COLD FLOW MODEL INVESTIGATION OF TWO INTERCONNECTED REACTORS FOR CALCIUM LOOPING HYDROGEN GENERATION WITH CO_2 CAPTURE

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Abstract – Calcium looping hydrogen generation (CaLHG) is a promising technology to produce hydrogen rich syngas with in-situ CO_2 capture. The concept of compact fluidized bed used as calcium looping gasifier for hydrogen generation from coal was proposed previously and the simulation results showed that the hydrogen purity could reach as high as 96vol%. The CLHG system consists of two interconnected fluidized beds: one is the gasifier, a compact fluidized bed, and the other is the regenerator, a fluidized riser. The CaO from regenerator flows into the middle of the gasifier and goes up in the riser, the upper of the compact fluidized bed. CaO absorbs CO_2 in the outlet gases from the bubble-fluidized bed, the lower of the compact fluidized bed, and drives the water-gas shift reaction forward, further improving the hydrogen purity. The solids from the upper of the compact fluidized bed, mainly comprised of CaO and $CaCO_3$, goes down to the bubble-fluidized bed after cyclone. In the lower bubble-fluidized bed, where coal gasification and carbonation occur, hydrogen rich gases are formed. The unreacted char, together with $CaCO_3$, goes down to the regenerator for CaO regeneration by oxygen-char combustion. In this paper, a cold flow model (CFM) has been built and tested to verify the feasibility of fluid dynamic of the system. Particles run in system were quartz sands (Geldart group B). Solid circulation rates, pressure profiles, gas leakage and mass distribution were measured. The results showed that the design of compact bed can operate stably under various operating conditions.

INTRODUCTION

Mankind's demands for energy are ever increasing and global warming has become a thorny problem which mainly caused by excessive emission of carbon dioxide found in (Arrhenius, S. and Holden, E.S., 1896). With the constant progress of energy generation science and technology, nuclear fusion has a great prospect for future energy generation with carbon dioxide zero-emission, but as found in (Dincer, I. and Acar, C, 2015), fossil fuel energy power generation will still be the main way to generate energy in 21st century. Therefore, carbon-dioxide capture and storage (CCS) project is proposed and analyzed in (Anderson, S. and Newell, R, 2003) to mitigate the worsening global climate change caused by fossil fuel carbon dioxide emission. In other previous studies, Dean, C.C. et al. (2011) wrote that calcium looping (CaL) is a CO_2 capture scheme using solid CaO-based sorbents to remove CO_2 inherently from flue gases producing a concentrated stream of CO_2 (~95%) suitable for storage and Johnston, B. et al. (2005) put forward that hydrogen is the energy source for this century. Based on this, finding a way to generate hydrogen with separate CO_2 inherently is a compelling subject. Currently, hydrogen is primarily produced from steam-natural gas reforming and coal gasification processes. However, these process is complex and expensive, especially when CO2 capture process is implemented. Therefore, in this paper, a reactor mainly for coal gasification with CaL was designed and constructed, which generate hydrogen and separate CO_2 simultaneously. The coal/CaO/steam gasification system consist of two reactors: a gasifier and a regenerator. In gasifier, the coal gasification process is achieved by reacting coal and steam at an appropriate temperature and pressure. During the gasification process, CaO is added into the reactor, absorbing CO_2 in form of $CaCO_3$. Then, $CaCO_3$ and the unburned char, which for combustion to provide the heat needed for CaO regeneration, flow into the regenerator. The schematic description of this process is shown in Fig.1. which is defined as calcium looping hydrogen generation (CaLHG).

