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Continuous Operation of Interconnected Fluidized Bed Reactor for Chemical Looping Combustion of CH\textsubscript{4} Using Hematite as Oxygen Carrier

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ABSTRACT: Chemical looping combustion (CLC) is a novel technology for CO\textsubscript{2} capture with low energy penalty. This technique involves the operation of the interconnected fluidized bed reactors, within which solid oxygen carrier particles circulate to provide active lattice oxygen for fuel combustion. An interconnected fluidized bed reactor was tested using natural hematite as oxygen carrier and CH\textsubscript{4} as fuel. The thermal power was between 1.00 and 1.50 kW\textsubscript{th} in the continuous operation of 100 h. During the operation, the CLC unit showed a good performance, in which the gas leakage varied between 1.81% and 3.20%, and the CH\textsubscript{4} conversion of 81.3% at maximum and the carbon capture efficiency of over 90% were attained. The effects of operational parameters on the performance of the new CLC reactor were investigated. The results indicated that the CH\textsubscript{4} conversion and CO\textsubscript{2} yield were influenced by the reactor temperature, bed inventory per unit thermal power, and the flow rate of the fluidizing gas agent in the fuel reactor. After the whole tests, no sintering and agglomeration of used particles were observed, and the thermogravimetric analyzer results of used samples showed the reactivity of oxygen carrier was well maintained.

1. INTRODUCTION

It is becoming more and more important to implement carbon capture and storage (CCS) due to the increasing concentration of carbon dioxide in the atmosphere, which has been identified as the one of the biggest contributors to the ongoing climate change.\textsuperscript{1} The main CO\textsubscript{2} emissions come from the combustion of fossil fuels.\textsuperscript{2} Chemical looping combustion (CLC) is a promising way of CO\textsubscript{2} capture with high efficiency and low energy penalty.\textsuperscript{3}

CLC is a process in which oxygen carriers (OC, usually metal oxides), rather than air, provide the active lattice oxygen for fuel combustion. Figure 1 shows the schematic map of CLC. The oxidized OCs are reduced by the fuel in the fuel reactor (FR) and transported to another reactor, namely, air reactor (AR), where the OCs are reoxidized by air. Generally, the reduction reaction is endothermic, the oxidation reaction is exothermic and the total amount of heat released in the two reactions is equal to the normal combustion heat released.\textsuperscript{4} The FR outlet gases consist mainly of CO\textsubscript{2} and H\textsubscript{2}O. After condensation, concentrated CO\textsubscript{2} can be attained for further disposal.

The success of the CLC system mainly depends on suitable OCs with high reactivity, resistance to agglomeration, sintering, fragmentation, and abrasion. For an industrial plant, the OCs should also have characteristics of low cost and environmental friendliness.\textsuperscript{5} Many OCs have been investigated in thermogravimetric analyzer (TGA),\textsuperscript{6,7} batch fixed/ fluidized bed reactors,\textsuperscript{8,9} and interconnected fluidized bed reactors.\textsuperscript{10−13} Some kinds of OC were synthetic oxides (like Ni-\textsuperscript{14}, Fe\textsuperscript{15,16}, Cu\textsuperscript{17−19}, Co\textsuperscript{20}, Mn-based\textsuperscript{21} oxides), and some were natural ores such as hematite,\textsuperscript{22} ilmenite,\textsuperscript{23} manganese ore,\textsuperscript{24} copper ore,\textsuperscript{25} and the mixture of iron ore and copper ore.\textsuperscript{26} The experimental results in TGA or batch-operated reactors provided useful information about, e.g., reduction and oxidation kinetics, which are essential for the design and operation of a real CLC reactor.\textsuperscript{27}

To further test the reactivity behavior of OCs during the continuously long-term operation as well as the feasibility of CLC technology, several groups have already built lab-scaled interconnected fluidized bed reactors, where the OCs continuously circulate in the units.\textsuperscript{12,14,28−31} CLC of gaseous fuels has been widely investigated using different OCs, such as NiO,\textsuperscript{32} Fe\textsubscript{2}O\textsubscript{3},\textsuperscript{33} CuO materials,\textsuperscript{34} and natural minerals (ilmenite,\textsuperscript{35,36} manganese ore,\textsuperscript{24} and so on).

