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Chemical looping combustion of coal in a 5 kW_{th} interconnected fluidized bed reactor using hematite as oxygen carrier

ABSTRACT



^a State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan, PR China ^b Department of Chemical Engineering, Monash University, Clayton, Victoria 3800, Australia

HIGHLIGHTS

- An interconnected fluidized bed reactor for iG-CLC was successfully operated.
- The unit showed low gas leakage and high cyclone separation efficiency.
- The combustion efficiency varied between 73.52% and 96.33%.
 The CO₂ yields in most of tests were
- higher than 85%.
- The reactivity of low-cost natural hematite maintained well during the 300 h.

G R A P H I C A L A B S T R A C T

A new configuration of interconnected fluidized bed for in-situ gasification chemical looping combustion (iG-CLC) was tested with Chinese bituminous coal as fuel and natural hematite as oxygen carrier. The thermal power of this unit was varied between 2.0 and 6.0 kW_{th}. The total operation time was more than 100 h in the hot mode fed with coal. This natural hematite displayed high reactivity. The effect of operational parameters, such as the fuel reactor (FR) temperature and coal feeding rate on three factors – combustion efficiency, carbon capture efficiency and CO_2 yield – were investigated. The results indicated this natural hematite was a good type of oxygen carrier.



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Keywords: Chemical looping combustion CO₂ capture A hematite, which has been operated in CH₄-fuelled Chemical Looping Combustion (CLC) for more than 200 h, was used as oxygen carriers for in-situ gasification chemical looping combustion (iG-CLC) of Chinese Bituminous coal in this study. The thermal power was varied between 2.0 and 6.0 kW_{th}. The total operation time was more than 100 h in the hot mode. Hematite displayed high reactivity with this bituminous coal attaining up to 96.33% of combustion efficiency. The carbon capture efficiency ranged from 72.84% to 89.36% as only CO₂ was used as coal gasification agent gas in the fuel reactor during the first tests. The CO₂ yield in the fuel reactor was up to 92.82% under the operational temperature was 1000 °C and the average coal feeding rate corresponding to the 2 kW_{th} of thermal power. The effect of operational parameters, such as the fuel reactor temperature, thermal power and the mass flow rates





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^{*} Corresponding author. E-mail addresses: klinsmannzhb@163.com, hzhao@mail.hust.edu.cn (H. Zhao).

Interconnected fluidized bed Coal Hematite

1. Introduction

 CO_2 was regarded as a greenhouse gas having significant effect on climate change. Combustion of fossil fuel was the major contributor to CO_2 emission. To stabilize the CO_2 concentration in the atmosphere, several measures has to be taken. Among them, carbon capture and storage (CCS) would contribute 15–55% to the cumulative mitigation effort worldwide until 2100 [1]. The chemical looping combustion (CLC) has been viewed to be one of the most economic ways of CO_2 capture having an advantage of inherent CO_2 separation [2].

The chemical looping combustion concept was proposed by Ishida et al. [3] and demonstrated amongst others by Lyngfelt and Thunman [4]. CLC was based on transferring oxygen from air to fuel by means of a solid oxygen carrier. There were different configurations for CLC system design [5,6], such as the interconnected fluidized bed reactor [7], which was the most widelyadopted reactor system for CLC. In the interconnected fluidized bed system, the two reactors were fuel reactor (FR) and air reactor (AR). In the fuel reactor the oxygen carrier was reduced by the fuel and then circulated to the air reactor, where it was re-oxidized by the air. The total heat released within the two chemical reactions was equal to that of normal combustion.

Initial work in CLC were mostly limited to laboratory scale work on oxygen carriers particles using thermo gravimetric analyser (TGA), and small fixed/fluidized beds to characterize over 1000 different materials based on Ni, Cu, Fe, Mn, and Co [8–16]. Later studies had progressed to low cost and environmentally friendly oxygen carrier, such as iron ore [17–19], manganese ore [20], copper ore [21], and the mixed iron and copper ore [22], including their use in entire CLC process systems at different scales [23].

Circulating fluidized bed reactors had been used to investigate the critical design parameters of a system such as solid inventory, solid circulation rate, as well as to identify stable operating conditions for various designs [7]. Lyngfelt et al. developed the first prototype unit with thermal power of 10 kW_{th} in 2004 for the combustion of gaseous fuels [24]. Other units used for CLC research of gaseous fuels varied in scale from 1 kW_{th} to over 120 kW_{th} scale at facilities in Europe, North America and Asia [25–28].

