Reactor Design, Cold-Model Experiment and CFD Modeling for Chemical Looping Combustion

Shaohua Zhang, Jinchen Ma, Xintao Hu, Haibo Zhao, Baowen Wang, and Chuguang Zheng

Abstract

Chemical looping combustion (CLC) is an efficient, clean and cheap technology for CO_2 capture, and an interconnected fluidized bed is more appropriate solution for CLC. This paper aims to design a reactor system for CLC, carry out cold-model experiment of the system, and model fuel reactor using commercial CFD software. As for the CLC system, the air reactor (AR) is designed as a fast fluidized bed while the fuel reactor (FR) is a bubbling bed; a cyclone is used for solid separation of the AR exit flow. The AR and FR are separated by two U-type loop seals to remain gas sealed. Considered the chemical kinetics of oxygen carrier, fluid dynamics, pressure balance and mass balance of the system simultaneously, some key design parameters of a CH_4-fueled and Fe_2O_3/Al_2O_3-based CLC reactor (thermal power of 50 kWth) are determined, including key geometric parameters (reactor cross-sectional area and reactor height) and operation parameters (bed material quantity, solid circulation rate, apparent gas velocity of each reactor). A cold-model bench having same geometric parameters with its prototype is built up to study the effects of various operation conditions (including gas velocity in the reactors and loop seals, and bed material height, etc.) on the solids circulation rate, gas leakage, and pressure balance. It is witnessed the cold-model system is able to meet special requirements for CLC system such as gas sealing between AR and FR, the circulation rate and particles residence time. Furthermore, the thermal FR reactor with oxygen carrier of Fe_2O_3/Al_2O_3 and fuel of CH_4 is simulated by commercial CFD solver FLUENT. It is found that for the design case the combustion efficiency of CH_4 reaches 88.2%. A few part of methane is unburned due to fast, large bubbles rising through the reactor.

Keywords

Chemical Looping Combustion • CO_2 Capture • CFD Modeling • Interconnected Fluidized Bed

1 Introduction

Chemical looping combustion (CLC), which has advantages of cascade utilization of chemical energy, inherent CO_2 separation, and low NO_x emission, has gained attention in recent years and regarded as one of the most promising ways of CO_2 capture. The system consists of two separate reactors—an air reactor (AR) and a fuel reactor (FR). Metal oxide particles that circulate between the two reactors act as an oxygen and heat carrier. The oxygen carriers (usually high oxygen-potential metal oxide, denoted by MeO) are reduced to zero-valent metal or low-valent metal oxide (denoted by Me) in FR and are re-oxidized by air in AR. In this way, classic direct combustion between fuel and

S. Zhang • J. Ma • X. Hu • H. Zhao (✉) • B. Wang • C. Zheng
State Key Laboratory of Coal Combustion, Huazhong University of Science & Technology, Wuhan 430074, China
e-mail: klinsmannzhb@163.com

H. Qi and B. Zhao (eds.), *Cleaner Combustion and Sustainable World*, DOI 10.1007/978-3-642-30445-3_159,

air is divided into two steps: reduction reaction (1) and oxidation reaction of oxygen carriers (2).

$$(2n + m/2)\mathrm{MeO} + \mathrm{C}n\mathrm{H}m \rightarrow (2n + m/2)\mathrm{Me} + m/2\ \mathrm{H_2O} + n\mathrm{CO_2} + \Delta H_{\mathrm{red}} \quad (1)$$

$$\mathrm{Me} + 0.5\mathrm{O_2} \rightarrow \mathrm{MeO} + \Delta H_{\mathrm{ox}} \quad (2)$$

The total amount of net heat (ΔH_c) evolved is equal to normal combustion of the same fuel (3):

$$\Delta H_c = \Delta H_{\mathrm{ox}} + \Delta H_{\mathrm{red}} \quad (3)$$

One beneficial feature of CLC is the cascade utilization of fuel chemical energy [1, 2]. Direct contact between fuel and combustion air is avoided, and the CO_2 produced from combustion are kept separated from the rest of gases (such as N_2). The products from FR contain the streams of vapor and CO_2 which could be capture with little additional energy through condensation.

As CLC technique is based on the circulation of oxygen carriers [3] between the two reactors, a interconnected fluidized bed (or a dual-fluidized bed) has been selected as CLC reactors. By now, the interconnected fluidized bed CLC systems with different thermal power (such as 10 kW [4], 50 kw [5], 120 – 140 kW) have been successfully operated. However, because different CLC system may be fed with different kinds of fuels, utilize different oxygen carriers, and operates with different modes (e.g., chemical looping combustion [6], chemical looping reforming [6], chemical looping combustion with oxygen uncoupling [7], chemical looping hydrogen generation, chemical looping gasification, etc.), they are largely differentiated between thermodynamics, chemical kinetics and fluid dynamics, and are thus required special reactor configuration and operation conditions to make them run well. It is very important to design the CLC reactors and operate the CLC system in an optimal way. Lyngfelt [6] first proposed a design methodology for the interconnected fluidized bed reactor (this system consists of a fast fluidized bed acting as the air reactor and a bubbling fluidized bed acting as the fuel reactor). The main idea is based on the chemical kinetic data to calculate the bed material quantity, oxygen carrier circulation rate and the fuel gas recirculation ratio in the FR, air-fuel ratio, and pre-set the cross-sectional area and the pressure balance of AR and FR, then get apparent gas velocity, the bed height, the fan power of AR and FR, so the method is empirical. Kronberger et al. [4] used the fluidized bed scaling laws [7] to enlarge the designed prototype system and got the similar cold model for CLC system, with a cold model experiment to test the gas leak of the actual circular flow process, the pressure point balance, the solids circulation rate, the particle abrasion, the particle residence time and so on, and then provided the basic parameters for the design and operation of the thermal CLC system. However, the design of cold-mode CLC is also according to the prior constraints parameters of the prototype system (based on the design theory of Lyngfelt et al. [8]).

