

Performance of a Cu-based oxygen carrier with pressurized CH₄ in a fixed bed CLC process

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Abstract. In order to broaden the operating temperature window of a Cu-based oxygen carrier (OC) in a chemical-looping combustion (CLC) process based on two fixed bed reactors, in which there exist great temperature distributions in radial and axial directions, through reducing its lower temperature limit, an experimental study on the performance of Cu₆₀/Al₄₀ with pressurized CH₄ was carried out in a CH₄ pressure range from 0.1MPa to 0.9MPa. Results showed that with CH₄ pressure increasing, the reduction rate of OC was improved, so the lower temperature limit was lowered from 555°C at 0.1MPa to below 500°C at 0.9MPa. Although carbon deposition in the reduction step became worse with the pressure increasing, it could be depressed with adding steam to CH₄, and when the reduction temperature was below 700°C, the deposited carbon could be completely removed in the following oxidation step. The fixed bed CLC process based on an OC that has a wide operating temperature window is applicable to the distributed medium & small scale hot water & steam gas-fueled boilers.

Introduction

Among the numerous technologies for carbon capture, utilization and storage (CCUS), most of which are often characterized by large energy penalties in the energy intensive processes, chemical-looping combustion (CLC) is a very promising one with nearly zero energy consumption and high capture efficiency as a CO₂ capture technology, in which the fuel does not contact with air directly and so the reduction product gas CO₂ does not diluted with the oxidation product gas N₂ [1-5].

For CLC, there are two reactor configurations, namely, the circulating fluidized bed reactors (CFBR) and the fixed bed reactor (FBR), and CFBR was widely studied under the background of application to a large scale power plant, in which the working temperature of CLC is generally above 1000°C [1,6,7]. Thus, agglomeration, sintering and pulverization of the oxygen carrier (OC) are always accompanied. However, considering that CLC can work under a much lower temperature in the applications to the field of heat supply, it is feasible to apply CLC to the distributed medium/small scaled gas-fueled boilers. From this prospective, FBR is a better choice because of its advantages of easy to design and operate, needless of gas/solid separation, flexibility in operation scale and possibility to operate at high pressures without significantly affecting the flow regime [8].

However, for a gas-fueled CLC process based on FBR, several subjects have to be concerned:

(1) With CH₄, the reduction reactions of most OCs except Cu-based OC are not exothermic [9]. If an OC except Cu-based OC was employed, heat supply from an external heat source would be necessary to maintain the required OC bed temperature in the reduction step, which is hard to realize. So, an OC using CuO as the main active component is required. Also, CuO enjoys the fast kinetics in lower temperature.

(2) Meanwhile, the corresponding oxidation reactions are strongly exothermic, hence in the oxidation step, a great temperature distribution along the radial and axial directions of the OC bed would be built with cooling the OC bed from the outer wall of reactor [10]. Thus, the OC is required to have good low temperature reactivity and good high temperature stability.

(3) On another hand, because of the low melting point of metallic copper (1085°C), Cu-based OCs easily suffer carbon deposition, agglomeration and sintering [11-13]. at high temperature. So, it is necessary to give the OCs a strong resistance to carbon deposition , agglomeration and sintering.

XM Zheng et al. [14] proposed a novel CLC process based on FBR by introducing a CH₄ pre-reforming step for transforming CH₄ to H₂ and CO, which could be operated in a much lower temperature of below 550°C. However, because of the system being complicate, its practical application is limited. On the basis of this process, authors [15] employed a Cu-Fe based OC to react with CH₄ directly and relieved the problems of sintering and carbon deposition for CuO at higher temperatures and thus the upper temperature limit of the OC was successfully raised. However, the lower temperature limit of its operating temperature window is still required to be lowered.