Previous works of the CLC reactor were widely designed with an interconnected fluidized bed reactor as CLC combustor proposed by Lyngfelt et al.\textsuperscript{32} These FRs were generally operated in the bubbling regime to achieve a high residence time and the configuration of the OC recirculation was

Figure 1. Schematic map of CLC.
Table 1. Configuration and Operational Experiences of the CLC Reactors

<table>
<thead>
<tr>
<th>Location</th>
<th>Size (kWth)</th>
<th>AR Configuration</th>
<th>FR Configuration</th>
<th>Recirculation Configuration</th>
<th>OC/fuels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalmers</td>
<td>10</td>
<td>bubbling fluidized bed</td>
<td>bubbling fluidized bed</td>
<td>overflow</td>
<td>Ni-based OC/natural gas</td>
</tr>
<tr>
<td>CSIC</td>
<td>10</td>
<td>bubbling fluidized bed</td>
<td>bubbling fluidized bed</td>
<td>overflow</td>
<td>Cu-based OC/CH4</td>
</tr>
<tr>
<td>Vienna</td>
<td>120</td>
<td>fast fluidized bed</td>
<td>circulating fluidized bed</td>
<td>lower loop seal</td>
<td>ilmenite/natural gas, et al.</td>
</tr>
<tr>
<td>Tsinghua</td>
<td>25</td>
<td>bubbling fluidized bed + riser</td>
<td>bubbling fluidized bed</td>
<td>rotary solid feeder</td>
<td>Fe-based OC/syngas</td>
</tr>
</tbody>
</table>

Figure 2. Interconnected fluidized bed reactor for CLC.

Although the synthetic OCs usually showed high reactivity with the gaseous fuel (actually, most units used synthetic OCs such as NiO/NiAl2O4, NiO/MgAl2O4, CuO/Al2O3, and attained very high fuel conversion of more than 90%), using natural ore as OC in larger CLC plants is preferred from the perspective of reducing the cost in investment and operation. Another objective of this work was to test the stability of a natural OC, namely, hematite in the interconnected fluidized bed reactor.

2. EXPERIMENTAL SECTION

2.1. Interconnected Fluidized Bed Reactor for CLC. In this CLC reactor system, there were four parts: the interconnected fluidized bed reactor; the preheating system of the gases and the electric furnace; the measurement and control system; off-gas analysis and treatment system. In the interconnected fluidized bed reactor system, the FR was operated in the bubbling fluidized bed regime, and the AR was operated in the turbulent fluidized bed regime. The riser was connected to each top of the reactors, which provided the driving force for solid circulation. The cyclone was used for the gas-solid separation, and the nonmechanical loop seal was located between the two reactors to prevent the gas leakage and transport the OC particles. Figure 2 shows the sketch map of this unit.

Also as shown in Figure 2, the whole interconnected fluidized bed reactor system was located within an electrically heated furnace. Each kind of gas was preheated in the electrical heaters. There were 21 pressure sensors and 21 thermal couples evenly and axially distributed in the reactor. The temperature of the thermal couple located on the FR bottom (the main reaction zone) was selected as the reaction temperature (TFR). All the gases were controlled by the mass flow meters. The outlet gases from the AR and FR were cooled by the heat exchanger, and the fine particles entrained were collected by filters.

At the start-up and shut-down stages, air was used as fluidizing gas agent in the reactors. During the continuous operation, air was also used to oxidize the reduced OC in the AR, and N2 and CO2 were used as OC/fuels.
as fluidizing agents when feeding CH₄ for combustion, where N₂ was used as the main fluidization agent and CO₂ was used as a carbon gasification agent. All gases were heated to 800 °C in preheating heaters before pumping into reactors, except CH₄. N₂ was also used as a fluidization agent in the two loop seals.

The operational conditions during the experiments were concluded in Table 2. \( P_{CH₄} \) was the thermal power input of the reactor (based on the low heating value of CH₄), ranging between 1.00 kW\(_{th}\) and 1.50 kW\(_{th}\). \( F_{AR} \) and \( F_{FR} \) were the flow rates in the AR and FR. The CO₂ flow rate in the FR was 5.0 L/min in the entire tests except tests No. 1 and No. 2. The N₂ flow rates in LS1 and LS2 were varied from 0.90 to 1.32 L/min in the transport chamber and from 1.50 to 2.20 L/min in the recycle chamber, respectively. The bed inventory in the FR (\( m_{FR} \)) was approximately 2.5 kg, and the total inventory in the reactor system was around 7.5 kg.

The gas leakage should be minimized in the interconnected fluidized bed reactor. During the initial hot tests No. 1 and No. 2 (\( T_{FR} \) was 900 °C), the fresh hematite was circulated in the interconnected fluidized bed reactor without CH₄ feeding in order to check the gas leakage between the AR and FR. The fluidizing agents to FR and two loop seals were high-purity nitrogen and the fluidizing agent to AR was air. The flow rate of N₂ to FR was 28 L/min during test No. 1 and 20 L/min during test No. 2.