The chemical looping combustion of solid fuels is more challenging because it involves the very possibly unsteady feeding of solid fuels, the rate-limiting char gasification in the fuel reactor and the separation of fly ash and oxygen carrier. However, adapting the CLC process to solid fuels seems more worthwhile due to low costs and abundance of solid fuels in the world. The first continuous pilot using solid fuels was retrofitted from the 10 kW_{th} pilot using natural gas as fuels, by making important modifications in the fuel reactor chamber and including an additional solids recirculation loop to adapt the system for solid fuels [29]. Recently, different units have been successfully operated for the combustion of solid fuels [30]. Shen et al. have constructed 1 kWth and 10 kWth units for the combustion of coal and biomass using Ni- and Fe-based oxygen carrier [31]. A 50 kW_{th} pressurized unit for chemical-looping combustion of coal was operated by Xiao et al. in Southeast University [17]. In CSIC, two units of 0.5 kW_{th} and 1.5 kW_{th} were used for iG-CLC and chemical looping with oxygen uncoupling (CLOU) of biomass and coal with different coal ranks [32]. Sébastien et al. in IFP has constructed a 10 kW_{th} pilot using coal as fuels and natural ore as oxygen carriers [33]. A 25 kW_{th} unit was operated with ilmenite and lignite in Hamburg University of Technology [34]. Two units of 2.5 and 25 kW_{th} using moving beds as fuel reactor were operated at Ohio State University [35].

Results from all the research facilities mentioned above demonstrated in principle the feasibility of direct coal use in the CLC system. Majority of the reactors were similar in configuration, where the air reactor was usually equipped with the fast fluidized bed riser and fuel reactor were usually operated in the bubbling mode, except the DCFB at Vienna University of Technology, which operated in the turbulent bed regime for the combustion of gaseous fuels [26]. The velocity in fuel reactor was much lower than the air reactor due to longer residence time requirement to achieve a higher fuel conversion. However, the transportation of oxygen carrier between the fuel reactor and air reactor by the overflow was an important area of proper system design. Relatively recently, Lyngfelt et al. proposed a $100 \text{ kW}_{\text{th}}$ reactor system with petcoke and bituminous coal as fuel [36,37]. In their design, the fuel reactor was a circulating fluidized bed and a four-chambered carbon stripper was implemented after the fuel reactor to further convert the lighter char particles leaving the fuel reactor. Technische Universität Darmstadt has also constructed a larger auto-thermal chemical looping combustion unit in the scale of 1 MW_{th} [38]. Here, the air reactor and fuel reactor were designed as two interconnected circulating fluidized bed reactors, between which a carbon stripper of a rectangular shaped bubbling fluidized bed was connected to improve the coal combustion efficiency and carbon capture efficiency.

In this study, a new dual circulating fluidized bed reactor for chemical looping combustion of coal was designed: the recirculation of OC was through the riser, which provided the driving force, and the cyclone, which separated the gas and solid, instead of the configuration of the overflow. It was also operated to validate design specification, achieve stable operation, and gain valuable operation experience. This unit was also tested for preliminary identification of the effect of operational parameters, e.g. fuel reactor temperature, the mass flow rates of the fluidization gas agent in the fuel reactor and coal feeding rates (corresponding to the thermal power) using the hematite as oxygen carrier. Some results on the performances of the same hematite oxygen carrier with CH₄ for almost 200 h were also provided.

2. Experimental

2.1. Setup of the 5 kW_{th} interconnected fluidized bed reactor for chemical looping combustion

The interconnected fluidized bed reactor unit consists of a fuel reactor, where the oxygen carrier was reduced by the fuel, and an air reactor, where the reduced oxygen carrier was oxidized by air. In the unit, the superficial gas velocity in the fuel reactor was operated in the bubbling bed regime and that in the air reactor was operated in the turbulent bed regime. The risers were installed followed the air reactor and fuel reactor to provide the driving force for the circulation of oxygen carriers, respectively. A cyclone connected with the riser was used for the separation of gas and elutriated solids. The particle outlet of the cyclone was connected with the down comer and loop seal. In the end, the oxygen carrier was transported to the other reactor through the loop seal. Two loop seals were presented between the two reactors in order to prevent the gas leakage and transport the oxygen carrier in the reactor unit. Fig. 1 showed the layout of interconnected fluidized bed reactor. The inner diameter of the air reactor was 45 mm with the height of 550 mm and the inner diameter of the fuel reactor was 55 mm with the height of 1000 mm. The inner diameters of the two risers were both 22 mm.