To improve the reactivity of the Cu-based OC in lower temperature, the measure to operate the reduction step at an elevated pressure should be effective. Several studies support the positive effect of pressure on CLC performance. Jin and Ishida [16,17] studied the influence of high pressure reduction of NiO/NiAl₂O₄ and CoO/NiO with H₂, CH₄ and syngas in a PTGA and a fixed-bed reactor. The reduction kinetics of H₂ in the PTGA favored elevated pressures of 0.3 and 0.9MPa. Nordness and Bollas [18] measured the reactivity of Cu-based OC in a fixed-bed reactor under various total pressures and found that high-pressure operation increased the fuel conversion for the OC. Siriwardane et al. [19] tested the reactivity of NiO/bentonite with simulated syngas and found that elevated pressure promoted the syngas combustion throughout the oxygen carrier reduction period. In addition, high-pressure reduction will enjoy other benefits on the CLC engineering application: Firstly, the pressurization energy of the pressurized natural gas from the high pressure gas pipelines can be utilized; Secondly, the captured CO₂ with a high pressure requires less power for further compression; At last, the heat efficiency and the temperature grade of the recovered heat from the product gas of the reduction step can be increased due to the dew point of the product gas being raised.

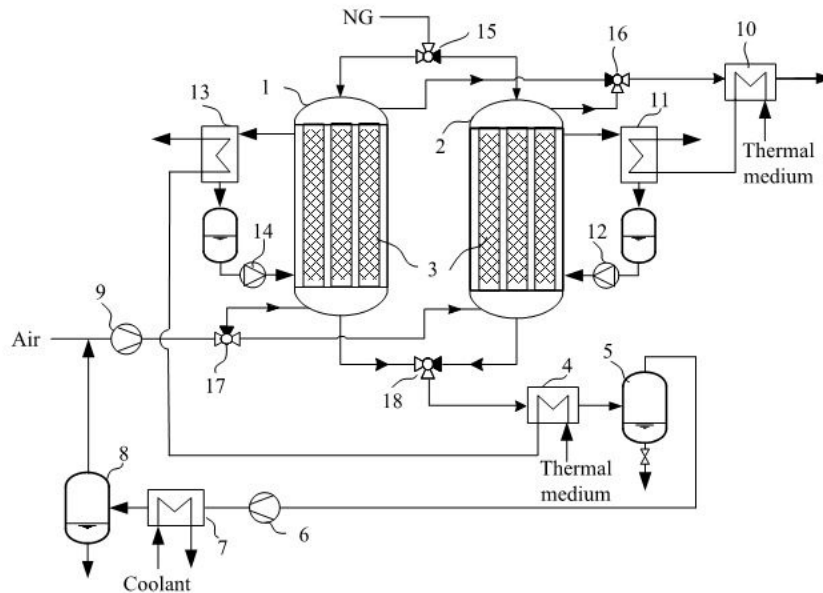


Figure 1. Flow sheet of a gas-fueled CLC process based on fixed bed reactors for the distributed medium&small scale boilers 1,2-CLC Reactor; 4,10,11,13-Heat exchanger; 5,8-Gas-liquid separator; 6,9-Compressor; 12,14-Water pump; 15,16,17,18-Three way valve

In our previous work¹⁵, a CLC process based on two FBRs was proposed and shown in Fig. 1. The reduction step proceeds in reactor 1. The gaseous reduction product is led into heat exchanger 4 and then gas-liquid separator 5, in which nearly pure CO₂ and condensate water are obtained. The obtained CO₂ is compressed with compressor 6 and then liquefied in cooler 7, then separated in gas-liquid separator 8. The rest of non-condensable gas (mainly CH₄ and CO₂) is introduced into

reactor 2, where the small amount of CH₄ left in reactor 1 is burned out. Meanwhile, the oxidation step proceeds in reactor 2. Based on this process, the reduction performance of a Cu-based OC with pressurized CH₄ was evaluated in a lab-scale FBR, and the effect of CH₄ pressure on the lower temperature limit of the operation temperature window of the OC was determined. The stability of the OC was also investigated.

