steam cycle (combined cycle) are necessary to ensure high overall energy efficiencies.² A number of materials have been identified as suitable oxygen carriers in a CLC system (see, e.g., refs 3–7): metal oxides based on iron, nickel, manganese, and copper oxides, supported on alumina, zirconia, silica, or titania. With several of these oxygen carriers, high reactivity under both reductive and oxidative conditions, good mechanical, chemical, and thermal stability over multiple cycles, and a high selectivity toward CO₂ could be combined.

In the literature, an interconnected fluidized bed system, schematically depicted in Figure 2a, has been proposed for CLC.³⁹ In this reactor concept the particles are transported between an air reactor (typically a riser), where hot air is produced via the oxidation of the particles, and a regeneration unit (typically a bubbling fluidized bed), where the particles are reduced with methane while producing CO₂. With this reactor system, a continuous production of hot air was achieved¹⁰ and the main problems associated with air/methane slip between the reactors

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were solved.\textsuperscript{11} However, the main drawbacks of this reactor concept are related to the transport of the oxygen carrier. Not only is an additional energy input required to transport the particles, but a cyclone is also required to separate the particles from the hot air stream. This particle separation is particularly difficult considering the required, extremely harsh reaction conditions (high pressure and very high temperature) and the fact that even fines (resulting from inevitable particle attrition) need to be removed to protect the downstream gas turbine.

In this work it is investigated whether CLC can be executed in reactor concepts based on packed bed reactor technology, where the solids are stationary and are alternately exposed to reducing and oxidizing conditions via periodic switching of the gas feed streams (Figure 2b). The main advantages of reactor concepts based on packed bed reactor technology are that the separation of gas and particles is intrinsically avoided, that the reactor design can be much more compact, and that they allow for better utilization of the oxygen carrier (i.e., a larger difference in the degree of oxidation between the reduced and oxidized forms of the oxygen carrier can be attained). To achieve a high process energy efficiency, a continuous high temperature gas stream supply to the downstream gas turbine is required. This can be achieved with packed bed operation by positioning at least two reactors in parallel. The main attention during the regeneration of the oxygen carrier is taken by the high temperature, high flow gas switching system. The objective of this study is to assess the feasibility of packed bed reactor technology for chemical-looping combustion.

Two important questions need to be considered first: (1) Can (very) high temperature air for the gas turbine be produced in a packed bed reactor filled with oxygen carrier particles, and what operating parameters can be effectively used to influence and control the air temperature? (2) For how long can an air stream of constant high temperature be generated relative to the total cycle time? First, these questions will be addressed by deriving analytical expressions for the maximum (plateau) temperature and the efficiency of the oxidation cycle, which is subsequently used to investigate the suitability of various oxygen carriers for packed bed CLC. Subsequently, a more detailed numerical model will be presented enabling the assessment of the model assumptions underlying the analytical expressions and to finally study in detail the complete process consisting of multiple oxidation–reduction cycles.

2. Analytical Approach

2.1. Maximum Temperature. First, it is investigated whether, in a CLC process based on dynamically operated packed bed reactors, production of a constant high temperature gas stream during the oxidation cycle is in principle possible and how the operating parameters and properties of the oxygen carrier should be tuned to control the temperature of the outlet gas stream. In the following analysis an analytical expression for the maximum temperature is derived from an energy balance, where it is assumed that the packed bed initially consists of the completely reduced form of the oxygen carrier, which will react with the oxygen supplied in the gas feed stream with an infinitely high reaction rate, as schematically depicted in Figure 3a. The exothermicity of this reaction causes the bed temperature to increase until complete particle conversion to the oxidized form has been attained. As a consequence of the convective gas flow, two heat fronts move through the reactor (see Figure 3b). In this analysis it is assumed that the heat capacity of the gas and solid and the solid density are constant and that the influence of the pressure drop and the variation of the mass flow rate, caused by the consumption of oxygen, can be neglected.