The gas concentration from the fuel reactor outlet was analysed for CO₂, CO, CH₄, O₂ and H₂, whereas the gas concentration from the air reactor outlet was analysed for CO₂ and O₂ by two separated on-line gas analysers. The gas composition from the reactor outlets after water condensation were continuously measured by the gas analyser (Gasboard-3151), with CO₂, CO, and CH₄ on dry basis being determined using nondispersive infrared analysis (NDIR) detector, H₂ by thermal gas conductivity (TCD) detector, and the O₂ with an electron capture detector (ECD).

2.2. Start-up and shut-down operation

The interconnected fluidized bed was supplied by an electrically heated furnace. During the preheating stage, air was used as fluidizing agent in the air and fuel reactors. The mass flow rates of fluidization gas agent in the air reactor/fuel reactor/loop seal were kept very low, which were operated in the bubbling bed regime (only 1-2 L/min, corresponding to $2-3 u_{mf}$) to prevent the agglomeration of the oxygen carrier. When the temperature in the fuel reactor reached the preset value, the mixture gas of N₂ and CO₂ were switched to the fluidization gas agent in the fuel reactor. The mass flow rates of the fluidization agents to the air reactor and fuel reactor were increased slowly to the optimal value along with increasing the mass flow rates of the fluidization agent to the loop seal (including the gas to the recycle chamber, which connected to the other reactor as shown in Fig. 1). After the CO₂

concentration of outlet gas from the fuel reactor became stable, the stable operating condition was deemed to have been reached and the fuel could be fed into the reactor. In the tests, the average coal feeding rates ranged between 5 g/min and 15 g/min, corresponding to the thermal power input between 2.0 kW_{th} and 6.0 kW_{th}. The fluidization gas agents of air and nitrogen can be preheated up to 800 °C. During the shut-down process, the air was changed as the fluidization agent in the fuel reactor which was operated in the bubbling regime until the furnace was cooled down.

2.3. Oxygen carriers

The oxygen carrier tested in the experiments was a low cost hematite. The fresh particles were prepared by drying in a furnace at 350 °C and sieved to a particle diameter range between 150 μ m and 250 μ m. The average oxygen carrier particle diameter was 180 μ m. The apparent density of the carriers was found to be 3742 kg/m³. The crushing strength was measured on the same size particles and the average of 20 measurements was 2.83 N by using the digital dynamometer (FGP – 100, Shimpo).

The minimum fluidization and terminal velocities were calculated according to the correlation of Kunii and Levenspiel [39]. The minimum fluidization velocity was 0.0187 m/s at 950 °C using nitrogen as fluidization gas and the terminal velocity was 1.12 m/s at 950 °C in air using the average particle diameter of 180 μ m.

It was noted that the same batch of the hematite had been tested previously more than 200 h of CH₄ operation in the same chemical looping unit without significant reactivity decrease [40].

2.4. Operating conditions

Table 1 described the operating conditions during the tests. P_{fuel} was the thermal power input of the reactor based on the low heating value of Chinese bituminous coal, whose composition was provided in Table 2. Nitrogen was used for the fluidized gas agent in the fuel reactor, and a mass flow rate of about 5 L/min CO₂ to improve the coal gasification rate. Air was used as fluidization gas agent of the air reactor, which provided enough oxygen to oxidize the oxygen carrier. F_{AR} and F_{FR} were the mass flow rates in the air reactor and the fuel reactor, respectively. Generally, nitrogen was selected as the fluidizing agent in loop seal. The temperature of the air reactor was between 900 °C and 1000 °C and the



Fig. 1. Layout of interconnected fluidized bed reactor for chemical looping combustion.

Table 1Test operating conditions in the reactor unit.

Operating condition	F _{AR} (L/min)	$F_{\rm FR}$ (L/min)	$T_{\rm FR,b}$ (°C)	$P_{\rm fuel}~(\rm kW_{th})$
Cyclone test	30	25	900	-
Hot test No. 1	30	28	900	3.25
Hot test No. 2	30	27	900	3.5
Hot test No. 3	30	25	950	2
Hot test No. 4	30	28	950	3.25
Hot test No. 5	30	25	950	4.75
Hot test No. 6	30	25	950	6
Hot test No. 7	30	25	1000	2.25
Hot test No. 8	30	24	1000	3.25
Hot test No. 9	30	24	1000	4.75

temperature of the fuel reactor was in the same range. Any additional heating to the air reactor and the fuel reactor was provided by an electric furnace. Based on this, the temperature measuring point in the bottom fuel reactor was selected as the standard temperature ($T_{\rm FR,b}$) because it was the main reaction zone.

The bed inventory in the fuel reactor was approximated 2.5 kg and the total inventory in the unit was around 7.5 kg.