Experiments

OC preparation method

The OC employed in this paper was prepared with a mechanical mixing method and denoted as Cu60/Al40. Preparation details were as follows: 60wt% CuO powder (particle size 105~177mm, purity≥99.5 wt%, Beijing ZhongKeHaoYun Co., Ltd.) was used as active components, and 40wt% Al₂O₃ powder (particle size 75mm minus sieve, purity≥99.5 wt%, Shandong Aluminum) was used as inert support. 2 wt% aqueous polyvinyl alcohol solution in a ratio of 20 wt% was added to the mixtures as binder. Then, the mixtures were pressed with a tablet machine at 10MPa for 2 minutes. The pressed flakes were dried at 120°C in a drying chamber overnight and calcined at 700°C for 5 h in a muffle oven, and then crushed and screened to particles with a size range of 0.1~1.0mm. In order to achieve a steady performance and a good repeatability, the OC sample will experience 5 redox cycles in the preset conditions to be fully activated.

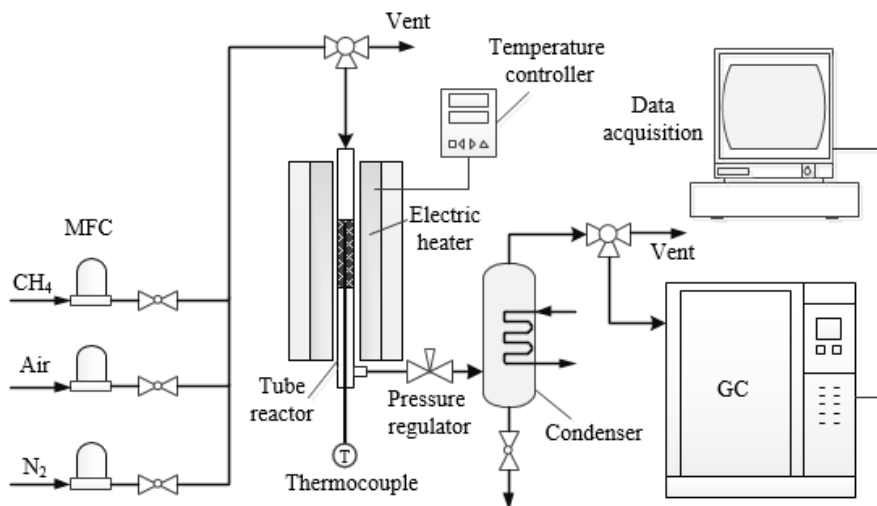


Figure 2. Apparatus for OC performance evaluation

Apparatus and method

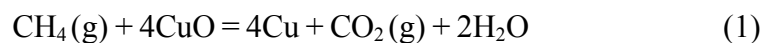
In the FBR experiments, the OC reactivity and stability were evaluated with a tube reactor, of which the diameter was 25mm and the length was 500mm, set in an electrical heating furnace shown in Fig.2. Along the longitude of the reactor, there existed a thermostatic section ($\Delta T < 10^\circ\text{C}$, length $\approx 80\text{mm}$) and the OC sample was packed in this section in order to avoid temperature difference. The OC layer, of which temperature was measured by a K-type thermocouple, was heated to the set temperature with $10^\circ\text{C}/\text{min}$ in flowing air of 225ml/min to ensure that the particles were fully oxidized before the reduction step. After N₂ of 1L/min was introduced for 10min to replace air in the reactor, CH₄ was fed to the reactor and the product gas from the reactor was led to a gas-liquid separator and a dehumidifier, where the moisture in the product gas was thoroughly removed, and then led to a GC-TCD (GC 6820, Agilent Technologies, Beijing) for analysis. After reduction step, N₂ was introduced for 10min and then the oxidation step began with air of 225ml/min. For a high pressure operation, the reactor pressure can be controlled by the pressure regulator at the end of the tube reactor.