Considering that the heat produced in the bed by the oxidation of the oxygen carrier is taken up by the solid material in the bed (neglecting the gas-phase volumetric heat capacity but not that of the solid phase) as described by the following energy balance

\[
\frac{\rho_v V_{g,O_2} \left( -\Delta H_R \right)}{M_{O_2}} = \epsilon \rho_s C_p (w_2 - w_1) (T_{\text{max}} - T_0)
\]

the expected maximum temperature increase in the packed bed reactor is given by eq 2, where \( w_1 \) and \( w_2 \) represent the heat front velocity and the reaction front velocity, respectively (see Figure 3b). Other symbols are explained in the Nomenclature. At the heat front the heat present in the solid material is transferred to the gas phase, and at the reaction front all the oxygen fed reacts with a known amount of solid material, so that

\[
\Delta T = T_{\text{max}} - T_0 = \frac{\rho_v V_{g,O_2} \left( -\Delta H_R \right)}{M_{O_2} \epsilon \rho_s C_p (w_2 - w_1)} \tag{2}
\]

where \( \xi \) represents the ratio of the number of moles of gas and solid needed for the oxidation reaction and \( w_{\text{act}} \) denotes the weight fraction of the reactive material in the oxygen carrier. For the latter parameter and the molecular weight of the active material in the solid, \( M_{\text{act}} \), an average value over the complete conversion should be adopted. Now, the expected temperature difference can be rewritten as

\[
\Delta T = \frac{-\Delta H_R}{C_p \xi \frac{M_{\text{act}}}{w_{\text{act}}}} - \frac{C_p \rho_s M_{O_2}}{\xi \rho_v w_{g,O_2} \frac{M_{\text{act}}}{w_{\text{act}}}} \tag{5}
\]

Remarkably, the maximum temperature increase due to the oxidation of the oxygen carrier in this packed bed CLC reactor is independent of the gas flow rate. This is very important in relation to the reactor’s flexibility to changes in production.
capacity. The maximum temperature is only influenced by the properties of the gas phase and, especially, the solid material (as long as the reaction front velocity, \( w_2 \), is larger than the heat front velocity, \( w_1 \)). Moreover, as long as the oxidation reaction is very fast, there is also no influence of the reaction kinetics, so that a possible decrease of the activity of the oxygen carrier will not directly affect the temperature increase obtained in the bed. This will be further verified with the numerical model, to be discussed in section 4.

2.2. Oxidation Cycle Efficiency. From the previous section it can be concluded that the desired temperature increase can be obtained; however, the second question is whether this high temperature air stream can be generated over a sufficiently long period of time to ensure efficient power production. It is anticipated that the heat accumulated in the particles at the moment the entire bed has been completely oxidized will be removed via the convective gas flow through the bed. The evolution of the temperature at the reactor exit, which is the temperature of the gas stream fed to the downstream gas turbine, can be evaluated by solving an unsteady energy balance over the solid packing, assuming an initially uniform temperature and that heat transfer limitations between the gas and solid phases can be accounted for with a pseudohomogeneous model. The outlet temperature will be equal to the initial temperature, as long as the reaction front has not yet reached the reactor exit. From that moment, the following energy balance applies (neglecting again the volumetric heat capacity of the gas phase) or using the heat front velocity, \( w_1 \), and effective thermal diffusivity, \( a (=\lambda_{\text{eff}}/\epsilon_{\text{eff}}C_{p,s}) \):

\[
\frac{\partial T}{\partial t} = -w_1 \frac{\partial T}{\partial x} + a \frac{\partial^2 T}{\partial x^2} \tag{6}
\]

This equation, supplemented with the initial condition \( T = T_0 \), can be solved analytically, again assuming constant physical properties and neglecting the influence of the pressure drop and changes in the gas mass flow rate due to the oxygen consumption, so that the temperature in the bed as a function of position and time is given by:

\[
T(x,t) = \frac{T_0 + T_{\text{max}}}{2} + \frac{T_{\text{max}} - T_0}{2} \text{sign}(x - w_1t) \text{erf}\left(\frac{|x - w_1t|}{4at}\right) \tag{7}
\]

for \( t > \frac{L}{w_2} \)