2.5. Performance indicators for fuel conversion

Gaseous species produced in the fuel reactor were either volatile compounds or products of char gasification. Volatiles mainly included CH₄, H₂, CO and CO₂. The oxygen demand,

$$\Omega_{\rm OD} = \left(0.5 \chi_{\rm CO} + 2 \chi_{\rm CH_4} + 0.5 \chi_{\rm H_2} \right) / \left(\Phi_0 \left(\chi_{\rm CO} + \chi_{\rm CH_4} + \chi_{\rm H_2} \right) \right)$$
(1)

 $\Omega_{\rm OD}$ was related to the gas conversion efficiency or the combustion efficiency ($\eta_{\rm comb, FR}$) in the fuel reactor, which was defined as,

$$\eta_{\text{comb},\text{FR}} = 1 - \Omega_{\text{OD}} \tag{2}$$

Here, χ_{CO} , χ_{CH_4} and χ_{H_2} were the volume fraction of gas of CO, CH₄, and H₂ from the outlet of the fuel reactor, respectively; Φ_0 was the oxygen/carbon ratio, i.e. the ratio of moles of oxygen needed to convert the fuel completely per mole of carbon in the fuel.

The carbon capture efficiency (η_{cc}) was the ratio of carbon containing gas flow leaving the fuel reactor to the total carbon containing gas flow leaving the unit,

$$\eta_{\rm CC} = \left(F_{\rm CO_2,FR} + F_{\rm CO,FR} + F_{\rm CH_4,FR}\right) / \left(F_{\rm CO_2,AR} + F_{\rm CO_2,FR} + F_{\rm CO,FR} + F_{\rm CH_4,FR}\right)$$
(3)

 $F_{CO_2,FR}$, $F_{CO,FR}$ and $F_{CH_4,FR}$ were the mass flow rates of CO₂, CO and CH₄ at the outlet of fuel reactor, respectively. $F_{CO_2,AR}$ was the mass flow rate of CO₂ at the outlet of the air reactor.

The CO₂ yield (γ_{CO_2}), which demonstrated the fraction of CO₂ of total gaseous carbon leaving the fuel reactor, was defined by

$$\gamma_{\text{CO}_2} = \chi_{\text{CO}_2} / \left(\chi_{\text{CO}} + \chi_{\text{CH}_4} + \chi_{\text{CO}_2} \right) \tag{4}$$

3. Results and discussion

The hematite as oxygen carrier was tested in the unit with a total running time of more than 300 h, during December 2013

Table 2

Proximate and ultimate analyses of the Chinese bituminous coal
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and January 2014, typically 8 h per day. The interconnected fluidized bed reactor unit worked well and stable operation was easily achieved. The investigation involved the different operational parameters, such as the reactor temperatures, the thermal power, and the mass flow rates of the fluidization gas agent of the fuel reactor. The combustion efficiency, the carbon capture efficiency and CO_2 yield were all calculated.

3.1. Gas leakage and cyclone separation efficiency

Gas leakage between the air reactor and fuel reactor should be minimized in the chemical looping combustion. During the initial operation (the temperature in the bottom fuel reactor was 900 °C), the hematite was added in the reactor to run the unit without fuel to check the gas leakage between the air reactor and fuel reactor. The inlet gas to fuel reactor and two loop seals were fed with high purity nitrogen and the inlet gas to air reactor was air, so the gas leakage can be calculated by the gas analyser measuring the oxygen concentration of outlet gas from fuel reactor based on the oxygen mass balance.

$$\eta = \left(F_{\text{FR,out}} \times \chi_{\text{O}_2,\text{FR}}\right) / \left(F_{\text{AR}} \times \chi_{\text{O}_2,\text{AR}}\right)$$
(5)

where the F_{AR} was the inlet flow rate of AR; $\chi_{O_2,AR}$ was the inlet O_2 concentration of AR, i.e., 20.9%; $F_{FR,out}$ was the outlet flow rate of FR; $\chi_{O_2,FR}$ was the outlet O_2 concentration of FR.

The gas leakage was tested in two operating conditions, which was the highest mass flow rate 28 L/min of the fluidization gas agent and the lowest mass flow rate 20 L/min of that in the fuel reactor. At the first 60 min test, the mass flow rate of the fluidization gas into the fuel reactor was 28 L/min and decreased to 20 L/min during the last 60 min, but the mass flow rate of the fluidization gas agent in the air reactor was always 30 L/min. The results showed the first stage of gas leakage averaged around 1.81% and then the second stage of that increased to 3.20% because the pressure fluctuation became larger when the mass flow rate of the fluidization agent decreased in the fuel reactor.