For all experiments of reduction and oxidation steps in this paper, the sample mass of the OC was 30ml of 37.80g and the flow rates of CH₄ and air were 25ml/min (GHSV=50h⁻¹) and 225ml/min (GHSV=450h⁻¹), respectively. According to Eq.1&2, the corresponding theoretical complete reduction time and oxidation time were 63min and 67min, respectively.

Data processing

In the FBR experiments, the reduction rate of OC (C_R , as shown in Eq.3), which varies with the outlet concentration of H₂ or CH₄, is one of the important parameters for the OC. 5% C_R was defined as the reduction rate at the time point when the H₂ or CH₄ outlet concentration exceeding 5%. Similarly, the oxidation rate (C_O , as shown in Eq.4) and 1% C_O were also defined. 5% C_R and 1% C_O were mainly used to evaluate how thoroughly the OC being utilized when switching.

Due to the great temperature distribution over FBRs in the practical application of CLC, the operating temperature window T_w was defined as follows: the OC is able to work efficiently and stably as long as the temperature distribution of the OC layer is kept within a certain temperature range, that is, T_w . Moreover, the lower temperature limit of T_w is the lowest temperature to achieve a 5% C_R of 40% for ensuring the reduction reaction of the OC being ignited, and the upper temperature limit of T_w is the highest temperature to ensure that little carbon deposition, agglomeration and sintering would occur below this temperature.



$$C_R = \frac{\int_0^t (V_{\text{CH}_4, \text{in}} - V_{\text{CH}_4, \text{out}}) dt}{22.4M_{\text{CH}_4}} \quad (3)$$

Where C_R is the reduction rate; V (mL/min) represents the flow rate and M (mmol) is the theoretical amount required for complete reduction conversion.

$$C_O = \frac{\int_0^t (V_{\text{O}_2, \text{in}} - V_{\text{O}_2, \text{out}}) dt}{22.4M_{\text{O}_2}} \quad (4)$$

Where C_O is the oxidation rate; V (mL/min) represents the flow rate and M (mmol) is the theoretical amount required for complete oxidation conversion.

Result and discussions

Operating temperature window of Cu60/Al40

In this section, the operating temperature window of Cu60/Al40 was investigated in a FBR at 0.1MPa in a temperature range of 500-800°C. Results were given in Fig.3.