The effects of operational parameters on the CLC performance were tested. Each test was continuously operated at least 30 min. Among tests No. 3, No. 4, and No. 5, three FR temperatures were investigated. The effect of CH₄ feeding rate (or thermal power input) was demonstrated in tests No. 5, No. 6, and No. 7 (all operated at 1000 °C). For the investigation of the flow rate of FR fluidizing gas agent, test No. 8 was compared to test No. 5 at 1000 °C, as well as No. 9 vs No. 4 at 950 °C and No. 10 vs No. 3 at 900 °C. In addition, tests No. 11 and No. 12 were conducted to indentify the effect of CH₄ feeding rates, in comparison with tests No. 10 (at 900 °C) and No. 4 (at 950 °C), respectively. During test No. 13 with the 100 min continuous operation, the solid circulation rates were regulated through the loop seals to identify the effect of the bed inventory on the performance of the unit.

Furthermore, the OC samples were collected from the FR during the continuous tests. The off-gas samples were pumped into the online gas analyzers after the filters, respectively. O₂ and CO₂ from the AR outlet were measured by the online gas analyzer (Cubic, Gasbroad-3151), with CO₂, CO, and CH₄ being determined using nondispersive infrared analysis (NDIR) detector, H₂ by thermal gas conductivity (TCD) detector, and O₂ with electron capture detector (ECD).

### 2.2. Oxygen Carriers.

In the tests, the natural hematite was selected as OC. The chemical analysis of hematite was analyzed by the X-ray fluorescence probe (XRF, EDAX EAGLE III) and X-ray diffraction (XRD, XpertPRO) analysis, as shown in Table 3. The particles were sieved in the size range between 150 and 250 μm, and the average particle diameter was 180 μm. The true density of the OC particles was 3472 kg/m³, measured by density analyzer (Micromeritics, AccuPyC1330). The crushing strength was 2.83 N by the digital dynamometer (Shimpo, FGP-100). The minimum fluidization velocity was 0.0187 m/s at 950 °C using nitrogen as fluidizing agent, and the terminal velocity was 1.12 m/s at 950 °C using air as fluidizing agent.

In consideration of using the natural hematite rather than the calcined hematite, there were two aspects: first, it was 7.5 kg OC for the total bed inventory in the 1–1.5 kW\(_{th}\) CLC reactor and about 300 kg OC of the bed inventory in the 50 kW\(_{th}\) (in built). It was too much work and consuming time of calcining the hematite at the muffule furnace; then, in the preheating stage (0–1000 °C) and starting up stage (1000 °C), the OC in the system was fluidized by the air agent, which was similar to the calcined stage of the hematite OC.

### 3. DATA EVALUATION

The gas leakage rate was calculated by the oxygen concentration from the FR outlet on the basis of oxygen balance. In the tests No. 1 and No. 2, the N₂ was used as the fluidized gas agent in the FR and two LS, and just air (79% N₂ and 21% O₂) used in the AR as fluidized gas agent. Thus, the O₂ can be viewed as tracer gas. On the basis of the definition of the gas leakage, eq 1 was used to calculate the gas leakage.

\[
\eta = \frac{F_{FR, out} \chi_{O₂, FR}}{F_{AR, in} \chi_{O₂, AR}} \tag{1}
\]

where \( F_{AR, in} \) was the flow rate of AR inlet; \( \chi_{O₂, AR} \) was the O₂ concentration of AR inlet; \( F_{FR, out} \) was the flow rate of FR outlet and \( \chi_{O₂, FR} \) was the O₂ concentration of FR outlet.

The relevant performance parameter in CLC operation was the CH₄ conversion, given by

\[
\chi_{CH₄} = 1 - \frac{\chi_{CH₄, FR}}{\chi_{CO₂, FR} + \chi_{CH₄, FR} + \chi_{CO₂, FR}} \tag{2}
\]

where \( \chi_{FR} \) was the concentration of gas i from FR outlet, \( i = CO₂, CO, \) or CH₄.