There was another key factor for achieving stable operation, cyclone separation efficiency. It was defined as

$$P_{\rm CY} = 1 - (\dot{m}_{\rm AR} + \dot{m}_{\rm FR}) / \sum (m_{\rm AR} + m_{\rm FR} + m_{\rm LS})$$
(6)

where \dot{m}_{AR} and \dot{m}_{FR} were the masses of collected oxygen carriers fines from the air reactor and fuel reactor cyclone every 15 min during the test, and m_{AR} , m_{FR} and m_{LS} were the preset condition of the masses of oxygen carrier particles loaded in the air reactor, fuel reactor and two loop seals in the test, respectively.

Fig. 2 showed the high cyclone separation efficiency, up to 99.6% during the first test. The operating conditions were shown in Table 1. In Fig. 2, the mass of collected fines from the first 15 min was relativity high due to some small particles surrounding the large particles loaded in the reactor unit, which was shown more clearly in SEM image of fresh sample in Fig. 9. As a result, the cyclone separation efficiency in the first 15 min was relativity lower. However, all the last experiments results reached a very high cyclone separation efficiency of over 99%. It demonstrated the feasibility of the interconnected fluidized bed reactor unit.

Solid fuel	Proximate (wt%, ad)				Ultimate (wt%, ad)				
	Moisture	Volatiles	Ash	Fixed carbon	С	Н	Ν	S	0
Chinese bituminous coal	1.66	15.54	34.34	48.46	55.26	2.12	0.79	0.44	5.39

3.2. Continuous operation

In this section, results from the continuous operation were presented. Fig. 3 showed the outlet gas concentrations of CO, CO_2 , CH_4 and H_2 from the fuel reactor and the outlet gas concentrations of CO_2 and O_2 from the air reactor was presented in Fig. 4. The operational parameters change were the temperature in the bottom of



Fig. 2. The high cyclone separation efficiency.



Fig. 3. The gas concentration of CO, CO₂, CH₄ and H₂ from fuel reactor.

fuel reactor and the thermal power, which were listed in Table 2. The temperature in the bottom fuel reactor varied among 900 °C, 950 °C and 1000 °C. Fig. 5 showed the pressure drop in the fuel reactor, which was correlated with the bed inventory in the fuel reactor.

The coal was introduced into fuel reactor in a somewhat unsteady manner because that the coal feeder design was far from perfect, so the coal feeding rate could not be smooth and steady at all times. However, the CO₂ concentration was always above 80% while CH₄ and H₂ concentrations were low. Generally, the CO concentration was higher than the CH₄ and H₂ concentrations. The reason may be ascribed to: (1) the amount of CH₄ released from coal devolatilization and pyrolysis was far less than that of CO; (2) the char gasification under the CO₂ atmosphere produced some CO (C + CO₂ \rightarrow 2CO); (3) the reactivity of hematite with CO was lower than that with hydrogen; (4) there was very limited time to allow the complete conversion of CO.

For comparing with tests No. 5 and No. 9, which were operated in the same fuel power input of 4.75 kW_{th} but at different temperatures in the fuel reactor, the CO₂ concentration from fuel reactor increased slightly and CH₄ and H₂ concentration decreased along with an increase of temperature in fuel reactor. It demonstrated that CH₄, CO and H₂ from coal devolatilization and pyrolysis were likely to be more reactive at a higher temperature. However, the CO concentration also increased due to the increase of char gasification rate at a higher temperature. In Fig. 4, the reduced concentration of CO₂ from the air reactor was explained by the reduced amount of char transported to air reactor as the temperature in fuel reactor increased.

In comparing with tests No. 3 and No. 5, which were operated with different fuel reactor pressure drop and thermal powers, the average CO₂ concentrations from fuel reactor was almost equal with the increase of the thermal powers at the same temperature 950 °C in the fuel reactor. However, the CO and H₂ concentrations in test No. 5 slightly decreased, which was ascribed to more bed inventory in the fuel reactor of test No. 5, as shown in Fig. 5. Basically, the CH₄ concentration in test No. 5 was equal to that in test No. 3. Thus, the results indicated that more bed inventory in fuel reactor should be adjusted to provide more lattice oxygen to convert these reducible gases when the thermal power increased. As shown in Fig. 4, the O₂ concentration from the air reactor outlet in test No. 5 decreased due to the more oxidation of oxygen carrier, which was explained by the more oxygen carrier reduced to low state iron oxide by more coal devolatilization and gasification



Fig. 4. The gas concentration of CO₂ and O₂ from air reactor and the temperature of fuel reactor.