The dimensionless temperature at the reactor exit, \( Y_L \), can now be written as:

\[
Y_L = \frac{T(x,L) - T_0}{T_{\text{max}} - T_0} = \begin{cases} 
0 & \text{for } t/\tau_h < \frac{\Delta \Theta_{\text{ad}}}{\Delta \Theta_{\text{ad}} + 1} \\
0.5(1 + \text{erf}[0.5(Pe\h)_{\text{ad}}]^{1/2}) \times \left(\frac{1}{(t/\tau_h)^{1/2} - (t/\tau_{\text{th}})^{1/2}}\right) & \text{for } \frac{\Delta \Theta_{\text{ad}}}{\Delta \Theta_{\text{ad}} + 1} < t/\tau_h < 1 \\
0.5(1 - \text{erf}[0.5(Pe\h)_{\text{ad}}]^{1/2}) \times \left(\frac{1}{(t/\tau_h)^{1/2} - (t/\tau_{\text{th}})^{1/2}}\right) & \text{for } t/\tau_h > 1
\end{cases} \tag{8}
\]

where the following dimensionless parameters have been introduced:

\[
Pe\h = \frac{w_1L}{a} \quad \Delta \Theta_{\text{ad}} = \frac{\Delta T_{\text{max}}}{\Delta T_{\text{ad}}^{*}} \quad \tau_h = \frac{L}{w_1} \quad \Delta T_{\text{ad}}^{*} = \left(\frac{-\Delta H_R}{C_{p,g}M_{\text{O}_2}}\right)^{1/2} \tag{9}
\]

Here, the heat Péclet number, \( Pe\h \), describes the ratio of convective heat flow and conduction and the dimensionless temperature increase, \( \Delta \Theta_{\text{ad}} \), describes the ratio of the maximum temperature increase (described by eq 5) and the adiabatic temperature rise that would be obtained if a gas-phase reaction with the same exothermicity were carried out in a stationary adiabatic packed bed reactor.

In Figure 4, the influence of the Péclet number, \( Pe\h \), and the dimensionless temperature increase, \( \Delta \Theta_{\text{ad}} \), on the evolution of the dimensionless temperature at the reactor exit during a complete oxidation cycle is depicted. The figure clearly shows that these parameters affect the outlet temperature differently: when the relative influence of convection over dispersion increases, the desired high temperature can be generated over a longer period of time. However, when a higher temperature increase in the bed is desired, the period that the high temperature air stream can be generated (with the same amount of active oxygen carrier) decreases. The efficiency of the oxidation cycle is defined as the ratio of the heat produced at the desired high temperature \( (Y_L \geq Y_L^{*}) \), with, e.g., \( Y_L^{*} \geq 0.95 \) and the total heat production. As the physical properties of both air and the oxygen carrier are assumed to be constant, this oxidation cycle efficiency is represented by the area under the curves in Figure 4, but left from the line where \( Y_L = Y_L^{*} \), relative to the adiabatic temperature rise.
to the total area under the curves. The influence of \( Pe_h \) and \( \Delta \Theta_{ad} \) on the oxidation cycle efficiency is shown in Figure 5. It is clear that it is desired to maximize \( Pe_h \) (which also means that the capacity of the bed is optimized) and to keep the dimensionless temperature increase as low as possible. Table 1 summarizes the qualitative effects of various parameters on the oxidation cycle efficiency. It is finally noted that the energy from the hot air stream when the outlet temperature has dropped below the design temperature \( Y_L < Y_L^* \) can be used to preheat the air stream (re recuperative heat exchange).

3. Oxygen Carrier Characteristics

From the previous sections it can be concluded that it is in principle possible to generate a constant high temperature air stream for a sufficiently long time in a packed bed CLC reactor, provided that the operating parameters and properties of the oxygen carrier are tuned. In this section, the consequences of these findings on the choice of a suitable oxygen carrier in a packed bed CLC reactor will be discussed.