### Table 2. Operational Parameters in the Tests

<table>
<thead>
<tr>
<th>test number</th>
<th>air reactor</th>
<th>fuel reactor</th>
<th>operating temperature</th>
<th>thermal power</th>
<th>bed inventory</th>
</tr>
</thead>
<tbody>
<tr>
<td>unit</td>
<td>( F_{AX} ) L/min</td>
<td>( F_{AR} ) L/min</td>
<td>( T_{FR} °C )</td>
<td>( P_{CH₄} ) kW(_{th})</td>
<td>( m_{FR} ) kg</td>
</tr>
<tr>
<td>No. 1 (60 min)</td>
<td>30</td>
<td>28</td>
<td>900</td>
<td>1.00</td>
<td>ca. 2.5</td>
</tr>
<tr>
<td>No. 2 (60 min)</td>
<td>30</td>
<td>25</td>
<td>900</td>
<td>1.00</td>
<td>ca. 2.5</td>
</tr>
<tr>
<td>No. 3 (30 min)</td>
<td>30</td>
<td>25</td>
<td>900</td>
<td>1.00</td>
<td>ca. 2.5</td>
</tr>
<tr>
<td>No. 4 (30 min)</td>
<td>30</td>
<td>25</td>
<td>950</td>
<td>1.00</td>
<td>ca. 2.5</td>
</tr>
<tr>
<td>No. 5 (30 min)</td>
<td>30</td>
<td>25</td>
<td>1000</td>
<td>1.00</td>
<td>ca. 2.5</td>
</tr>
<tr>
<td>No. 6 (30 min)</td>
<td>30</td>
<td>25</td>
<td>1000</td>
<td>1.25</td>
<td>ca. 2.5</td>
</tr>
<tr>
<td>No. 7 (30 min)</td>
<td>30</td>
<td>25</td>
<td>1000</td>
<td>1.50</td>
<td>ca. 2.5</td>
</tr>
<tr>
<td>No. 8 (30 min)</td>
<td>30</td>
<td>20</td>
<td>1000</td>
<td>1.00</td>
<td>ca. 2.5</td>
</tr>
<tr>
<td>No. 9 (30 min)</td>
<td>30</td>
<td>20</td>
<td>950</td>
<td>1.00</td>
<td>ca. 2.5</td>
</tr>
<tr>
<td>No. 10 (30 min)</td>
<td>30</td>
<td>28</td>
<td>900</td>
<td>1.00</td>
<td>ca. 2.5</td>
</tr>
<tr>
<td>No. 11 (30 min)</td>
<td>30</td>
<td>28</td>
<td>900</td>
<td>1.25</td>
<td>ca. 2.5</td>
</tr>
<tr>
<td>No. 12 (30 min)</td>
<td>30</td>
<td>25</td>
<td>900</td>
<td>1.25</td>
<td>ca. 2.5</td>
</tr>
<tr>
<td>No. 13 (100 min)</td>
<td>30</td>
<td>25</td>
<td>900</td>
<td>1.00</td>
<td>ca. 2.5–2.0</td>
</tr>
</tbody>
</table>

### Table 3. Chemical Analysis of Hematite

<table>
<thead>
<tr>
<th>Composition</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>65.9</td>
</tr>
<tr>
<td>SiO₂</td>
<td>25.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.4</td>
</tr>
<tr>
<td>others</td>
<td>3.5</td>
</tr>
</tbody>
</table>
The carbon capture efficiency was calculated as the ratio of carbon containing gas flow leaving the FR to the total carbon containing gas flow leaving the system,

\[ \eta_{CC} = \frac{F_{AR,\text{out}}(x_{CO,\text{AR}} + x_{CH_4,\text{AR}})}{F_{FL,\text{in}}(x_{CO,\text{FR}} + x_{CH_4,\text{FR}})} \]

Here, \( F_{AR,\text{out}} \) was the flow rate of AR outlet; \( x_{CO,\text{FR}} \) was the \( CO_2 \) concentration of AR outlet.

The fraction of \( CO_2 \) of total gaseous carbon leaving the FR\(^{41} \) was defined by

\[ x_{CO_2} = \frac{x_{CO,\text{FR}}}{x_{CO,\text{FR}} + x_{CH_4,\text{FR}} + x_{CO_2,\text{FR}}} \]

4. RESULTS AND DISCUSSION

4.1. Gas Leakage. The gas leakage was tested at varying flow rates of FR fluidizing agent, which was 28 L/min during the first 60 min (test No. 1) and then decreased to 20 L/min during the second stage (60–120 min, test No. 2). As shown in Figure 3, the average gas leakage rate in the first stage was 1.81% and then rapidly increased to 3.20% with the decrease of \( F_{FL} \) to 20 L/min. Factually, as the flow rate of FR fluidizing agent decreased, the standard deviation of pressure drop in the FR was much larger due to the growth and break of more bubbles, which resulted in a larger pressure fluctuation in the FR. The pressure fluctuation lead to quite unsteady pressure differences between the FR and loop seal and then fluctuant bed height in the downcomer of the FR cyclone, which more easily caused gas leakage between two reactors.

4.2. Effects of Operational Parameters. The continuous operation of the unit was more than 300 h, including the cold-model running, the heating running, the fuel-feeding running (nearly 100 h) and the cooling-down running. The natural hematite showed a stable and acceptable reactivity during the long-term operation, without obvious sintering or agglomeration.