Fig. 5. The pressure drop in the fuel reactor.

products. The concentration of CO_2 from the air reactor in test No. 5 also slightly increased, which was attributed to that more unconverted char was transferred to the air reactor. This result indicated that there was still the limitation of the char residence time in the fuel reactor.

Furthermore, the effect of the mass flow rate of fluidization gas agent in fuel reactor was investigated during the continuous test. By comparing with tests No. 4 and No. 5, the CO_2 concentration performed a considerable decrease as the mass flow rate of fluidization agent in the fuel reactor increased from 25 L/min in test No. 5 to 28 L/min in test No. 4. The CO, CH₄ and H₂ concentration also increased obviously in this case of test No. 4. In addition, the higher CO_2 concentration from the air reactor indicated that more unconverted char in test No. 4 than that in test No. 5 was entrained from the fuel reactor. The explanation for these was that a higher mass flow rate of the fluidization gas agent of fuel reactor resulted in a shorter residence time of oxygen carrier particles and char particles in fuel reactor, and thus more unconverted reducible gases and char escaping from fuel reactor.

In conclusion, the operational results were affected by a number of factors, such as temperature and the bed inventory in the fuel reactor, the mass flow rate of the fluidization gas in the fuel reactor, and the thermal power (calculated based on the coal feeding rates). Another important factor is the type of fluidization agent in the fuel reactor, which could be the steam reported by Markstrom et al. [36].

3.3. The combustion efficiency at different temperatures of the fuel reactor and thermal powers

The average combustion efficiency, carbon capture efficiency and CO_2 yield during the continuous operation as a function of the temperature of the fuel reactor and the thermal power were shown in Figs. 6–8, respectively.

The combustion efficiency increased with temperature and the results were over 90% during the 1000 °C tests. It was generally expected a higher reactivity of the oxygen carrier at a higher temperature. At the same time, the higher gasification rate of the char was attained at higher temperatures. As a result, the coal char was almost gasified in fuel reactor and the reducible gases were almost converted by hematite at 1000 °C, and a very high combustion efficiency of more than 92.5% was attained, as demonstrated by the results of tests No. 7, 8 and 9.

The combustion efficiency was also affected by the bed inventory in the fuel reactor per unit of thermal power. By comparing the results of tests No. 7, 8 and 9 at 1000 °C as well as tests No. 3, 4, 5, and 6 at 950 °C, the combustion efficiency performed a decreasing tendency in general when the thermal power increased. The test No. 4 performed apparent low combustion efficiency because that a higher superficial velocity of fuel reactor was adopted, compared to these in tests No. 3, 5, and 6.



Fig. 6. Average combustion efficiency as a function of thermal power and temperature of the fuel reactor.



Fig. 7. Average carbon capture efficiency as a function of thermal power and temperature of the fuel reactor.



Fig. 8. Average CO_2 yield as a function of thermal power and temperature of the fuel reactor.

3.4. Carbon capture efficiency at different temperatures of the fuel reactor and thermal powers

The carbon capture efficiency is highly dependent on the CO_2 level in the air reactor. The CO_2 detected at the air reactor outlet came from two ways: the burnt out of char, which was entrained from the fuel reactor to the air reactor; the gas leakage from the fuel reactor to the air reactor.

As known, a faster char gasification rate and a higher char conversion degree were attained at a higher temperature. Thus, less unconverted char was entrained from the fuel reactor to the air reactor at higher temperatures. Most of the results reflected the effect of temperature, that is, the higher the reactor temperature was, the higher the carbon capture efficiency was achieved. However, the carbon capture efficiency was also affected by the operation of the interconnected fluidized bed reactor, such as the bed inventory, the gas leakage caused by the pressure fluctuation and the mass flow rate of the fluidization gas agent in the fuel reactor. For example, the carbon capture efficiency in test No. 3 was higher than that in test No. 7 even though the temperature increased 50 °C in test No. 7, because the pressure drop of the fuel reactor in test No. 3 was higher than 500 Pa that in No. 7. Thus, more char could be converted in the fuel reactor of test No. 3. leading to less char entrained to the air reactor.

Moreover, the carbon capture efficiency in test No. 4 was also higher than that in the test No. 8, although the temperature increased from 950 °C in test No. 4 to 1000 °C in test No. 8. It was because that the pressure fluctuation in the loop seal connected to the air reactor was larger during test No. 8, which resulted in slightly unsteady running of the loop seal. Thus, more serious gas leakage from fuel reactor to air reactor due to the lower mass flow rate of the fluidization gas in fuel reactor in test No. 8, as mentioned in Section 3.1.