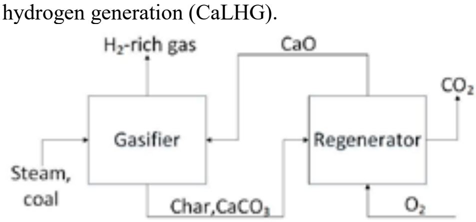


Fig.1. The schematic description of coal/CaO/steam system

The reactors for CaLHG are mainly divided into three type configurations: 1) A bubbling fluidized bed (BFB) and a circulating fluidized bed (CFB). Bidwe, A.R. et al. (2014) constructed a system comprised of a BFB gasifier and a CFB regenerator. The configuration was standpipe-loop seal-return leg arrangement of the regenerator as internal circulation. They also studied the residence time and segregation of the light particles in the BFB with bed material exiting from the bottom. It was found that the light particles have more residence time than the heavy particles since the light particles have a tendency to float in a BFB. Charitos, A. et al. (2010) built a dual fluidized bed (DFB) utilizing a CFB carbonator, and a BFB regenerator. They used a double exit loop seal with an orifice at its bottom. The opening size of the orifice is controlled by a cone valve. In addition, the absolute pressure of the BFB is set by a pressure control valve. 2) Two CFBs. Pröll, T. et al. (2009) studied the fluid dynamics of a system consisting of two interconnected CFB reactors with two loop seal and an internal circulation in fuel reactor (FR). They found a partly paradoxical behavior with respect to the dependence of the FR's internal solid circulation rate on the total solids inventory and on the global circulation rate between air reactor (AR) and fuel reactor (FR), i.e., the operating point at 10 Nm^3/h shows an opposite dependence on both bed inventory and lower loop seal fluidization than the operating point at 15 Nm^3/h. 3) Two BFBs. Yazdanpanah, M. M. et al. (2011) analyzed a CFM configuration of two interconnected bubbling fluidized beds with double L-valve and loop seal. The interest of their study is that they found when aeration below the supply chamber of the loop seal was lower than aeration of horizontal pipe of the loop seal, gas leakage will occur at loop seal. Inversely, when aeration below the supply chamber of the loop seal was equal or greater than the aeration of horizontal pipe of the loop seal, the best gas tightness was achieved. Ryu, H. J. et al. (2007) studied a relatively simple configuration of two BFB reactors comparing to the configuration researched by Yazdanpanah M. M. et al. (2011). They compared different characteristics of injection nozzle and found that the solid circulation rate increased as the size and number of nozzle increased.

The novelty of our system is the extra upper riser above the gasifier. The hydrogen-rich syngas flows up to the upper riser. Regenerated CaO from the regenerator is led to the upper riser above the gasifier; it is raised by hydrogen-rich syngas from the gasifier and absorbs the rest CO_2 in the mixed gases, further improving the hydrogen purity. At the outlet of gasifier cyclone, nearly pure hydrogen, where the hydrogen purity can reach 96 vol% found in (Chen SY et al., 2011), could be obtained after water condensation and the separated solids $CaO/CaCO_3$ fall into the gasifier for gasification process. However, because of the complex hydrodynamic of system, it is necessary to set up a cold flow model (CFM) to validate the feasibility of design configuration. In this paper, a CFM configuration has been constructed (shown in Fig.2). The pressure profile under standard operating condition has been draw. The pressure drop in the upper riser varies with gas flow rate in gasifier has been recorded with time and analyzed. Solid circulation rate, mass distribution and gas leakage has also been investigated.

PREPARATION

In other previous studies, Glicksman rules presented in (Glicksman, L. R. et al., 1994) were applied to scale-down the hydrodynamic parameters for the cold flow model. The scaling rules of fluidized bed reactors usually have three subprocesses:1) fluid dynamic gas-to-solid contact, 2) heat and mass transfer and 3) chemical reactions. In a word, Glicksman rules require parameters shown in Eq. (1) should be kept constant.

$$\mathrm{Fr},\ \mathrm{Re_p},\ \frac{L}{d_p},\ \frac{D}{d_p},\ \Phi,\ \mathrm{PSD, bed\ geometry} \qquad (1)$$

Of special interest, the reactor will be set in an oven. The scaling ratio between hot and cold reactor is 1:1 since this CFM configuration is used to verify the performance of compact bed, not used for refined calculation of chemical reaction. The riser, i.e. regenerator, is 1.95 m high and its internal diameter is 22 mm. The gasifier is 160 mm long, 80 mm wide and 350 mm high. The diameter and the height of the storage silo (viz. standpipe of upper loop seal) above the upper loop seal is 41 mm and 180 mm respectively. The diameter of other tubes in our configuration is 20 mm uniformly. The configuration is made by perspex and fixed with brackets on the steel frame.

Table.1: Properties of bed materials

Property (Unit)	Value	Measurement method
$\rho_{s,real}$ (kg/m^3)	1364	Supplier data sheet
d_p (μm)	330	Laser granulometry
U_{mf} (m/s)	0.06	Pressure drop variation method
U_t (m/s)	3.37	Haider and Levenspiel

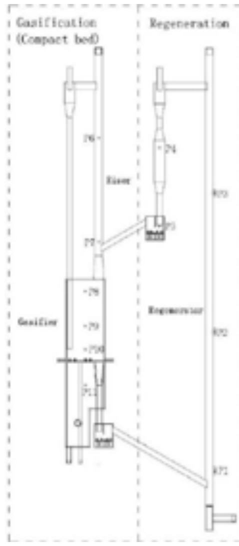


Fig.2. Experimental facility of CFM   Fig.3. Distribution of pressure taps

Experiments were carried out at ambient temperature and pressure conditions using air as the fluidization gas. Quartz sand particles was used and its properties was listed in Table.1. Fluidization air was supplied from an air pump with constant pressure. Gas flow rate into gasifier, regenerator and loop-seal was measured and controlled by rotor flow meters and manual valves. Pressure drops were measured by digital pressure transducers and were automatically transferred to a computer with adjustable frequency. Locations of pressure taps corresponding to each section of the system are illustrated in Fig.3. The bottled CO_2 gas and flue gas analyzer are utilized to measure gas leakage in the CFM.