The purpose of this article is to put forward an improved design concept for CLC (Fig. 1): firstly, the bed material quantity of AR and FR, solid circulation rate and residence time and so on are calculated based on the design theory of Lyngfelt et al. [8]. secondly, the proper reactor height, cross-sectional area, fuel flow, air flow and other factors of CLC system are designed, basing on traditional fluidization theory and experience and fluid dynamics theory while overcome the presupposition of geometric parameters in the design theory of Lyngfelt et al. [8]. An interconnected fluidized bed reactor system representing a 50 kWth prototype was designed, using Fe_2O_3/Al_2O_3 as oxygen carriers and CH_4 as fuel. A cold-model bench was then built at the same size as the thermal-model bench. And pressure balance, gas leakage and various operation conditions of the interconnected fluidized bed were investigated. On one hand, this experiment verified the improved design. On the other hand, proper

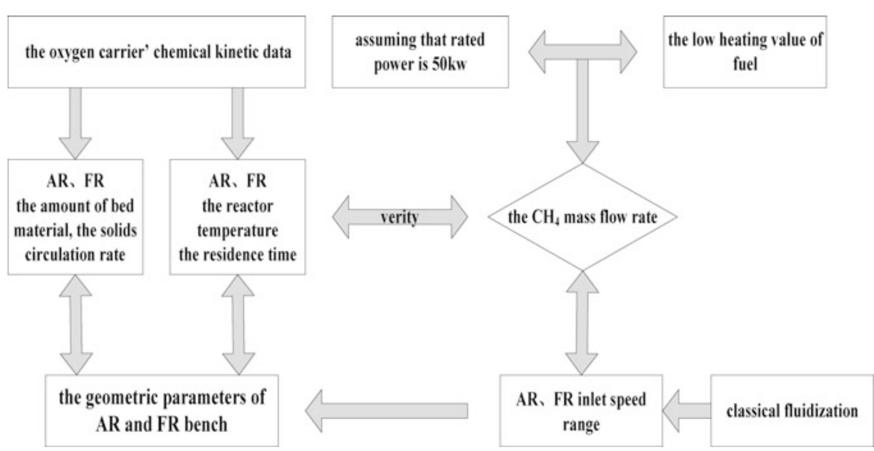


Fig. 1 Designing flow of CLC

operation conditions were found to prepare for thermal design and operation. In the end, the thermal fuel reactor was simulated by commercial CFD solver FLUENT. The working condition of fuel reactor was simulated to investigate the action of multiphase flow and the efficiency of combustion. Besides, a further consideration was taken to test the validity and reliability of the approach to design the reactor.

2 Reactor Design

The interconnected fluidized bed is comprised of air reactor, fuel reactor, a cyclone and two U-type loop seals. In the air reactor, the oxygen carrier is reoxidized by air, fluidizing while chemical reacting. In this process, the reaction rate is relatively fast, therefore, a fast fluidized bed can match it well and provide main power for the oxygen carrier circulation. In the fuel reactor, gaseous fuel is oxidized by an oxygen carrier. In this process, the reaction rate is relatively slow, so a bubbling fluidized bed can match it well and guarantee the particles residence time and particles reaction time. Figure 2 shows the specific thermal system structure: the operating temperature in the left air reactor is set at 1,000°C, the operating temperature in the right fuel reactor is set at 900°C. CH_4 is used as fuel, Fe_2O_3 supported on Al_2O_3 is applied as oxygen carrier (mass ratio is 60%: 40%, the average diameter of about 213 μm and the material density is 4369.1 kg/m^3) [9–12].

Figure 2 shows the interconnected fluidized bed design method: firstly, based on the conceptual design (50 kW), the CH_4 mass flow rate can be calculated, oxygen flow and air flow are then calculated. secondly, the bed material quantity, solid circulation rate and the residence time should be calculated on the basis of the oxygen carrier (Fe_2O_3/Al_2O_3) chemical kinetic. Afterwards, gas fluidization velocity is calculated in line with basic fluidization theory. Finally, the geometric parameters of AR and FR bench can be calculated and accessories are needed to match.

So far, most theoretical design of bench is preliminarily complete. But processing technique, the experience of the continuous operation CLC etc. are needed to combine in order to identify the final dimension and operation condition (such as wind speed range, exhauster wattage and power etc.). Now, the value of the thermal power 50 kWth is summarized in Table 1.

A cold-flow model was built based on the above value of thermal reactor (prototype bed). The aim of the cold-flow model is to checkout hydrodynamics law, pressure balancing and gas leakage etc. In this paper, the cold-flow model (simulate bed) and the thermal reactor (prototype bed) are the same size. The circulation particles are quartz (particle