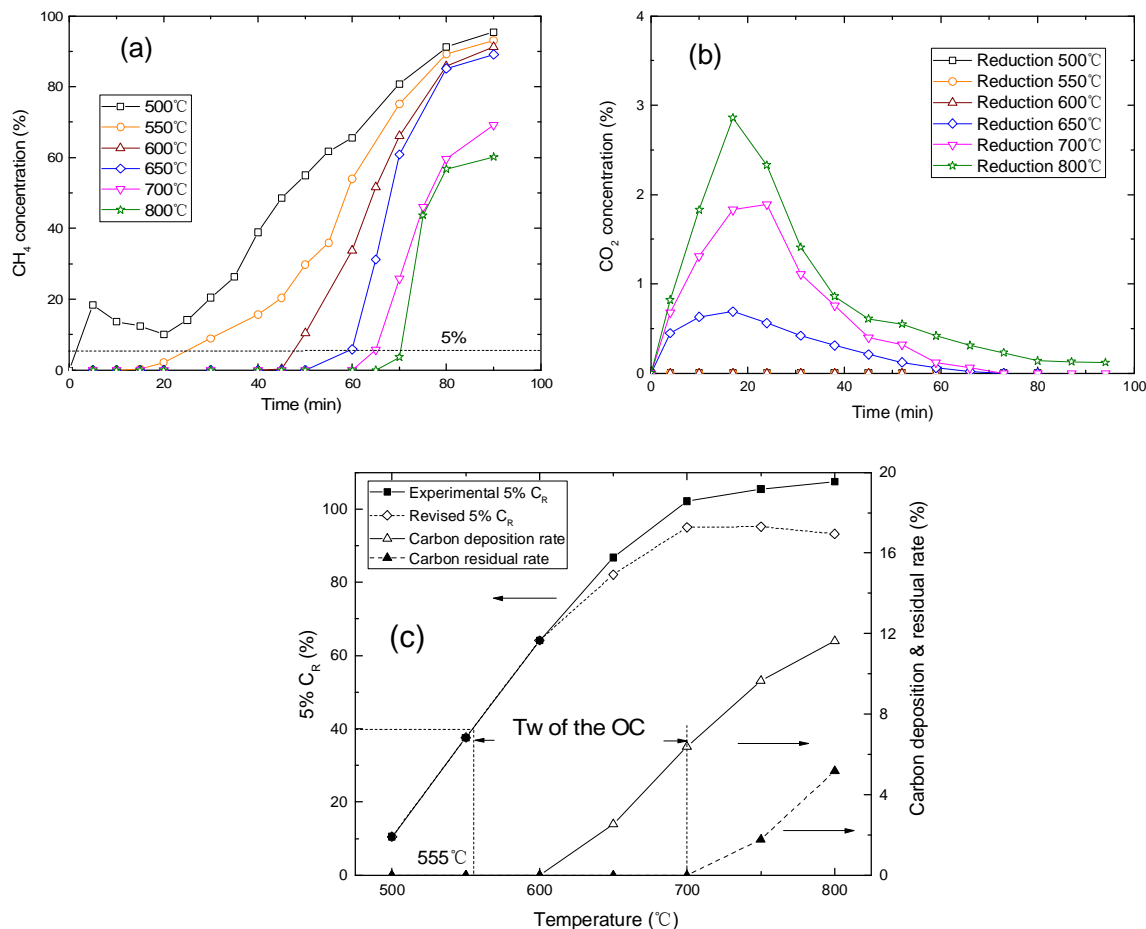


Figure 3. Performance of Cu60/Al40 with 0.1MPa CH₄ from 500°C to 800°C. (a) CH₄ outlet concentration; (b) CO₂ outlet concentration in the following oxidation step; (c) Experimental & revised 5%*C_R* and carbon deposition in the reduction step & carbon residual rate in the following oxidation step

From Fig.3a, CH₄ of more than 5% escaped from the beginning at 500°C, which can be attributed to the limited low temperature reduction reactivity of Cu60/Al40 [20]. With the temperature increasing, 5%CH₄ escape time gradually increased from 20min at 550°C to 60min at 650°C, which was close to the theoretical complete reduction time of 63min, and then exceeded 63min at above 700°C. It can be inferred that CH₄ thermolysis occurred on the surface of metallic copper at high temperature and led to a prolonged escape time. To confirm this assumption, oxidation of the reduced OC at different reduction temperatures was carried out at 500°C to observe the outlet CO₂ concentration. From Fig.3b of the oxidation step, CO₂ was detected in the outlet gas when the corresponding reduction temperature was above 650°C, and the CO₂ concentration increased with the reduction temperature increasing. In Fig.3c, the carbon deposition rate represents the ratio of the total mole of CO₂ escaped in the whole oxidation step to the total mole of CH₄ introduced in the whole reduction step, and the carbon residual rate represents the ratio of the deposited carbon, which could not be removed in the following oxidation step, to the total mole of CH₄ introduced in the whole reduction step. As shown in Fig.3c, carbon residual rate was 0% at below 700°C, while increased from above 750°C, and finally reached 5.7% at 800°C. If the deposited carbon could not be completely removed, it would accumulate with the redox cycle going on, finally leading to the fixed bed blockage as well as the reactivity loss.