Several important parameters were influenced by operating conditions, i.e. gas flow rate into each reactor and total solid inventory (TSI), have been investigated in our studies, such as pressure profile, operational map, solid circulation rate, mass distribution and gas leakage. Pressure was measured using Beijing star sensor technology® pressure transmitters and pressure signals was converted into electric signals to computer to record. The measured pressures in this paper were all gage pressure. Solid circulation rate was measured using batch calibration method. The aeration under the storage silo (viz. standpipe of upper loop seal) was shut down during the stable operation. The time (t) for particles to accumulate with a certain distance (h) was measured. Since the bulk density (ρ_{bulk}) of bed materials and cross section aera (S) of storage silo was known, the solid circulation rate (G_s) can be calculated using Eq. (2).

$$G_s=\frac{S\rho_{bulk}H}{t} \qquad (2)$$

Gas leakage was measured using bottled CO_2 as tracer gas. Flue gas analyzer was set at the two outlets of bed to test the concentration of CO_2. If the concentration of CO_2 in the gasifier plenum is equal to that at the outlet of gasifier, the gas tightness at the compact part can be proven well. Gas flow rate in every plenum was measured by rotor flow meter, sectional area of tube or box was known and Eq. (3) was used to calculated superficial velocity.

$$v=\frac{F}{S} \qquad (3)$$

When system in the stable operation, air supply was shut down and bed materials fluidized in the bed was full down and stack spontaneously. The stack height in every reactor was measured, then the mass distribution was obtained by Eq. (4).

$$M=\hbar_m S\rho_{bulk} \qquad (4)$$

RESULTS AND DISCUSSION

Pressure

Pressure is a key parameter during the operation because it is the driving force in the whole bed. In the other hand, it is impossible to observe the running status in thermal experiment because of the reactor constructed by non-transparent metal. Pressure can reflect the operation status in the reactor. In our CFM experiment, the pressure profile has been measured under standard operating condition according to table.2. The first aeration is under standpipe of loop seal and the second aeration is near to the discharging pipe.

Table.2: Standard operating condition

Parameter (Unit)	Standard Value	Variation
Total solids inventory (kg)	3.5	2.5-7
Gas flow rate in gasifier (m^3/h)	6	3.2-10
Gas flow rate in regenerator (m^3/h)	4	2.5-6
First aeration in upper loop seal (L/h)	280	100-500
Second aeration in upper loop seal (L/h)	200	0-1000
First aeration in lower loop seal (L/h)	150	100-500
Second aeration in lower loop seal (L/h)	220	0-1000

The pressure profile under standard operating condition is shown in Fig.4. The pressure tap locations are shown in Fig.3. The dotted line represents the pressure in fuel reactor (FR) and the dash line represents the pressure in regenerator (air reactor, AR). The AR shows a typical distribution for a fast fluidized riser. In the FR, the gasifier is a bubbling bed and the upper riser is a fast fluidized bed. Most of bed materials are found in the bottom region of gasifier and the pressure tap P10 buried in the inventories. The entrainment of upper riser is higher compared to the regenerator. From P4 to P5, the pressure drop in the standpipe of upper loop seal reflects the wall friction of particles flowing through the loop seal and this significant pressure drop in the upper loop seal indicates a higher global solid circulation rate in this system. In other words, this reactor can operate stably at high global circulation rate.