So far, most of the development of oxygen carriers has been done aiming at the selection of a material that would be suitable for application in an interconnected fluidized bed reactor (IFBR).\(^3\)\(^-\)\(^7\) However, for use in a packed bed reactor (PBR), different demands and specifications apply. An important difference between both concepts is that, in a PBR, use is made of the complete oxidation range of the particles, whereas, in an IFBR, only a part of the oxygen carrier’s oxidation potential is utilized. Although the stability of the oxygen carrier (e.g., resistance against coke formation, \( CO_2 \) selectivity) needs to be assured over the entire oxidation range of the material used, the number of reduction/oxidation cycles that the oxygen carrier must undergo (per unit of time) is much smaller in the packed bed system. On the other hand, particle replacement is probably easier in the IFBR. Further on, in view of the downstream turbine, the prevention of fines production is crucial in the process, which especially poses a problem for the IFBR, where the mechanical stresses exerted on the particles are significantly higher than in the PBR. In the packed bed reactor, the particle size needs to be large enough to avoid a large pressure drop.

In Table 2 and Figure 6 the influence of the oxygen carrier material properties on the temperature increases and the oxidation cycle efficiency is given. Here, it is assumed that a temperature increase of 600 K is necessary for an efficient energy production process. Since different support materials can be used for the different metal oxides used as oxygen carriers, the heat capacity of the solid material, \( C_p,s \), was taken constant for all materials. Optimization of the heat capacity of the support material can however be very important.

The desired high temperature increase can be obtained with all of the suggested oxygen carriers, although the amount of active material that is required in the particles is considerably larger when the oxygen capacity of the carrier is smaller. This however does not affect the oxidation cycle efficiency, which is comparable for iron, nickel, and manganese oxide; only the maximum oxidation cycle efficiency of copper oxide is significantly smaller. Considering the high oxidation cycle efficiency (> 85%), these oxygen carriers show good potential for application in a packed bed CLC reactor. The final selection of the
most suitable oxygen carriers needs to be made considering the stability and selectivity of the materials.

It is well-known that on nickel oxide significant coke formation can occur during the reduction reaction with methane. Deposition of carbonaceous compounds must be avoided considering that it may not only negatively affect the performance of the oxygen carrier, but also decreases the overall CO₂ capture efficiency due to the combustion of coke during the oxidation reaction. It is believed that the addition of steam to the reducing gas stream may suppress coke formation, but the increase of the mass flow through the reactor may result in a substantial pressure drop and the costs associated with the production and transportation of steam may be significant. On the other hand, it must be noted that, in most other CO₂ capture processes, a CO₂ capture efficiency of 90% is considered acceptable, so that small amounts of CO₂ in the air stream may be tolerated.

With oxygen carriers based on iron oxide, multiple reduction states will be encountered, and from thermodynamic calculations it is expected that the selectivity toward carbon dioxide and steam deteriorates when the reduction from Fe₃O₄ to FeO, and it is expected that the selectivity toward carbon dioxide and steam deteriorates when the reduction from Fe₃O₄ to FeO, and from thermodynamic calculations it is expected that the selectivity toward carbon dioxide and steam deteriorates when the reduction from Fe₃O₄ to FeO, and further, occurs. In contrast to the interconnected fluidized bed reactor, this may not be a problem with the packed bed reactor. The further reaction of hydrogen and carbon monoxide will take place with the oxygen present in the oxygen carrier downstream in the bed. This means that full conversion of the fuel is still possible as long as the reaction fronts are sharp and the addition of fuel is stopped once CO starts to break through. As with nickel oxide, also coke formation during the reduction of iron oxide may occur.

With manganese oxide, the weight fraction of active material in the particle, \( w_{\text{act}} \), needs to be considerably larger than with the other oxygen carrier candidates, but when particles with these active/inert material ratios can be produced, manganese oxide is very well suited for application in this process.