Thus, the upper temperature limit of *T_w* for Cu60/Al40 was determined to be 700°C from the aspect of carbon deposition. On the other hand, from the revised 5%*C_R* curve, which was obtained by subtracting the carbon deposition rate from the experimental curve of 5%*C_R* (the solid line), the lower

temperature limit of T_w for Cu60/Al40, that is, the temperature corresponding to 40% of $5\%C_R$ was 555°C.

Performance evaluation of Cu60/Al40 at higher CH₄ pressure

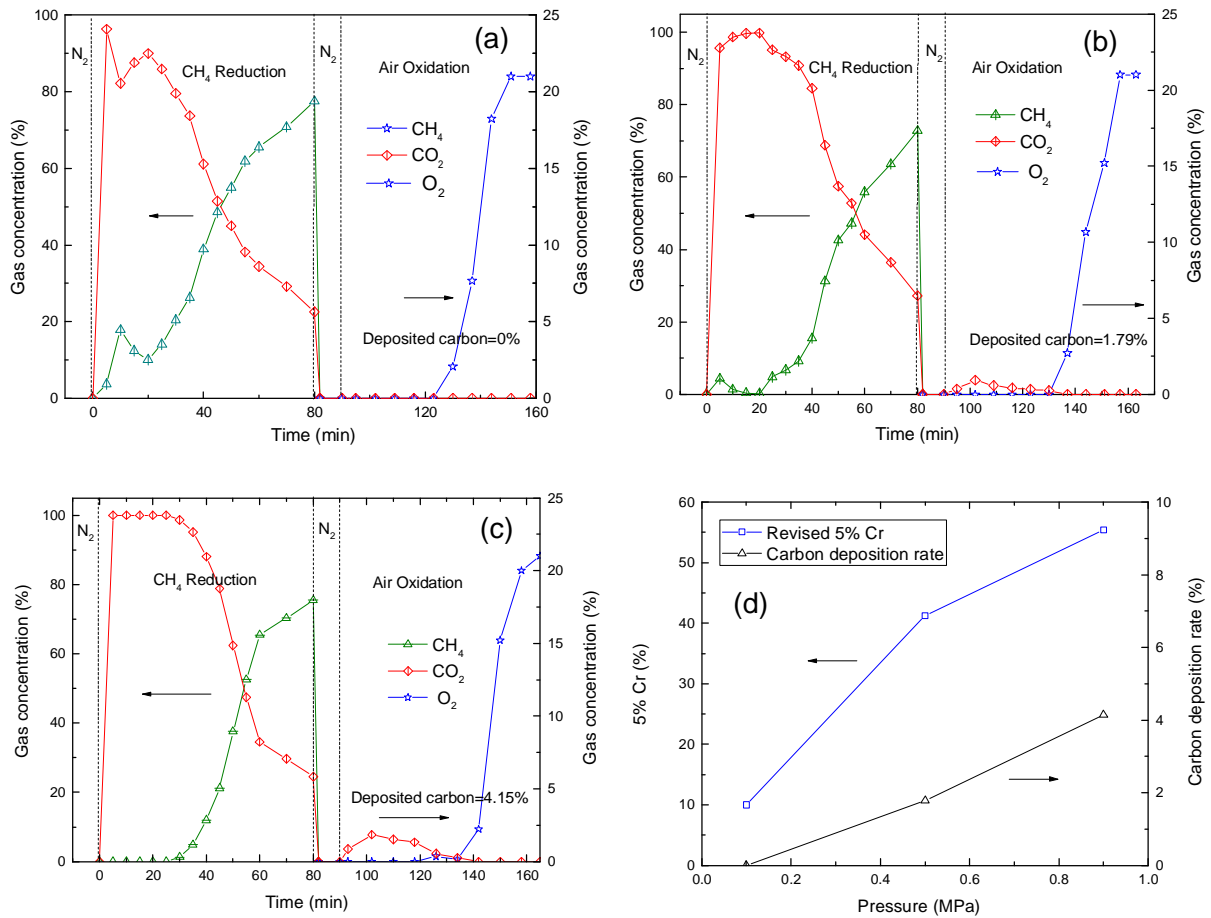


Figure 4. Redox performance of Cu60/Al40 with CH₄ at different CH₄ pressures in the reduction step and with 0.1MPa air in the oxidation step: (a) 0.1MPa CH₄; (b) 0.5MPa CH₄; (c) 0.9MPa CH₄; (d) the corresponding revised 5% C_R and carbon deposition rate in the reduction step