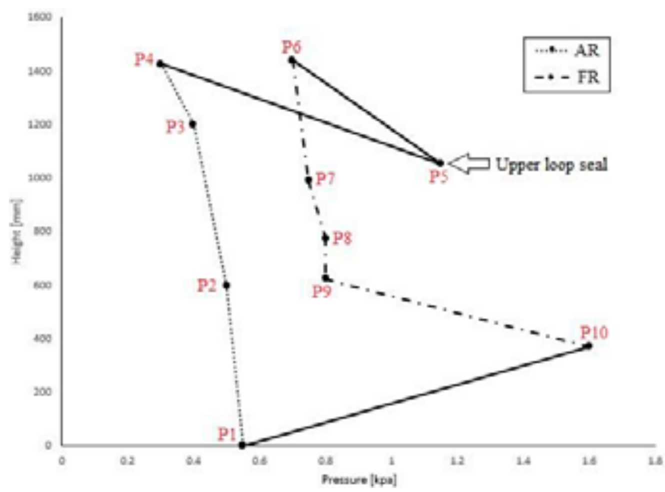


Fig.4. Pressure profile measured under standard operating condition

In this paper, the feasibility of compact bed (viz. an upper riser above a bubbling bed) has been studied. The original intention of compact bed is to fluidize bed materials coming from the upper loop seal, which is good for improving hydrogen purity in thermal state. In CFM experiments, the relationship between gas flow rate in upper riser and the pressure drop variation from P8 to P7 against time was researched. The system was operating under standard condition.

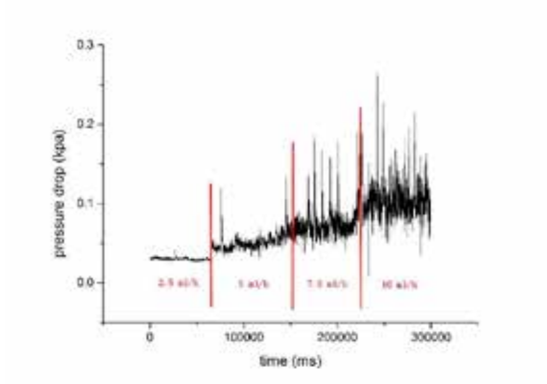


Fig.5. Pressure drop variation against time from pressure tap 8 to tap 7

Fig.5. shows the pressure drop variation against time from pressure tap 8 to tap 7. The gas flow rate in the gasifier increases from 2.5 m^3/h to 10 m^3/h with a step size of 2.5 m^3/h. The two aerations in the upper loop seal are constant to keep the discharging solids entrainment unchanged. Fig.6. shows the route of discharging solids from upper loop seal under different superficial velocities in upper riser. Fig.6.(a) to Fig.6.(d) are corresponding to the four different gas flow rate mentioned above respectively (e.g. the gas flow rate in Fig.5.(a). is 2.5 m^3/h and so on). An increase of gas flow rate in gasifier increases the pressure drop in the upper riser and the fluctuation of pressure drop have grown bigger and bigger. The reason for the gradually growth fluctuation mostly attributes to the design of connection between the gasifier and the upper loop seal. The specific reason for this phenomenon will be researched in our continuous works. In Fig.6.(a), a part of the discharging materials from upper loop seal has drop into gasifier when the gas flow rate in gasifier is 2.5 m^3/h and the pressure drop is less than 0.05 kpa. This is not the design operating condition because the regenerated CaO from regenerator cannot further absorbing CO_2 in the upper riser. When the gas flow rate in gasifier reaches 10 m^3/h, the elutriation of materials in gasifier happens, which is also undesired because of $CaCO_3$ and unreacted char cannot fully flow down to regenerator through the lower loop seal and decrease the thermal efficiency in the regenerator. In conclusion, experimentally, the range of gas flow rate in gasifier for desired operation is from 3.2 m^3/h to 10 m^3/h, i.e., the superficial velocity range in upper riser is from 2.34 m/s to 8.85 m/s.

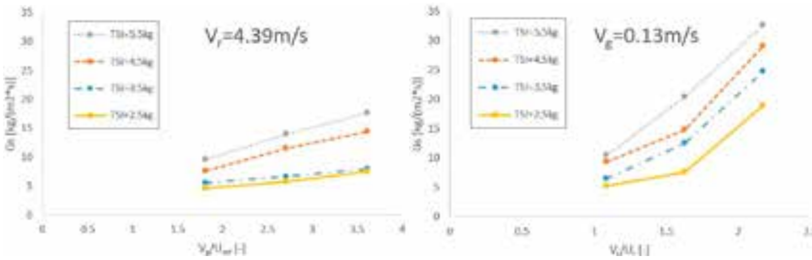
(a) 2.5m^3/h (b) 5m^3/h (c) 7.5m^3/h (d) 10m^3/h

Fig.6. The route of discharging solids from upper loop-seal under different gas low rate in gasifier

Solid circulation rate

Solid circulation has two main tasks during the thermal operation:1) Giving sufficient oxygen transport capacity for complete oxidation of the fuel in the gasifier. 2) Providing energy transfer between the two reactors in order to keep the temperature at the desired values. Based on this background, higher solid circulation in favor of increasing thermal and production efficiency. Therefore, it is very important to research the solid circulation rate between two compartments with respect to different total solid inventories

(TSI), superficial velocities ratio in gasifier and regenerator, etc. In this paper, solid circulation rate (G_s) is plotted against the fluidization number under different solid inventories in Fig.7.