Figure 4 showed the pressure drop of the AR, FR (including the bottom part and the riser) and two LS during the continuous operation of tests No. 3, No. 4 and No. 8. The operating temperatures were also shown in Figure 4. During each test, the pressure drops were almost steady with some pressure fluctuation. In tests No. 3 and No. 4, the average pressure drop of the FR was 4500 Pa when the flow rate of the FR was 25 L/min. In comparison to test No. 8, in which the flow rate of the FR was 20 L/min, the average pressure drop of the FR was increased to 5000 Pa. At the same time, the pressure drop in the AR was slightly decreased. During the whole continuous operation, the pressure drops in the LS1 and LS2 were high enough to prevent the gas leakage between the AR and FR. The pressure fluctuations in the LS1 and LS2 were explained by the changes of the pressure at the outlet of the recycle pipes, which connected the reactors, and the growth and break of the bubbles in the recycle chamber, which was operated in the bubbling bed regime.

The gas concentrations from FR and AR of six tests are shown in Figure 5. The effect of reactor temperature was first investigated. Figure 5 showed the \( CO_2, CO \) and \( CH_4 \) concentrations from the FR outlet and the \( CO_2 \) and \( O_2 \) concentrations from the AR outlet during the hot tests No. 3, No. 4 and No. 5, which were operated at 900, 950 and 1000 °C, respectively. The main reactions associated with the fuel combustion in the fuel reactor, including OC reduction (eq 5, 6 and 7), \( CH_4 \) decomposition (eq 8), gasification of the deposit carbon (eq 9), et al., and the reactions occurred in the air reactor (eqs 10 and 11) were as follows.

\[
\begin{align*}
CH_4 + 12Fe_2O_3 & \rightarrow CO_2 + 2H_2O + 8Fe_3O_4 \\
CO + 3Fe_2O_3 & \rightarrow CO_2 + 2Fe_3O_4 \\
H_2 + 3Fe_2O_3 & \rightarrow H_2O + 2Fe_3O_4 \\
CH_4 & \rightarrow C + 2H_2 \\
C + CO_2 & \rightarrow 2CO \\
O_2 + 4Fe_3O_4 & \rightarrow 6Fe_2O_3 \\
C + O_2 & \rightarrow CO_2
\end{align*}
\]

It was obvious that the \( CO_2 \) concentration exiting from the FR in test No. 3 was lower, while the \( CO \) and \( CH_4 \) concentrations were considerably higher than in other two tests No. 4 and No. 5. These were ascribed to the reactivity of the OC being relativity lower at 900 °C. However, the \( CO_2 \) concentrations from the FR were almost the same in tests No. 4 (950 °C) and No. 5 (1000 °C). The explanation for this was that more \( CO_2 \) was reacted with carbon produced from the \( CH_4 \) decomposition (\( CH_4 \rightarrow C + 2H_2 \)), which was also demonstrated by a slightly higher CO concentration from the FR in test No. 5 (\( CO_2 + C \rightarrow 2CO \)). Because of the limited residence time, there was still unconverted CO exiting from the FR. The \( CH_4 \) concentration decreased with the increase of FR temperature.

The \( CO_2 \) was found in the AR outlet, which indicated that there was gas leakage from the FR to the AR or the carbon deposited was transported to the AR through OC entrainment. The \( CO_2 \) concentration from the AR decreased with the increase of the reactor temperature. It was because of that that the carbon deposited on the surface of OC particles in the FR was more easily gasified at higher temperatures, reducing the amount of carbon entrained to the AR.
Tests No. 5, 6 and 7 were organized to investigate the effect of the thermal power input (or the CH₄ feeding rates) on the performance of CLC reactor, as shown in Figure 5. Different CH₄ feeding rates from 1.67 L/min (1.00 kWth) to 2.50 L/min (1.50 kWth) were tested at 1000 °C. As shown, the FR CO₂ concentration decreased as the increase of thermal power. There was an obvious increase of CH₄ concentration from the FR outlet with an increase of thermal power, which corresponds to the decrease of CH₄ conversion. The CO concentration of the FR outlet was around 10%. On the other hand, the CO₂ concentration from the AR outlet increased with the thermal power, which indicated that the carbon transported to the AR increased. It seemed that the CH₄ decomposition increased at a higher CH₄ concentration in the FR. Factually, the CH₄ decomposition was caused by the limitation of the bed inventory and the chemical reactivity of OC in the FR. The same trends were found at different operational temperatures (tests No. 10 and No. 11 at 900 °C, tests No. 4 and No. 12 at 950 °C).

Figure 4. Pressure drops during the continuous tests.