As a result, the operation of interconnected fluidized bed should be optimum to keep the gas leakage and the entrained char from the fuel reactor to air reactor minimum simultaneously. It was noted that in other successful reactor units the carbon stripper was configured to improve the carbon capture efficiency, where char can be further gasified by steam [36,38].

3.5. CO_2 yield at different temperatures of the fuel reactor and thermal powers

During the operation, the CO_2 yield was investigated as a function of reaction temperatures of the fuel reactor and thermal power. It related to the unconverted gases concentrations in the fuel reactor according to Eq. (4). Therefore, the CO_2 yield was basically influenced by the reactivity of the oxygen carrier, the bed inventory and the residence time.

When the fuel reactor temperature was over $950 \,^{\circ}$ C, the CO₂ yield increased about 4% when the temperature in the fuel reactor increased from 950 °C to 1000 °C. However, the CO₂ yield increased about 34% when the temperature increased from 900 °C in test No. 1 to 950 °C in test No. 4. It was because of the higher coal devolatilization and gasification rates and higher reactivity of oxygen carrier at higher temperatures [41]. As shown in Fig. 3, the CO₂ concentration from the fuel reactor outlet in test No. 9 was higher than that in test No. 5, however the CO and CH₄ were lower.

The bed inventory per unit of thermal power was another influencing factor on the CO_2 yield. For comparing tests No. 3 and No. 5, which were tested at the same temperature and the mass flow rate of the fluidization agent in the fuel reactor, but the bed inventory and the thermal power in test No. 5 were higher than these in test No. 3, as shown in Fig. 5 and Table 1 respectively. However, the CO_2 yields in these two tests were almost equal even though the thermal power in test No. 5 was higher than that in test No. 3. Factually, the less reducible gases (such as CH_4 and CO) were escaped from the fuel reactor outlet when there was enough oxygen carrier to provide the lattice oxygen.

The CO₂ yield was also affected by the mass flow rate of the fluidization agent in the fuel reactor. As shown in Fig. 3, the concentrations of unconverted gases, such as CH₄ and CO, were higher in the fuel reactor outlet in test No. 4 (F_{FR} = 28 L/min), as compared to these in test No. 5 (F_{FR} = 25 L/min). Obviously, the residence time of unconverted gases was lower at a higher superficial velocity of the fuel reactor.

To summarize, these operation variables including reaction temperature, bed inventory per unit of thermal power and the mass flow rate of the fluidization gas agent in the interconnected fluidized bed reactor unit were mutually related and jointly determined the final performance of chemical looping combustion of coal. It seemed that the combustion efficiency, carbon capture efficiency and CO_2 yield were more sensitive to the reactor temperature. It is necessary to optimize the operation conditions to attain a better performance in the future research.

3.6. Characterization analyzes of oxygen carrier

The fresh and used oxygen carrier particles were subjected to characterization techniques using a laser diffraction particle size analyser (LDSA), a Scanning Electron Microscope (SEM), Energy Dispersive X-ray (EDS), X-ray Diffraction (XRD) and Accelerated Surface Area and Porosimetry (ASAP).

After the whole tests, the used particles were collected from the unit and the particle size distribution of the fresh and used samples were analysed by laser diffraction particle size analyser (Master Min, Malvern), as shown in Table 3. It was obvious that the used particles had more small particles compared with the fresh OC. The explanation for this was the collision and attrition between the particles and the wall, especially in the cyclone due to the high gas velocity. However, in the industrial CLC plant attrition is likely to be lower due to the relatively low velocity and circulation of small particles will be low due to the high separation efficiency of the cyclone.

The structural and morphological changes of the particles were investigated by the scanning electron microscope (SEM, FEI Quanta 200) with 20.0 kV of accelerating voltage. Fig. 9 showed the micrograph obtained at two magnification levels (500X and 5000X) for the fresh particles (before tested more than 200 h in the CLC of methane) and used particles (the used samples were collected by the fuel reactor filter during the tests), respectively. Fig. 9(A) and (B) showed that the fresh particle was rough with presence of smaller particles on its surface, some of which were observable in the higher magnification image. This together with the irregularities on the surface would result in the particle having a higher surface area. Comparing this with the used samples, as shown in Fig. 9(C) and (D), the surface had become smoother and no longer had observable smaller grains on its surface. This was due to the abrasion experienced by the collisions between the particles and with the metallic surfaces of the reactor at high velocities over multiple redox cycles.

Table 3Particle size distribution of the fresh and used samples.