Copper oxide is actually the only oxygen carrier that seems less suitable for CLC considering the desired very high temperatures, because of its low oxidation cycle efficiency and its low melting point, even though it is the only material of which the reduction reaction is exothermic.

From this analysis it is concluded that Fe/Fe₂O₃, Ni/NiO, and MnO/Mn₃O₄ oxygen carriers show the highest potential for application in a packed bed CLC reactor. With all these candidates though, problems need to be solved. Moreover, in this system, as well as in the interconnected fluidized bed reactor, the performance of the oxygen carrier is crucial for the feasibility of the process. Not only is it necessary that the reactions proceed at sufficiently high rates, but also the particle behavior must be constant and reliable over a large number of oxidation/reduction cycles and the chemical, mechanical, and thermal stability of the solids is of great importance, especially when, as is the case with the packed bed reactor, replacement of the particles can be costly. Finally, to be able to profit from the advantages of different materials, combinations of oxygen carrier materials may be considered as well.

### Table 3. Governing Equations

<table>
<thead>
<tr>
<th>Kinetic constant</th>
<th>Expression</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k )</td>
<td>( \frac{k_{\text{eff}}}{C_{\text{p,ox}}} )</td>
<td>Energy balance of ( F_{\text{g,ox}} ) at ( T = 600 \text{ K} )</td>
</tr>
<tr>
<td>( k_{\text{eff}} )</td>
<td>( \frac{k_{\text{eff}}}{C_{\text{p,ox}}} )</td>
<td>Volume balance of ( F_{\text{g,ox}} ) at ( T = 600 \text{ K} )</td>
</tr>
<tr>
<td>( k_{\text{eff}} )</td>
<td>( \frac{k_{\text{eff}}}{C_{\text{p,ox}}} )</td>
<td>Mass balance of ( F_{\text{g,ox}} ) at ( T = 600 \text{ K} )</td>
</tr>
</tbody>
</table>

### Table 3. Required \( w_{\text{act}} \) and Corresponding Oxidation Cycle Efficiency for Different Oxygen Carriers

<table>
<thead>
<tr>
<th>Reductive state</th>
<th>Oxidative state</th>
<th>Capacity ( % )</th>
<th>( \Delta H_{\text{ox}} ) (kJ/mol of ( \text{O}_2 ))</th>
<th>( \Delta H_{\text{red}} ) (kJ/mol of ( \text{CH}_4 ))</th>
<th>( \Delta T_{\text{red}} ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>CuO</td>
<td>20.1</td>
<td>-296</td>
<td>-209</td>
<td>100</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe₂O₃</td>
<td>30.1</td>
<td>-539</td>
<td>277</td>
<td>-135</td>
</tr>
<tr>
<td>MnO</td>
<td>MnO₂₃O₄</td>
<td>7.0</td>
<td>-449</td>
<td>97</td>
<td>-55</td>
</tr>
<tr>
<td>Ni</td>
<td>NiO</td>
<td>21.4</td>
<td>-468</td>
<td>135</td>
<td>-74</td>
</tr>
</tbody>
</table>

* Oxygen capacity = 1 - \( M_{\text{red}}/M_{\text{ox}} \). * At \( T = 1000 \text{ °C} \). * With \( C_{\text{p,ox}} = C_{\text{p,red}} = 1000 \text{ (J/kg)/K} \). * Oxidation cycle efficiency at \( Pe_{\text{θ}} = \infty \). * Using \( w_{\text{act}} \).
discussed in the previous section, but the availability of kinetic data for both the oxidation and the reduction reactions (García-Labiano et al.\textsuperscript{13}) made this system well suited for these introductory calculations. The choice of the oxygen carrier is not expected to affect the conclusions drawn in a qualitative sense. In this study it was assumed that only the oxidation of copper to copper(II) oxide proceeds and that reaction is completely selective to carbon dioxide and steam. The contributions of the oxidation of Cu to Cu$_2$O, or coke deposition, which may occur during the reduction reaction, or the possible degradation of the oxygen carrier (e.g., because of the high temperatures) are neglected. It was assumed that the availability of the solid material does not affect the reaction rate ($m = 0$), and in the source term, the possible influence of internal and external mass transfer limitations was accounted for. The pressure drop was calculated with Ergun’s equation, a uniform temperature profile was assumed as the initial condition, and the usual Danckwerts-type boundary conditions were applied. The input simulation parameters for a test case are given in Table 4.