Figure 5. Gas concentrations of the FR and AR during the continuous tests.
A series of tests were designed to investigate the effects of the flow rates of FR fluidizing agent, which were varied from 20 L/min to 28 L/min (as shown in Table 1). The CO₂ concentration from the FR outlet was 80% at a lower flow rate in test No. 8 (20 L/min N₂), over 10% than that in test No. 5 of 25 L/min N₂. Accordingly, the CH₄ concentration from the FR outlet was also decreased to around 10% in test No. 8, in comparison with test No. 5. These were ascribed to the CH₄ residence time increasing when the FR flow rate decreased. For the CO₂ concentration of the AR, it decreased from 0.25% (in average) in test No. 5 to 0.15% in test No. 8. It was due to the longer carbon gasification time at a smaller FR flow rate to make less carbon entrained to the AR.

The test No. 13 was continuously run for 100 min to investigate the effects of the FR bed inventory. The FR bed inventory was regulated by controlling the flow rates of the fluidizing agents in the loop seal. As shown in Figure 2, \( F_{\text{LS, tran}} \) was the flow rate of the fluidizing agent in the transport chamber of loop seal (which connected the down comer of cyclone), and \( F_{\text{LS, rec}} \) was the flow rate of the fluidizing agent in the recycle chamber of loop seal (which connected the other reactor). On the basis of our previous cold-model experiments, the solid circulation rate increased with the flow rates of the fluidizing agent in the loop seal. Thus, an increase of the flow rates of the fluidizing agent in the loop seal (LS2) would lead to the solid circulation rate from the FR to the AR being higher than that from the AR to the FR, and then a gradual increase in the FR bed inventory. In test No. 13, the \( F_{\text{LS, tran}} \) was 1.1 L/min in LS1 and 1.26 L/min in LS2; the \( F_{\text{LS, rec}} \) was 1.5 L/min in LS1 and 1.7 L/min in LS2.

The pressure drop of the FR, which was relevant to the bed inventory, was monitored during the hot tests. As shown in Figure 6, the average pressure drop was decreased from ca. 4500 Pa in the initial stage to ca. 3500 Pa. It was estimated that the bed inventory in the FR was decreased by 0.5 kg according to the reduced FR bed height when the test was stopped.

Figure 7 showed the gas concentrations from the FR and AR outlets during the continuous test No. 13. The CO₂ concentration from the FR continuously decreased from the peak value of 70% to almost 50%. It was attributed to insufficient bed inventory that cannot provide enough lattice oxygen for CH₄ combustion. Therefore, the unconverted CH₄ increased in the FR. At the same time, more carbon deposited on the OC particles was transported to the AR, as result of the increase of CO₂ concentration from the AR outlet. Because of the same reason, the unconverted CO from the FR outlet increased gradually.

### 4.3. Performance of Interconnected Fluidized Bed Reactor

The CLC performance of the interconnected fluidized bed reactor was shown as functions of operational parameters (the reactor temperature, the thermal power input, the flow rates of the fluidizing agent, and the bed inventory). The CH₄ conversion, the carbon capture efficiency and CO₂ yield are discussed below, respectively.

#### 4.3.1. CH₄ Conversion

The CH₄ conversion was affected by three factors: the reactor temperature, which is highly relevant to the OC reactivity; the flow rate of FR fluidizing agent (or the FR superficial gas velocity), which determines the CH₄ residence time in the FR; the FR bed inventory, which determines the amount of lattice oxygen to oxidize the reducing gases (CH₄, CO (the product of carbon gasification) and H₂ (the product of CH₄ decomposition)). A series of tests were well organized to investigate the effects of the three factors.

The average CH₄ conversion for 10 tests (each with 30 min continuous operation) is shown in Figure 8. The tests were

![Figure 6. Pressure drop in the FR as a function of time.](image)

![Figure 7. Gas concentrations of the FR and AR during the continuous test.](image)

![Figure 8. CH₄ conversion at different operational parameters.](image)
operated at three typical reactor temperatures, 900, 950, and 1000 °C. At the FR flow rate of 25 L/min and the thermal power of 1.00 kWth, the CH4 conversion increased from 71.38% to 78.58% when the reactor temperature increased from 900 to 1000 °C. The same trend also held at the thermal power of 1.25 kWth.

Furthermore, the flow rates of FR fluidizing agent had an impact on the CH4 conversion. This operational parameter was varied from 20 L/min, 25 L/min, to 28 L/min at the thermal power of 1.00 kWth. The highest CH4 conversion of over 80% was achieved at the lowest FR flow rate (20 L/min) at 950 and 1000 °C. When the FR flow rate was higher, the CH4 conversion was decreased to below 80% and even lower than 40% at 900 °C. It was explained by the insufficient CH4 residence time. In addition, there was more unconverted CH4 at the FR outlet in test No. 5, compared with test No. 8, as shown in Figure 4. However, the almost same CH4 conversions were obtained at tests No. 8 and No. 9, only with different reactor temperatures (950 and 1000 °C). The experimental result indicated that the temperature variation (in the range of 950–1000 °C) was not crucial when the time for CH4–oxygen carrier contact was sufficient at the flow rate of 20 L/min in the FR.