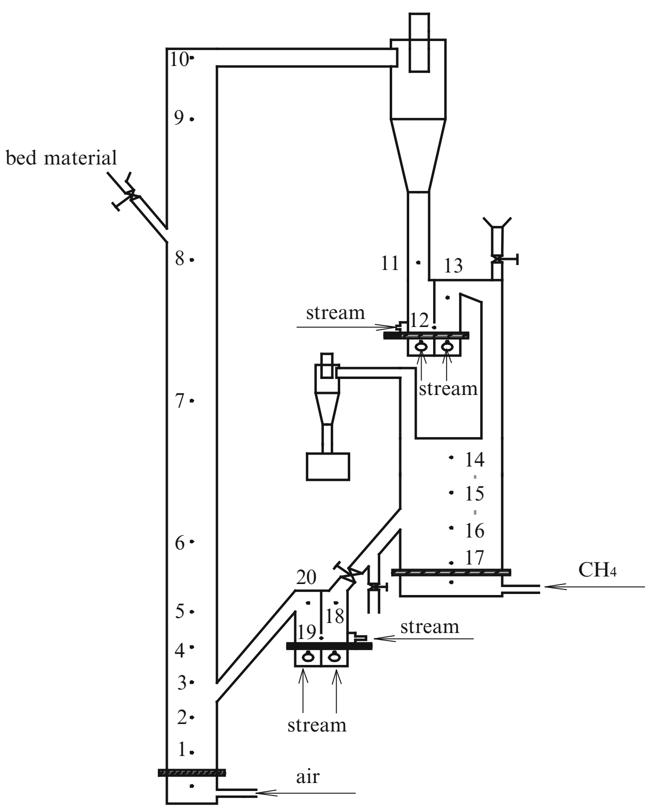


Fig. 2 The sketch map of CLC

Table 1 Design value of the 50 kW CLC prototype bed and simulate bed

Project	Symbol	The cold-flow-model value	The thermal reactor value
ARvoidage	ε_{AR}	0.9	0.9
FRvoidage	ε_{FR}	0.55	0.55
solids circulation rate from AR to FR	$\dot{m}_{sol}$	0.274 kg/s	0.41 kg/s
solids circulation rate from FR to AR	$\dot{m}_{sol,ret}$	0.274 kg/s	0.406 kg/s
AR mass quantity	$m_{bed,\ AR}$	4 kg	6 kg
FR mass quantity	$m_{bed,\ FR}$	6.68 kg	10 kg
minimum	$u_{mf,\ AR}$	0.051 m/s	0.024 m/s
fluidization velocity	$u_{mf,\ FR}$	0.051 m/s	0.053 m/s
terminal	$u_{t,\ AR}$	1.68 m/s	2.01 m/s
velocity	$u_{t,\ FR}$	1.68 m/s	1.93 m/s
Velocity in AR	u_{AR}	3.02 m/s	3.62 m/s
AR times	u_{AR}/u_t	1.8	1.8
Velocity in FR	u_{FR}	0.153 m/s	0.159 m/s
FR times	U_{FR}/u_{mf}	3	3
AR diameter	D_{AR}	0.09 m	0.09 m
FR diameter	D_{FR}	0.19 m	0.19 m
AR pressure	P_{AR}	4,530 Pa	9,252 Pa
FR pressure	P_{FR}	3,950 Pa	3,462 Pa
AR height	$h_{AR,\ min}$	2.20 m	2.20 m
FR height	$h_{FR,\ min}$	0.39 m	0.39 m

density is 2,917 kg/m^3, particle sphericity is 0.7) and average diameter is 213 um in order to ensure the fluidization similar between the cold-flow model and the thermal reactor. With regard to the cold-flow model and the thermal reactor, the apparent gas velocity in FR and minimum fluidization velocity ratio is a constant value ($u_{FR}/u_{mf} = 3$ in this paper). the apparent gas velocity in AR and terminal settling velocity ratio is a constant value ($u_{AR}/u_t = 1.8$ in this paper). The bed material height is kept the same between prototype bed and simulate bed in AR and FR in order to guarantee the fluid dynamics similar specific value of cold-flow model are also summarized in Table 1 [13–15].

3 Results and Discussion

The cold-flow model has been built based on design concept in this paper, which guarantee the fluid dynamics similarity to the thermal reactor, and an extensive tests program have been done. First, the system pressure point is measured which is the key for stable and continuous operation. If the system pressure rises and falls frequently, it is difficult to control the system. U-type loop seals guarantee particle flow smoothly and remain gas sealed in the two reactors. So the pressure at the both ends of loop seal (as the point 11 and 13 in Fig. 2) should be balanced and lower than that in the horizontal orifice (as the point 12 in Fig. 2). Figure 3 shows the system pressure distribution. When the velocity in AR is 1.8 times u_t (apparent gas velocity is 3.70 m/s), voidage and pressure difference between every two points along the AR is not significant. The particle kinestate in the AR presents dilute-phase pneumatic conveying and this situation should be avoided. The pressure is lower and the voidage is larger in the higher part compared to the lower part of the FR, due to that the two gradient stops in the higher part are over the bubbling height and at the freeboard. while the pressure in the lower part increases sharply, due to that the two gradient stops in the lower part are at the bubbling, where the voidage is relatively small and directly proportional to the pressure.

U-type loop seal's function is to remain gas sealed and keep the oxygen carrier flowing smoothly. As Fig. 4 shows, with the analysis of the pressure distribution under the four cases in U-type loop seal and it is found out that the pressure at outlet (1.34 m) and inlet (1.44 m) are always above that at the horizontal orifice (1.26 m), so the AR and FR are separated by two U-type loop seals to remain gas sealed. The larger pressure difference is, the better gas sealed is. Figure 3 also suggests the loop seal can balance the system pressure between the two reactors.

All numbers for the particle flow in this section represent averaged values from a minimum 15 measurements.