4.2. Oxidation Reaction. The oxidation reaction of copper on alumina was studied using the settings given in Table 4. From the axial concentration and temperature profiles obtained in this simulation, depicted in Figure 7, it is clear that the oxidation reaction proceeds at a sufficiently high rate to conclude that the assumptions made for the derivation of the analytical expressions for the maximum temperature increase are reasonable.

In Figure 8, the correspondence between the analytical solution and the numerical simulation is shown and it is found that the temperature increase, the front velocities, and the effect of conduction can be predicted very well with the analytical solution. Apparently, the effect of the reaction kinetics, pressure drop, and variations of the physical properties of the gas and particles, which are implemented in the model, is of secondary importance during the oxidation reaction. That the influence of the reaction kinetics is small during the oxidation reaction was validated as well; the results are presented in Figure 9. It is found that the maximum temperature increase obtained is indeed independent of the reaction rate. This is a very interesting feature of packed bed CLC, since a (small) decrease in activity of the oxygen carrier (e.g., due to coke formation) will not affect the temperature of the hot air produced. The decrease in the oxidation cycle efficiency that must be accepted when the oxidation reaction rate is smaller is relatively small, as the time needed to completely oxidize the bed is small compared to the time during which a high temperature air stream can be produced.

When the temperature profile is not uniform when the oxidation cycle is started (as a consequence of the preceding regeneration step), temperature variations in the gas leaving the reactor may occur. From Figure 10 it can be discerned that, while small temperature effects may still be leveled out, larger deviations from the ideal situation may have an important influence on the temperature profile obtained at the reactor exit, when this temperature effect is situated both at the beginning and at the end of the packed bed. Of course, temperature effects can be canceled out more easily when the residence time of the heat front in the bed is larger (e.g., increased reactor length), but considering that the temperature the particles are subjected to is considerably larger than in the ideal situation, it may be preferred to start the oxidation cycle with a uniform temperature profile. This may be accomplished via mild fluidization of the bed just after the reduction reaction (preferably with steam and close to incipient fluidization conditions) for a short period, so

<table>
<thead>
<tr>
<th>Table 4. Input Simulation Parameters</th>
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<tr>
<td><strong>oxidation</strong></td>
</tr>
<tr>
<td>$\rho_{\text{d}O_2}$ [(kg/m$^3$)/s]</td>
</tr>
<tr>
<td>$T_{\text{red}}$ (K)</td>
</tr>
<tr>
<td>$w_{\text{in}}$</td>
</tr>
<tr>
<td>$\Delta H$ (kJ/mol of O$_2$)</td>
</tr>
<tr>
<td>$k_0$ (s$^{-1}$)</td>
</tr>
<tr>
<td>$E_{\text{act}}$ (kJ/mol)</td>
</tr>
<tr>
<td>$n$</td>
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that the temperature profile can be leveled off. During the last stage of the oxidation reaction (Figure 8, \( t > 1600 \text{ s} \)), the temperature of the produced hot air stream drops below the specified optimal temperature for the downstream gas turbine. Efficiency calculations involving the downstream turbine will determine at what temperature the reaction should be stopped. Moreover, it may be useful to level off the temperature profiles in the bed just before the oxidation cycle, because in this way essentially the heat is reused by efficient back-mixing of the stored energy.