Particle size distribution (µm)	Percentage distribution of the fresh sample (%)	Percentage distribution of the used sample (%)
0-40	2.75	0.63
40-150	15.93	20.75
150-200	50.75	62.61
200-250	30.08	16.01
>250	0.49	0



Fig. 9. Fresh and used iron ore samples: (A) fresh sample, X500; (B) fresh sample, X5000; (C) used sample, X500; (D) used sample, X5000.



Fig. 10. EDS spectra of the fresh and used samples.

Fig. 10 showed the representative EDS spectra (GENESIS XM, EDAX Inc) taken for two samples. It can be observed that both spectrums were very similar except for the relative elemental composition. The samples contained primarily O, Fe, Si, Ca, Mg, and Al, with the C coming from the C-tape used on the sample stub. Both samples contained less amounts of Ca, Al and Mg from the ore, which indicated that ash deposition was not apparent. There was no more carbon on the used sample, which indicated the char was not deposited on the surface of oxygen carrier. In addition, it can be seen that the chemical composition of the oxygen carrier had not altered significantly over the course of the experiment.

As presented in Fig. 11, X-ray diffraction (XRD, X'Pert Pro) was carried out for both samples by using Cu K α radiation (λ = 1.542 nm) in a 2 θ range of 10–90° with an accelerating voltage of 40 kV and the tube current of 40 mA. As mentioned in the experimental section, the oxygen carrier used was a hematite ore. Based on the analysis that was performed for the fresh sample,



Fig. 11. XRD of the fresh and used samples.

it can be seen that it was composed of Fe_2O_3 and SiO_2 . The used sample on the other hand contains Fe_2O_3 , Fe_3O_4 and SiO_2 . Again, this showed that there was no significant interaction with the ash as these would be neither deposited on the surface of the oxygen carrier nor formed compounds with the oxides present in the oxygen carrier.

The Brunauer, Emmett and Teller (BET) surface area as well as the average pore diameter were obtained from the ASAP measurements (Micromeritics, ASAP-2020). The sample particles had a surface area of $3.4 \text{ m}^2/\text{g}$ and $1.5 \text{ m}^2/\text{g}$ for the fresh and used particles, respectively. The average pore diameter reduced from 42.1140 Å to 32.0294 Å going from the fresh to used particles. This conformed to the results from the SEM which showed that the fresh particle was rougher than the used particle which had lost most of its small particles. This corresponds with the decrease average pore diameter which was most likely due to shrinkage of the pores from the

Fig. 12. Oxygen transport rate of the fresh and used sample in TGA.

thermal and chemical stresses during the tests. This showed that even though the surface area and pore diameter had decreased, it was sufficient to react with the gases from the coal.

Fig. 12 showed the oxidation and reduction characteristics of both the fresh and used oxygen carrier sample in TGA (TGA, BOIF WCT-1D/2D). A gas composed of 35 vol% CO, 25 vol% H₂ and 40 vol% CO₂ for reduction and air for oxidation were used. It can be clearly seen that the fresh and used hematite showed high reactivity during both the oxidation and reduction stages. The reaction time of complete conversion for reduction stage was about 150 s, while that for the oxidization stage was lower than 70 s. However, the oxygen transport capacity of the used sample was slightly decreased both in the reduction and oxidation stages due to the decrease on the surface area. In the end, the results also indicated that the hematite after continuous operation over 300 h did not show a significant decrease in reactivity.

4. Conclusion

An interconnected fluidized bed reactor unit for chemical looping combustion was successfully operated using a hematite ore. The reactor unit was continually operated with CH_4 and coal as fuels for a total duration exceeding 300 h. Although some difficulties were faced relating to the pre-heating system and the instability of the coal feeder, it was found that stable operation was easily achievable.

The operational parameters were changed to investigate the effects on combustion efficiency, carbon capture efficiency and CO_2 yield. The combustion efficiency varied between 73.52% and 96.33%. The temperature in the fuel reactor, the bed inventory per unit of thermal power and the mass flow rate of the fluidization gas agent in the fuel reactor were the variables, which had the most impact on the performance of the unit.

The oxygen carrier displayed high reactivity towards the reducible gases as well as being resistant to unacceptable levels of sintering and agglomeration. The results from the TGA showed that the reactivity of the used oxygen carrier was not significantly changed relative to the fresh sample. The analytical techniques complemented the experimental results and it was found that the even though the BET surface area was reduced by a factor of 2.27, the reactivity of the hematite ore was not significantly affected.

The hematite sample was a low cost oxygen carrier which made it a good choice as an oxygen carrier for chemical looping combustion of coal. Our future work included determination of the optimum operating conditions for the reactor unit used in this study and the investigation of the effect of steam as the gasification agent.

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