When gas velocity changes in the inlet of the two reactors, it will affect the fluidization, the residence time, the particle circulation rate and so on. When the system is in the stable operation, the circulation of the particle is determined by abruptly stopping the fluidization of the upper loop seal and measuring the time of particle accumulation between defined levels in the cylindrical downcomer after the upper loop seal. As Fig. 5 shows, when the gas velocity in AR and other parameters are unchanged, the particle circulation rate increases with the gas velocity in FR increasing. But when the gas velocity in AR is 1.8 times u_t, the gas velocity in FR is not directly influencing the particle

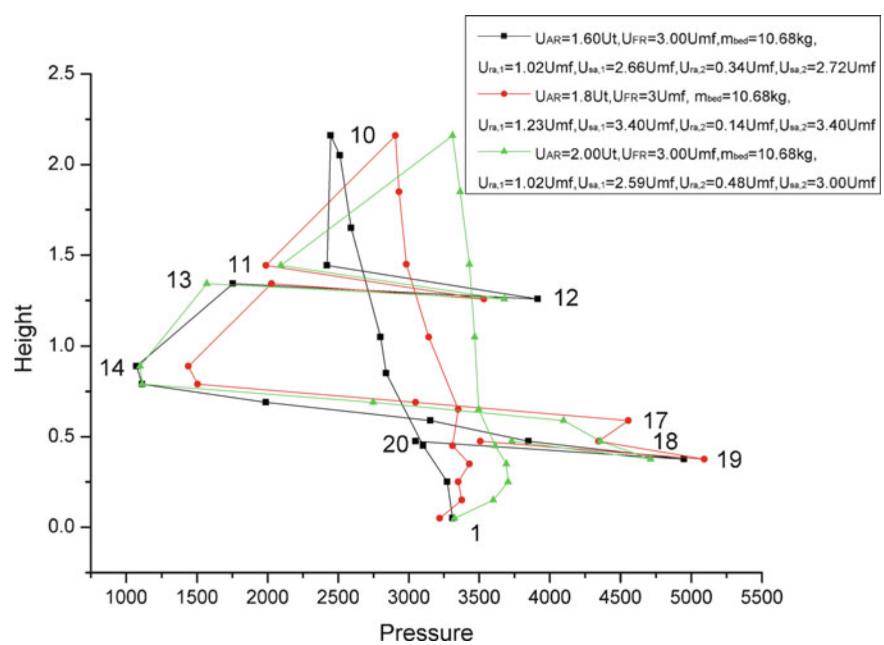
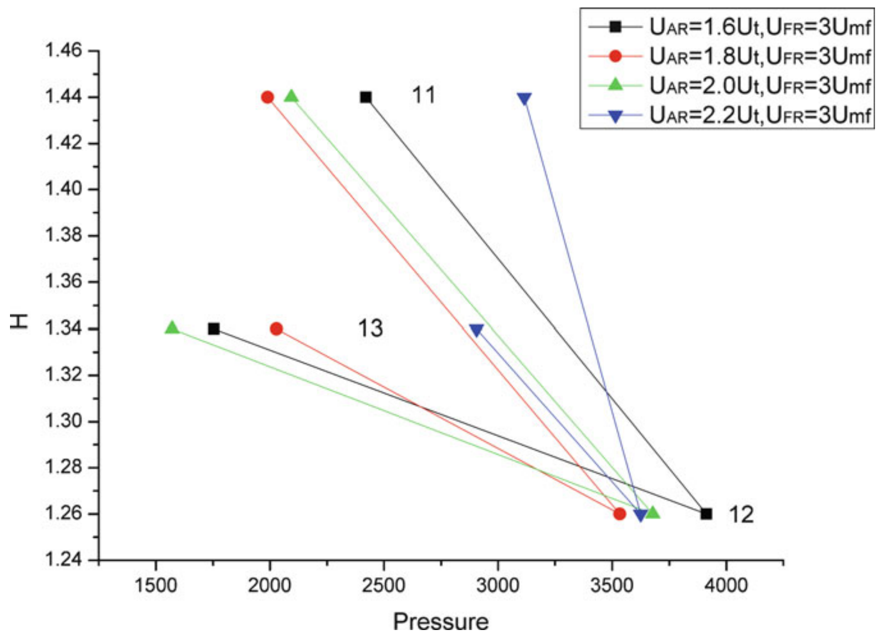