According to test No. 13 (continuous 100 min at 1.00 kWth and 900 °C), there was an obvious decrease of the CH4 conversion with a decrease of the pressure drop in the FR (see Figure 6), which is relevant to the bed inventory. The CH4 conversion was reduced by 14% when the bed inventory was reduced by 0.5 kg as mentioned above. Similar trend was observed when the thermal power increased from 1.00 kWth to 1.50 kWth at 1000 °C. No matter when the bed inventory decreased or the thermal power increased, both of them resulted in the lower bed inventory per unit of thermal power.

4.3.2. Carbon Capture Efficiency. The carbon capture efficiency, which is highly relevant to the CO2 concentration from the AR outlet, was influenced by a few factors, such as methane conversion and decomposition, which resulted in the amount of carbon entrained to the AR, and the fluidizing velocity, which had the impact on the gas leakage as discussed in section 4.1. Considering the methane conversion and decomposition, it was better that the FR was operated at the higher temperatures, because the lower amount of carbon generated in the FR resulted in less carbon entrained to the AR. For another factor, the gas leakage should be minimized.

In Figure 9, when the flow rate of the FR fluidizing agent was 20 L/min at 950 and 1000 °C and with the thermal power of 1 kWth, 96% of carbon capture efficiencies were attained, indicating that more carbon was gasified by CO2 (C + CO2 → 2CO) due to more carbon residence time compared with tests under 25 L/min. However, the highest carbon capture efficiencies were achieved in the tests with the highest flow rate of FR fluidizing agent (28 L/min) and the lowest reactor temperature (900 °C). The explanations for this were (1) the smallest gas leakage at 28 L/min, as discussed in section 4.1; (2) less methane decomposition at 900 °C.

The bed inventory per unit thermal power was defined as the ratio of the bed inventory and the thermal power. The results showed that the increase of the thermal power (from the 1.00 kWth to 1.5 kWth) and the decrease of the bed inventory in the FR (test No. 13) will cause the decrease of the bed inventory per unit thermal power, resulting in the decrease of the carbon capture efficiency, as shown in Figure 9.

4.3.3. CO2 Yield. The influencing factors to the CO2 yield were almost the same to those of CH4 conversion. However, some differences were observed.

When the thermal power was 1.00 kWth and the flow rates of FR fluidizing agent were 25 L/min, the CO2 yield at 950 °C was the highest (70.85%). This was different with the varying trend of the CH4 conversion. It can be explained by the competition between the CH4 reduction and the CH4 decomposition. As known, the higher the reactor temperature, the higher the reactivity between CH4 and OC (resulting in more CO2 and less CH4), however the faster CH4 decomposition (resulting in less CH4 and more carbon formation) and the higher reactivity between carbon and CO2 (resulting in less CO2 and more CO). Factually, as a result, there was less CO from the FR in test No. 4 at 950 °C, compared to other two cases. Similar results were found in tests No. 8 (1000 °C) and No. 9 (950 °C) both with flow rate of 20 L/min.

When the flow rate in the FR was 28 L/min, the CO2 yields were both below 35% in tests No. 11 and 12. The results showed that a higher gas superficial velocity in the FR resulted in a lower CH4 residence time. Thus, the CO2 yield significantly increased with the decrease of the FR flow rates.

During the continuous operation in test No. 13, the CO2 yield was reduced from 70% to 51% as the decrease of the bed inventory. It was also because more bed inventory could provide more lattice oxygen to CH4 reduction in FR.

4.4. OC Characterization. Characterization analysis of the OC particles was performed to investigate the structure and composition changes between the fresh and used OC particles. The oxidized sample and reduced sample were collected from the AR and FR at the end of the experiments, respectively.

When all tests were finished, the used particles were collected to analyze the particle size distributions of the fresh and used samples by laser diffraction particle size analyzer (Master Min, Malvern), as shown in Figure 11. It was obvious that the percentage of the small used particles (below the 200 μm) increased compared with the fresh sample, while that between 200 and 250 μm was decreased. An explanation is that the OC collided and attrited in the reactor, especially in the cyclone due to the high gas velocity. However, the natural hematite showed high strength during circulation in the real CLC reactor.
The microstructure of fresh and used samples after the continuous CLC tests were investigated by scanning electron microscopy (SEM, FEI Quanta 200) with 20.0 kV accelerating voltage. The fresh OC sample contained amounts of fines although it had been screened thoroughly before the test. There were many small particles to be adhered on the surface of the fresh OC, and a compact structure existed. Under the influence of thermal effect and mechanical abrasion, the surface of the OC became porous and the irregular protrusions structure became smooth to some extent. In the SEM image of the used OC sample, small particles were not found, which indicated a high separation efficiency of the cyclone. It was worth noting that no sintering or agglomeration was observed for these used OCs.