4.3. Reduction Reaction. During the regeneration of the bed all fuel fed to the reactor should be converted, not only to realize the maximal energy efficiency, but also to ensure the maximum CO\(_2\) capture efficiency. Moreover, the cycle time for the regeneration should be kept as short as possible, the pressure drop must remain limited, and a sufficiently high temperature must be ensured in the entire bed so that the reduction reaction can indeed take place. Different regeneration strategies can be envisaged.

The first regeneration strategy is to stop the fuel supply once methane is detected at the reactor exit and accept that the packed bed is not regenerated completely (no methane slip). The fraction of the bed that is not reduced and remains in the (partly) oxidized form is determined by the mass flow through the system and the reaction kinetics. In Figures 11–13, the influence of the mass flow on the axial (dimensionless) methane concentration profile, the methane slip, and the oxidation degree is depicted, calculated with the numerical model. The methane slip has been defined as the fraction of the fuel added that leaves the reactor unconverted, and the oxidation degree is the fraction of the bed material that is still in the oxidized form. The time has been normalized with the time required to feed the minimum amount of fuel with the selected mass flow rate to completely reduce all the solid material in the bed (equal to \( \tau_r \)). With higher mass flow rates, the reduction of the bed material can be achieved in a shorter time; however, the relative extent of axial dispersion increases, resulting in an undesired increase in the methane slip and oxidation degree of the bed material.

Another strategy for the regeneration is to strive for complete regeneration of the bed and accept some methane slip. An extra
bed could be used to combust the unconverted methane and use the heat for preheating the air or fuel stream, or it is accepted that a small amount of fuel remains in the CO₂ product stream. A detailed economic evaluation based on overall energy efficiency calculations needs to be performed to find out which of these options should be preferred.

4.4. Multiple Cycles. With the numerical model the performance of the CLC packed bed reactor after multiple oxidation/reduction cycles has been investigated. In this simulation, the oxidation cycle was stopped when the outlet air temperature dropped below 1200 K and the reduction cycle was stopped when the methane mass fraction at the reactor outlet exceeded 0.05, assuring a methane slip below 1.5%. After the oxidation and reduction cycles, it was assumed that the system was shortly fluidized with steam, leveling the concentration and temperature profiles. In Figure 14 the evolution of the outlet gas temperature as a function of time is depicted, and in Figures 15 and 16 the axial concentration and temperature profiles at the end of the oxidation and reduction cycles are shown. It is found that, with this operation, the degree to which the packed bed has been regenerates influences the temperature and concentration profiles in the subsequent cycles only to a small extent. After only a small number of cycles, the cyclic steady state is reached and the oxidation range converges to a constant value (0.85) and correspondingly the plateau temperature during the oxidation reaction converges to 1270 K. Moreover, as anticipated, the time during which an air stream of the desired high temperature can be generated (1300 s) is large compared to the time needed to oxidize and reduce the bed (1800 s), so that, with a small number of reactors, continuous power generation can be accomplished.

5. Conclusion/Discussion

In this study the possibility was investigated to perform chemical-looping combustion with dynamically operated packed bed reactors, where the solids are stationary and are alternately exposed to reducing and oxidizing conditions via periodic switching of the gas feed streams. Via the derivation of analytical expressions validated with a more detailed numerical model of the packed bed CLC reactor, it was found that during the oxidation cycle an air stream of constant, very high temperature can be generated. A very advantageous feature of the packed bed CLC reactor is that this maximum temperature is independent of the gas mass flow rate and the oxidation kinetics of the oxygen carrier, offering a high flexibility to changes in the production capacity and little disturbance by changes in the reaction kinetics (e.g., due to coke formation). Moreover, the high temperature air stream can be produced during a time that is large compared to the time needed to oxidize and reduce the bed. It was shown that with oxygen carriers based on nickel, iron, and manganese oxide the highest oxidation cycle efficiencies can be attained. The final selection of the oxidation carrier material may be dictated by its reactivity, stability, resistance against coke formation, and material costs.