Fig. 3 The static pressure loops in the system

Fig. 4 Six different operation mode pressure at U-type loop seal



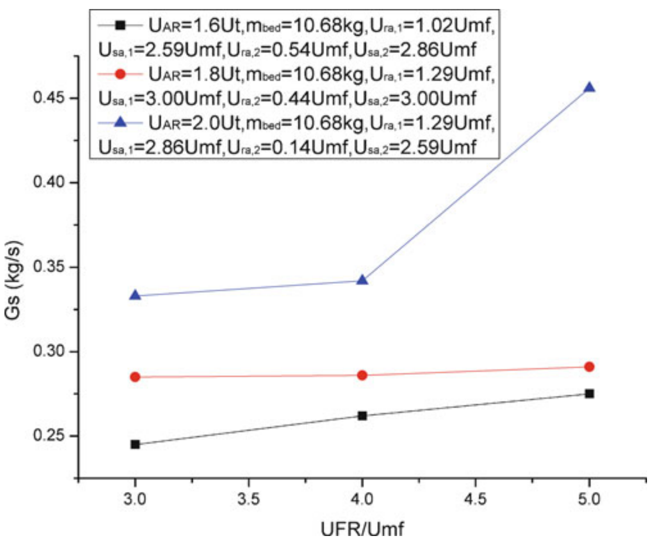


Fig. 5 The particle circulation rate versus gas velocity in FR

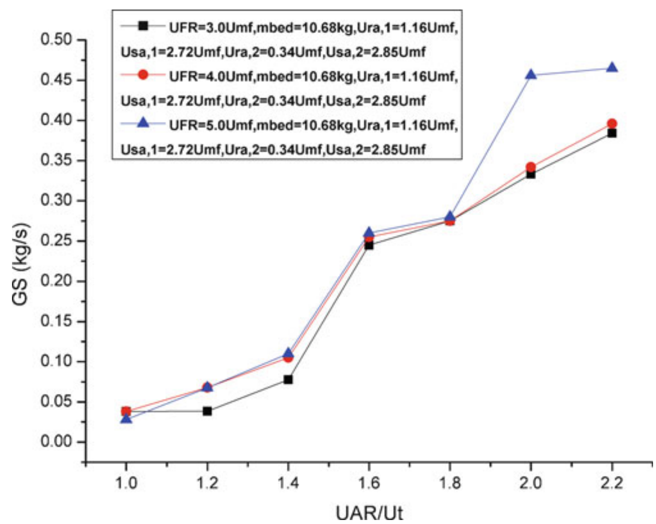


Fig. 6 The particle circulation rate versus gas velocity in AR

circulation rate. It can be observed that the system is stable when the gas velocity in AR is the value of design condition. When the the gas velocity in AR increases (such as 2.0 times u_t) or decreases (such as 1.6 times u_t), the gas velocity in FR mainly affect the particle circulation rate. Particularly, the higher gas velocity in AR and the higher gas velocity in FR (such as 5 times u_{mf}) lead the sudden increases of particle circulation rate [16–18].

Figure 6 shows the increase of gas velocity in AR results in the particle circulation rate increase to a constant value. When the gas velocity in AR is 2.0 times u_t (the gas velocity in FR is 5.0 times u_{mf}), the particle circulation rate tends stable.

It was found that the particle circulation rate (about 2.7 kg/s) can provide enough oxygen transport capacity for complete oxidation of the fuel and sufficient energy transfer between the two reactors to keep the temperatures at desired values. And a wide range of stable and suitable operating conditions was identified: when the gas velocity in AR or the gas velocity in FR properly increases, the particle circulation rate will also increase. In this case, the oxygen carrier can provide more oxygen transport capacity for complete oxidation of the fuel in the FR, which is helpful to complete combustion or leading to increasing the CH_4 flow (this refers to increase reactor power). while the gas velocity in AR or the gas velocity in FR properly decreases, the particle circulation rate will also decrease, implying the CH_4 flow should be decrease to complete combustion for CLC. During the cold-flow model test runs, it could be proved that the suitable gas inlet velocity range in FR is 3 – 5 times u_{mf} and the suitable gas inlet velocity range in AR is 1.6 – 2.2 times u_t.

4 CFD Simulation

1. The simulation of the design case
   This paper adopted User Defined Function (UDF) to realize the chemical reaction, the pre-exponential factor and activation energy were employed from the experiment data which were given by Son et al. [19] in 2006. The initial and boundary conditions are in the Table 2 below:
2. The simulation result and discussion
   As Fig. 7 shows, the mole fraction of CH_4 at the bubbling is higher than the freeboard, due to the reaction occurring at the bubbling area (Figs. 8, 9, 10, 11, and 12).
   As Fig. 13 shows, it is obvious that the mole fractions of gas phase fluctuate conspicuously in the first 1 s, due to the impact of initial condition. Then the mole fractions of gas phase become stable after 1 s.
   Figure 13 also exhibits that when the inlet gas is pure methane, the average mole fraction of water vapor in the outlet is 0.58 and the average mole fraction of CO_2 which is 0.29. The mole ratio of vapor to carbon dioxide is in accordance with that in the chemical equation. It is also demonstrated that the conversion rate X_{CH_4} as a key factor [20] in the fuel reactor design is 88.2%, a few part of methane is unburned due to fast-moving, large bubbles [21] rising through the reactor. Thus it is a good approach to reduce inlet gas velocity after achieving the circulation rate. Additionally, this result agrees well with the optimum fuel gas velocity (2 – 3) recommended by Sung Real Son.

Table 2 The initial and boundary conditions

Height of Bed (m)	0.19
Width of Bed (m)	0.39
The Initial Temperature (K)	1173.15
Diameter of Particles (m)	0.000213
The Density of Solid Phase (kg/m^3)	4369.1
Minimum Fluidization Velocity-u_{mf} (m/s)	0.053
Terminal Velocity-u_t (m/s)	1.93
Initial Solid Height (m)	0.155
Initial Gas Volume Fraction	0.47
Restitution Coefficient (e)	0.9
Time Step (s)	0.001
Grid Size	0.5 × 0.5 cm
Initial Mass Fraction of Fe_2O_3 in the solid phase	60%
Initial Mass Fraction of Al_2O_3 in the solid phase	40%
Inlet Methane Temperature (K)	973.15
Initial Fraction of N_2 in the reactor	100%
Drag Model	Gidaspow