The Brunauer–Emmett–Teller (BET) surface area analysis (Micromeritics, ASAP-2020) was consistent with the SEM characterization. The specific surface areas were 3.390 m$^2$/g for the fresh particles but 1.768 m$^2$/g for the used one. Actually, the fresh sample was surrounded by many small particles, which led to a higher BET surface area. Note that, even enough the surface area and pore diameter were decreased, the used OC showed an acceptable reactivity with CH$_4$.

The crystalline phase compositions of the fresh iron ore samples, used samples collected from AR and used samples collected from FR during the continuous tests were determined by X-ray diffraction (XRD, X’Pert Pro) using Cu K$_\alpha$ radiation ($\lambda$ = 1.542 nm) in a $2\theta$ range of 10–90$^\circ$ with an accelerating voltage of 40 kV and a tube current of 40 mA. It can be seen that the fresh ore mainly contains Fe$_2$O$_3$, although a small amount of Fe$_3$O$_4$ still exists, which may be explained by incomplete oxidation in the OC preparation step. For the used iron ore sampled from AR, the XRD results indicated that the reduced ore from FR can mostly be oxidized into Fe$_2$O$_3$ in AR by air in the continuous operation. Meanwhile, as shown above, the OC was mostly reduced from Fe$_2$O$_3$ to Fe$_3$O$_4$ by CH$_4$ in FR.

Figure 14 showed the redox reactivity of both the fresh and used iron ore OC sample in a thermogravimetric analyzer (TGA, BOIF WCT-1D/2D). $\omega$ is the mass-based degree of conversion,$^{43}$ eqs 12 and 13; $dX/\omega$ and $dX/\omega$ are the conversion rates in the reduction stage and the oxidation stage.
stage, respectively, eq 14. The OC was alternately exposed in the mixture gases of 25% H₂ + 35% CO + 40% CO₂ for reduction and the air for oxidation, both at the temperature of 900 °C. It can be clearly seen that the fresh and used hematite showed acceptable reactivity during both the oxidation and reduction stages. The conversion rate of the used sample was slightly higher than that of fresh sample in both the reduction stage and the oxidation stage. However, the oxygen transport capacity of the used sample was decreased in both the reduction stage and the oxidation stage due to a decrease of the surface area, as shown in Figure 15. Overall, the reactivity of hematite was well maintained after continuous operation of over 100 h. It could be a suitable choice as OC after improving the reactivity by decorating copper⁴⁴ or nickel⁴⁵.

\[ X_r = \frac{(m_i - m_f)}{m_{\text{initial}}} \times 100\% \quad (12) \]

\[ X_o = \frac{(m_i - m)}{m_{\text{initial}}} \times 100\% \quad (13) \]

\[ \frac{dX}{dt} = \frac{dm}{m_{\text{initial}} \, dt} \times 100\% \quad (14) \]

where \( m_i \) and \( m_f \) represent the weight of OC at the oxidized state and reduced state; \( m \) is the weight of the OC at time \( t \); \( m_{\text{initial}} \) is the weight of the OC at the beginning.

5. CONCLUSION

An interconnected fluidized bed reactor for chemical looping combustion has been operated with the hematite as oxygen carrier and CH₄ as fuel. A series of tests fed with CH₄ have been performed at different operational parameters, such as the FR temperature, the thermal power input, the flow rate of the gas agent in the FR, and the bed inventory, to investigate the influence of different operational parameters on the performance of the interconnected fluidized bed reactor for CLC. The almost same batch of hematite had been used for the whole operation without sintering and agglomeration. The operation continued for 30 days, with typically 12 h per day. The following conclusions were drawn:

- The highest CH₄ conversion of 81.4% was achieved at 1000 °C with sufficient residence time and bed inventory.
- The carbon capture efficiencies were dependent on the CH₄ decomposition, the bed inventory in the FR, and the gas leakage in the unit.
- The flow rate of the fluidizing gas agent and the bed inventory were the important factors in the CO₂ yield. However, the operational temperature should be optimized to control the CH₄ conversion and CO₂ yield when the hematite was used as OC and CH₄ as gas fuel, because a higher temperature is beneficial to CH₄ conversion as well as CH₄ decomposition.

This work showed the successfully continuous operation and the different operational parameters during the tests, which made contributions to the scale-up of the CLC reactor. In further research, the steam as a gasification agent could be favorable to achieve high carbon capture efficiency, which can limit the methane decomposition, and a carbon stripper should be adopted to reduce the carbon entrained by the reduced OC from the FR to the AR.

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Notes
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