During the regeneration of the oxygen carrier, methane slip needs to be limited to maximize the CO₂ capture efficiency and to ensure efficient use of the fuel. It was proposed to fluidize the bed for a very short period after both the reduction and the oxidation cycles, to level off temperature and concentration differences. The cyclic steady state was obtained after only a small number of oxidation/reduction cycles, and continuous power generation can be realized with only two packed bed reactors in parallel.

The main advantage of packed bed reactor technology for CLC over an interconnected fluidized bed system proposed in the literature is that the separation of the gas and particles is intrinsically avoided. This particle separation is particularly difficult considering the extremely harsh reaction conditions (high pressure and very high temperature) and the fact that even fines resulting from inevitable particle attrition need to be removed to protect the downstream gas turbine. Thus, packed
bed CLC shows great potential as an alternative for the interconnected fluidized bed system.

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Nomenclature

\[ a = \text{effective thermal heat conductivity (m}^2/\text{s}) \]
\[ a_0 = \text{external specific area (m}^2/\text{m}^3) \]
\[ a_p = \text{internal specific surface area (m}^2/\text{m}^3) \]
\[ C_p = \text{heat capacity of the gas/solid phase [J/kg/K]} \]
\[ C_i, C_j = \text{concentration gas/solid component (mol/m}^3) \]
\[ D_{ax} = \text{axial dispersion coefficient (m}^2/\text{s}) \]
\[ d_p = \text{particle size (m)} \]
\[ E_{act} = \text{activation energy (J/mol)} \]
\[ \Delta H_R = \text{reaction enthalpy (J/mol)} \]
\[ k_0 = \text{preexponential factor (s}^{-1}) \]
\[ k_{eff} = \text{effective reaction constant (s}^{-1}) \]
\[ L = \text{reactor length (m)} \]
\[ m = \text{reaction order in the solid phase} \]
\[ M_i = \text{molecular weight of component } i \text{ (kg/mol)} \]
\[ M_i' = \text{molecular weight of component } i, \text{ based on one metal atom (kg/mol)} \]
\[ n = \text{reaction order in the gas phase} \]
\[ p = \text{pressure (Pa)} \]
\[ P_{en} = \text{Peclet number, } P_{en} = w_1 L/a \]
\[ t = \text{time (s)} \]
\[ T = \text{temperature (K)} \]
\[ \Delta T_{max} = \text{maximum temperature increase (K)} \]
\[ \Delta T_{ad} = \text{adiabatic temperature increase (K)} \]
\[ v_g = \text{gas velocity (m/s)} \]
\[ w_{ax} = \text{weight fraction of reactive material in the solid} \]
\[ w_{in} = \text{weight fraction of the reactive component in the gas at the inlet} \]
\[ w_i, w_j = \text{weight fraction of the gas/solid component} \]
\[ w_1 = \text{heat front velocity (m/s)} \]
\[ w_2 = \text{reaction front velocity (m/s)} \]
\[ x = \text{axial position (m)} \]
\[ Y_L = \text{dimensionless temperature at the outlet (} x = L \text{)} \]

Greek Letters

\[ \Delta \Theta_{ad} = \text{dimensionless temperature increase} \]
\[ \epsilon = \text{porosity} \]
\[ \xi = \text{stoichiometric factor} \]
\[ \eta = \text{oxidation cycle efficiency} \]
\[ \lambda_{eff} = \text{effective heat dispersion [W/m/K]} \]
\[ \rho = \text{density (kg/m}^3) \]
\[ t_h = L/w_2 = \text{heat front time (s)} \]
\[ t_r = L/w_1 = \text{reaction front time (s)} \]

Subscripts

\[ g = \text{gas phase} \]
\[ s = \text{solid phase} \]
\[ i = \text{component in the gas phase} \]
\[ j = \text{component in the solid phase} \]
\[ ox = \text{oxidized state} \]
\[ red = \text{reduced state} \]

Abbreviations

CLC = chemical-looping combustion
IFBR = interconnected fluidized bed reactor
PBR = packed bed reactor

Literature Cited


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