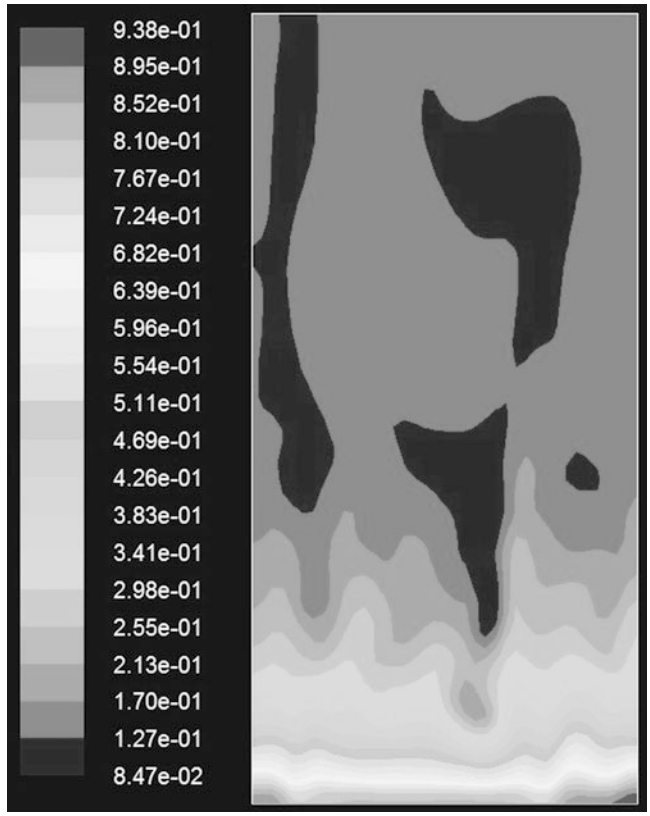


Fig. 7 Mole fraction of CH_4 at 5 s

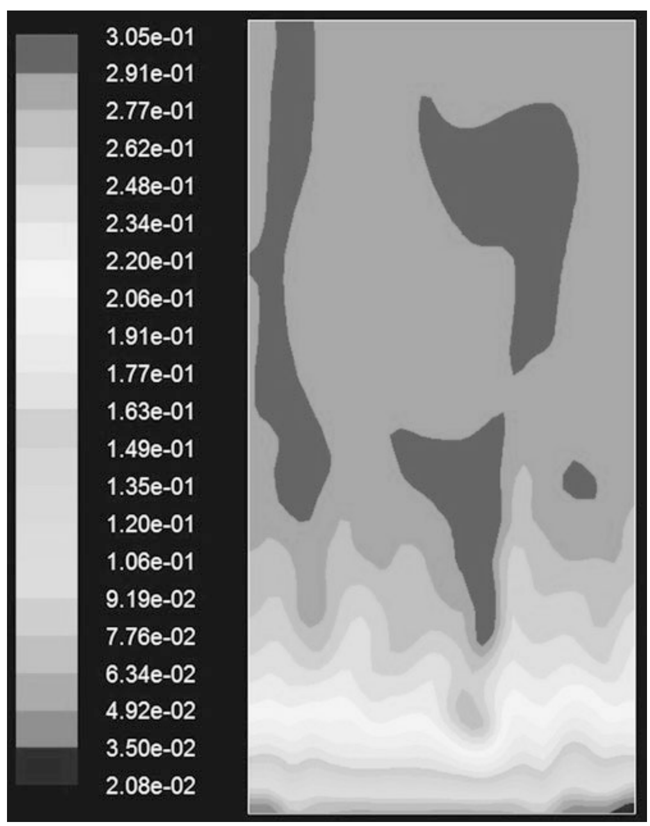


Fig. 8 Mole fraction of CO_2 at 5 s

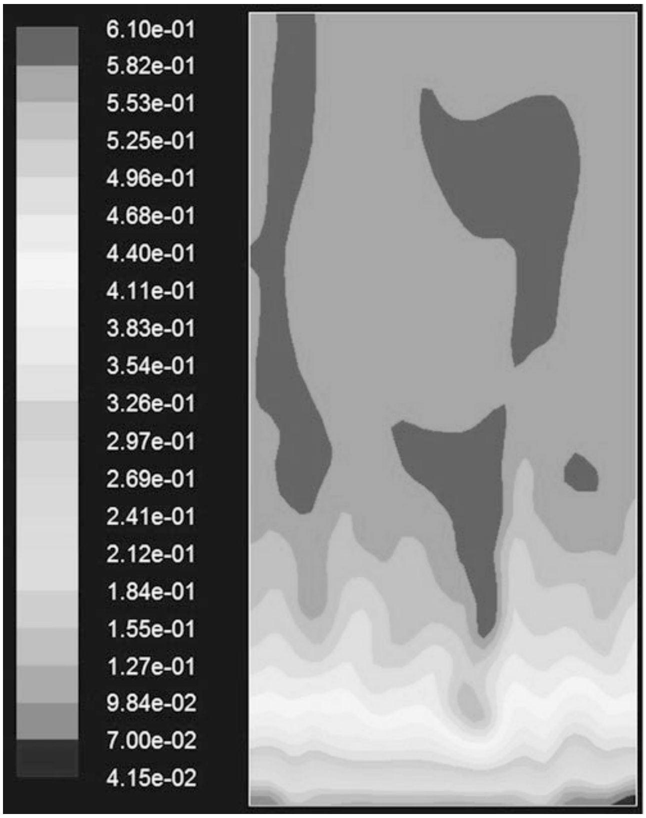


Fig. 9 Mole fraction of H_2O at 5 s

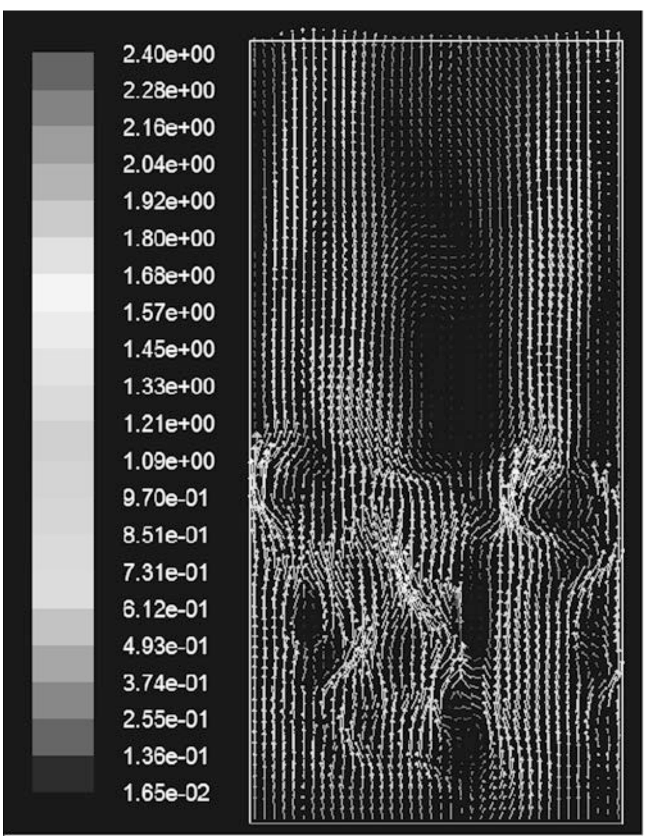


Fig. 10 The velocity of gas phase at 5 s

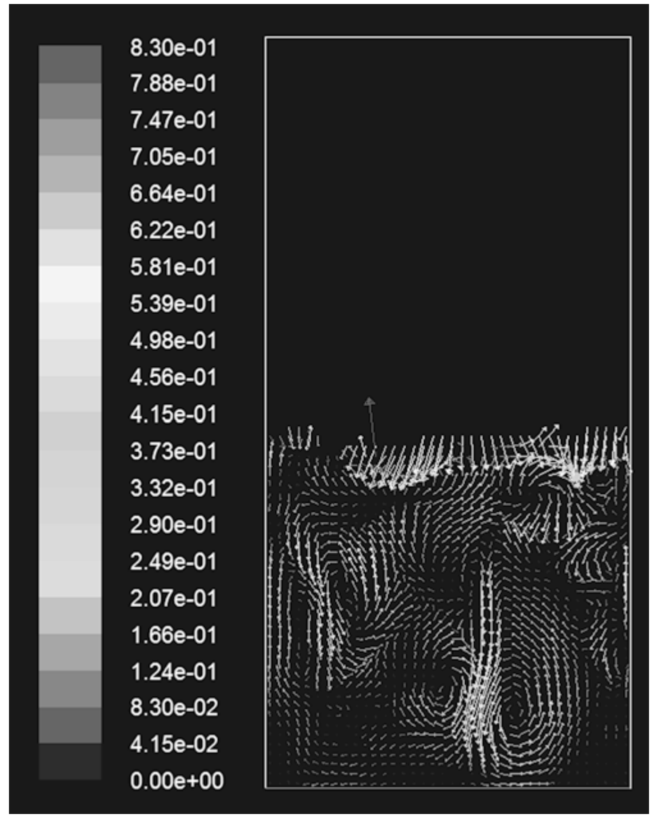


Fig. 11 The velocity of solid phase at 5 s

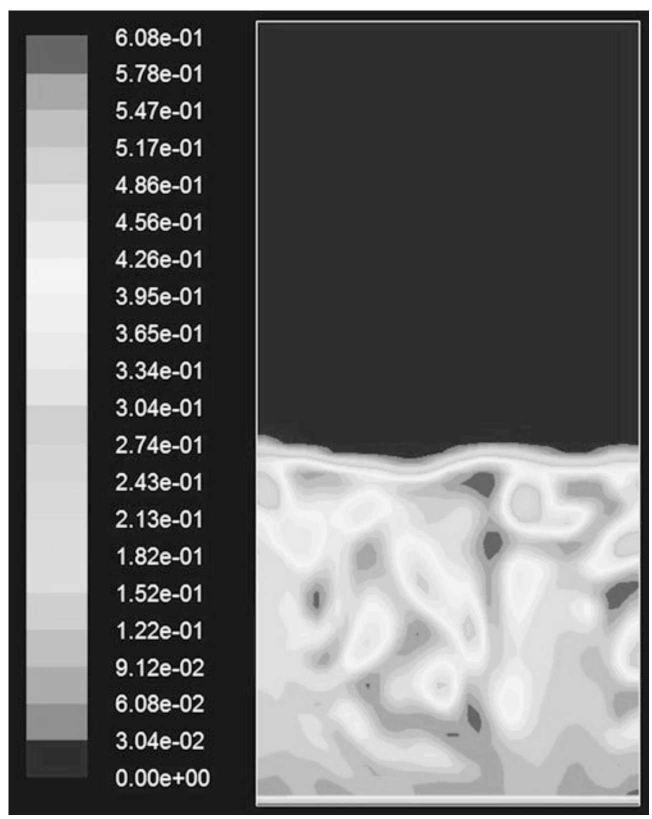


Fig. 12 The volume fraction of solid phase

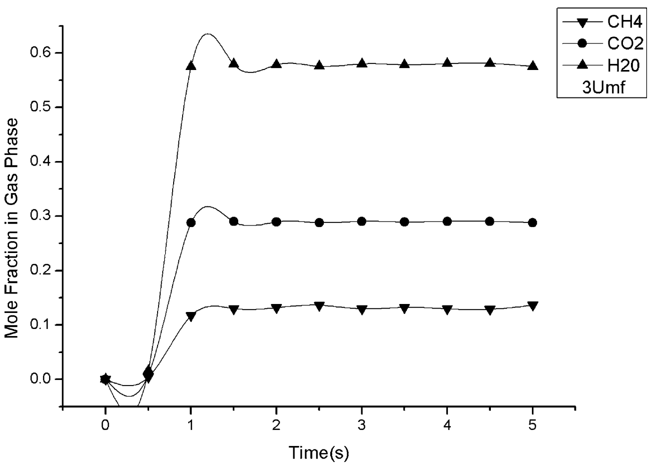


Fig. 13 Mole fraction in gas phase as a function of time at the outlet

5 Conclusion

Considered the chemical kinetics of oxygen carrier and fluid dynamics, the geometric parameters and various operation conditions of the interconnected fluidized bed are designed and calculated, overcoming the presupposition of geometric parameters in the design theory of Lyngfelt et al. [8], at certain extent. A CH_4-fueled and Fe_2O_3/Al_2O_3-based CLC reactor (thermal power of 50 kWth) has been designed, and a cold-model bench having same geometric parameters with its prototype is used to do many repeated experiments. The experimental investigation on the new CLC reactor is conducted to verify the rationality of various operation conditions including gas velocity in the reactors and loop seals. The bed material quantity and solid circulation rate can satisfy the chemical looping combustion requirements. The AR and FR are separated by two U-type loop seals to remain gas sealed and the particle flow smoothly through U-type loop seals. A certain range of stable and suitable operating condition was identified: the suitable gas velocity in FR is 3 – 5 times u_{mf} and the suitable gas velocity range in AR is 1.6 – 2.2 times u_t. In these cases, the particle circulation rate ranges from 0.25 to 0.45 kg/s.