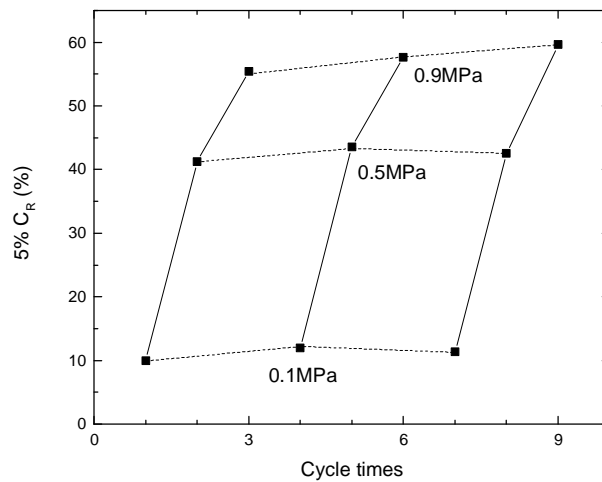


Figure 5. Repeatability of the reduction performance of Cu60/Al40 with the pressurized CH₄ in the range of 0.1-0.9MPa at 500°C

The T_w for Cu60/Al40 with 0.1MPa CH₄ was 555°C-700°C from the last section. In this section, as shown in Fig.4, experiments with 0.5MPa and 0.9MPa CH₄ Fig.4 shows were conducted at 500°C, at which the reduction reaction of Cu60/Al40 with 0.1MPa CH₄ could not be ignited.

With 0.1MPa (Fig. 4a), CH₄ escaped significantly from the beginning of the reduction step. In the whole following oxidation step, no CO or CO₂ was observed, meaning that no deposited carbon was formed during the reduction. And with 0.5MPa CH₄ (Fig. 4b), much less CH₄ escaped within 30 min, while a slight carbon deposition occurred. In contrast, with 0.9MPa CH₄ (Fig. 4c), CH₄ was completely converted to CO₂ until 30min. In Fig.3d, it can be seen that the 5%*C_R* increased from 10% with 0.1MPa CH₄ to 41% with 0.5MPa CH₄ and then to 55% with 0.9MPa CH₄. The repeatability of above performance was assured with the results of repeating experiments as shown in Fig.5. That is to say, the reduction reaction of Cu60/Al40 can be ignited with 0.5MPa CH₄ at 500°C and with 0.9MPa CH₄ at a temperature even lower than 500°C. These results showed that through elevating CH₄ pressure, the reduction rate of Cu60/Al40 can be obviously raised and so the lower temperature limit of Cu60/Al40 can be reduced. Clearly, it is attributed to the improvement of kinetic conditions of the reaction, because of the increase of pressure does not thermodynamically benefit the reaction of Eq.4, which is a volume increase reaction. In summary, according to the definition of lower temperature limit of *T_w* for an OC, the lower temperature limit of Cu60/Al40 was 500°C with 0.5MPa CH₄ and was further reduced to a temperature lower than 500°C with 0.9MPa CH₄. However, at the same time the carbon deposition became more serious with the pressure increasing. The deposited carbon can be removed in the following oxidation step or depressed by adding steam to the inlet CH₄ [21].