The results of simulation reveal that under the design situation the conversion rate of CH_4 reaches 88.2% and unburned methane escapes from the reactor with large bubbles. In order to gain a higher conversion rate, the recirculation of unburned methane [22] will be a promising approach.

Acknowledgments The authors were supported by "National Key Basic Research and Development Program (Grant No. 2011CB707300)", "National Natural Science Foundation (Grant No. 50936001 and 50721005)" and "New Century Excellent Talents in University (Grant No. NECT-10-0395)" for funds.

References

1. Hossain MM, de Lasa HI. Chemical-looping combustion (CLC) for inherent CO_2 separations – a review. Chem Eng Sci. 2008;63 (18):4433–51.
2. Kronberger B, Lyngfelt A, Loffler G, et al. Design and fluid dynamic analysis of a bench-scale combustion system with CO_2 separation-chemical-looping combustion. Ind Eng Chem Res. 2005;44(3):546–56.
3. Liu L, Zhao H, Zheng C. The research advances in oxygen carriers in chemical looping combustion. Coal Convers. 2006;29(003): 83–93 (in Chinese).
4. Berguerand N, Lyngfelt A. Design and operation of a 10 kWth chemical-looping combustor for solid fuels-testing with South African coal. Fuel. 2008;87(12):2713–26.
5. Ryu HJ, Jin GT, Yi CK. Demonstration of inherent CO2 separation and no NOx emission in a 50 kW chemical-looping combustor: continuous reduction and oxidation experiment. Amsterdam: Elsevier Ltd; 2005.
6. Lyngfelt A, Leckner B, Mattisson T. A fluidized-bed combustion process with inherent CO_2 separation. Application of chemical-looping combustion. Chem Eng Sci. 2001;56(10):3101–13.
7. Rydén M, Lyngfelt A, Mattisson T. Synthesis gas generation by chemical-looping reforming in a continuously operating laboratory reactor. Fuel. 2006;85(12–13):1631–41.
8. Mattisson T, Lyngfelt A, Leion H. Chemical-looping with oxygen uncoupling for combustion of solid fuels. Int J Greenh Gas Control. 2009;3(1):11–9.
9. Kolbitsch P, Bolhàr-Nordenkampf J, Pröll T, et al. Comparison of two Ni-based oxygen carriers for chemical looping combustion of natural gas in 140 kW continuous looping operation. Ind Eng Chem Res. 2009;48(11):5542–7.