Stability test of Cu60/Al40 at high pressure

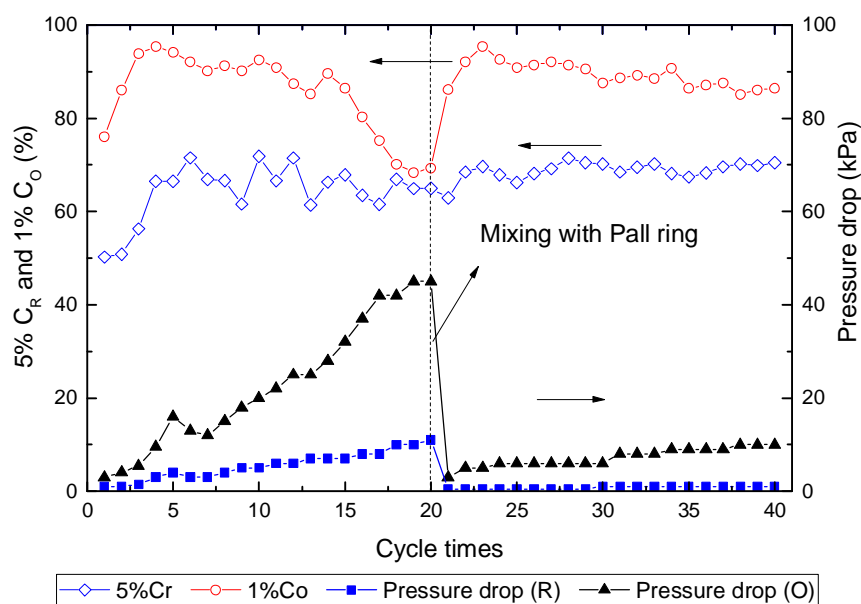


Figure 6. Stability and pressure drops of Cu60/Al40 with 0.9MPa CH₄ in the reduction step and with 0.1MPa air in the oxidation step at 500°C

In this section, the stability of Cu60/Al40 with 0.9MPa CH₄ in the reduction step and with 0.1MPa air in the oxidation step was evaluated for 40 redox cycles at 500°C. As shown in Fig.6, 1% *C_O* decreased and the pressure drop of the OC layer in the oxidation step increased with the redox cycle going on, indicating that the OC suffered pulverization and sintering. It is interesting that 5%*C_R* was relatively stable, and it can be supposed that the reduction performance of OC suffers little influence from OC's pulverization and sintering if the reduction is under a high pressure. Through mixing OC particle with a packing material of Pall rings with a volume ratio of 1:1, the oxidation performance of the degraded OC was recovered and both pressure drops of reduction and oxidation steps were much relieved.

Conclusions

For broadening the operating temperature window T_w of OC in a CLC process based on the fixed bed reactors, so as to make the process more applicable to the distributed medium & small scale gas-fueled hot water & steam boilers, the reduction performance of Cu60/Al40 with the pressurized CH₄ was investigated in a CH₄ pressure range of from 0.1MPa to 0.9MPa. Main results were obtained as follows:(1) With CH₄ pressure increasing, the lower operating temperature limit of T_w for Cu60/Al40 was extended from 555°C at 0.1MPa to lower than 500°C at 0.9MPa, due to the reduction rate of Cu60/Al40 being raised; (2) Carbon deposition in the reduction step became worse with CH₄ pressure increasing, but it could be depressed with adding steam to CH₄, and when the reduction temperature was below 700°C, the deposited carbon could be removed completely in the following oxidation step; (3) Stability tests of OC for 40 redox cycles showed that the reduction performance of Cu60/Al40 under a high pressure was stable and suffer little degradation from OC's pulverization and sintering. The pressure drop of the OC layer could be significantly reduced by mixing the packing material of Pall rings with the OC particles. In addition, through using the pressurized nature gas from the high pressure pipeline of nature gas, the heat efficiency and the temperature grade of the recovered heat from the product gas of the reduction step can be increased due to the dew point of the product gas being raised, and the pressurization energy of CO₂ in CCUS can be reduced, because CO₂ from CLC has been pre-pressurized.

Acknowledgements

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