10. Ryu HJ, Lee SY, Park YC, et al. Solid circulation rate and Gas leakage measurements in an interconnected bubbling fluidized beds. Int J Appl Sci Eng Technol. 2008;4(2):113–18.
11. Adánez J, et al. Optimizing the fuel reactor for chemical looping combustion. In: Proceedings of the 17th international conference on fluidized bed combustion. ASME, 2003.
12. Wu J, Shen L, Xiao J. Control the gas-solid two-phase flow in the interconnected fluidized bed. Chem Eng J. 2007;58(011):2753–8 (in Chinese).
13. Cho P, Mattisson T, Lyngfelt A. Comparison of iron-, nickel-, copper-and manganese-based oxygen carriers for chemical-looping combustion. Fuel. 2004;83(9):1215–25.
14. Jang L, Zhao H, Zhang S. Study on the oxygen carrier (Fe2O3/ Al2O3) circulation reactivity in CH4. J Eng Thermophys. 32(002): 329–32 (in Chinese).
15. Liang B, Duan T, Tang S. Chemical reaction engineering. Science Press; 2003 (in Chinese).

16. Guo, Li H. Handbook of fluidization. Beijing: Chemistry Industry Press; 2007 (in Chinese).
17. Glicksman LR. Scaling relationships for fluidized beds. Chem Eng Sci. 1984;39(9):1373–9.
18. Horio M, Nonaka A, Sawa Y, et al. A new similarity rule for fluidized bed scale-up. AIChE J. 1986;32(9):1466–82.
19. Son SR, Kim SD. Chemical-looping combustion with NiO and Fe_2O_3 in a thermobalance and circulating fluidized bed reactor with double loops. Ind Eng Chem Res. 2006;45(8): 2689–96.
20. Jung J, Gamwo IK. Multiphase CFD-based models for chemical looping combustion process: fuel reactor modeling. Powder Technol. 2008;183(3):401–9.
21. Deng Z, Xiao R, Jin B, Song Q, Huang H. Multiphase CFD modeling for a chemical looping combustion process (fuel reactor). Chem Eng Technol. 2008;31(12):1754–66.
22. Kruggel-Emden H, Rickelt S, Stepanek F, Munjiza A. Development and testing of an interconnected multiphase CFD-model for chemical looping combustion. Chem Eng Sci. 2010;65 (16):4732–45.