(a) (b)

Fig.7. Solid circulation rate under different total solid inventories against increasing fluidization number

In the Fig.7. (a), the velocity in regenerator is kept constant at 1.3 times U_t and in the Fig.7. (b), the velocity in the gasifier is kept constant at 2.17 times U_{mf}. Meanwhile, the superficial velocity in upper riser (V_{ur}) is controlled between 3.66 m/s and 7.31 m/s, conforming to the operation range presented above. It is obviously demonstrated in Fig.7. that an increase of total solid inventory (TSI) increases the solid circulation rate (G_s). Comparing two figures above, an increase of superficial velocity in the regenerator has more impact on solid circulation rate (G_s) than that in the gasifier. As mentioned above, G_s is measured at the storage silo (viz. standpipe of upper loop seal), so the entrainment to the storage silo is a key parameter effecting on G_s. The gases in gasifier fluidize the bed materials from upper loop seal and exhaust from the cyclone. The gases in regenerator entrain bed materials to cyclone for gas and solid separation. An increase of fluidization in regenerator increases the entrainment to storage silo, particles accumulating for a fixed height in storage silo cost less time than before, i.e., the solid circulation rate (G_s) increases. In contrast, an increase of fluidization in gasifier only increases the entrainment in upper riser and have little effect on G_s.

Mass distribution

Mass distribution indicates the remaining time of bed materials (viz. solid residence time) in each reactor. In thermal experiment, the solids residence time reflects the reaction extent. In this paper, the superficial velocity in regenerator influencing the mass distribution has been studied since the fluidization in regenerator has larger impact on G_s obtained above. Fig.8. shows the mass distribution variations with different total solids inventories and fluidization number in regenerator. The superficial velocity is 4.39 m/s in upper riser and is 0.13 m/s in gasifier constantly. An increase of total solid inventory (TSI) both increases solid residence time in gasifier and regenerator. Furthermore, an increase of superficial velocity in regenerator increases the solids mass in gasifier and decreases the solids mass in regenerator. In other words, an increase of gas superficial velocity in regenerator increases solid residence time in gasifier and decreases the residence time in regenerator. But this effect was not distinct and for controlling residence time without help. In addition, the study of the influence of aerations in two loop seals on mass distribution will continue in the future.

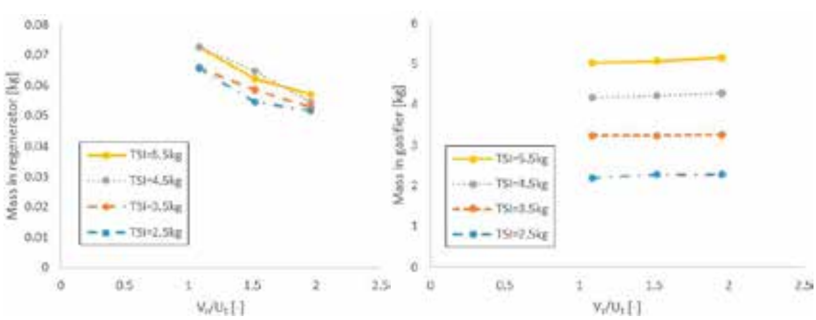


Fig.8. Mass distribution with different TSI and gas flow rate in regenerator

Gas leakage

The gas tightness of system makes the bed operate under design condition. In this paper, the CFM has two loop seals to prevent gas leakage and to ensure the solid flow orientation. The test of gas leakage from gasifier to storage silo under different gas superficial velocity in gasifier has been done. 600 mL/min of carbon dioxide from gas cylinder was pumped into the plenum constantly. The gas flow rate of air in gasifier is 6 m^3/h, 8 m^3/h and 10 m^3/h respectively since gas leakage happened mostly at higher gas flow rate. The gas was gathered at the exit of two cyclones and flow into the flue gas analyzer. Fig.9. shows the gas leakage result from gasifier to storage silo (viz. standpipe of upper loop seal). With the increase of gas superficial velocity in gasifier, the ratio of carbon dioxide gathered at gasifier cyclone decreases since the gas flow rate of air increases and the gas flow rate of carbon dioxide is constant. The carbon dioxide ratio of gas gathered at regenerator cyclone is maintained at 0.05%, which is typically the carbon dioxide ratio of air. This test has proven that this system can probably operate under higher gas flow rate without gas leakage from gasifier to storage silo. This characteristic in favor of higher solid circulation rate, which increases thermal and production efficiency.

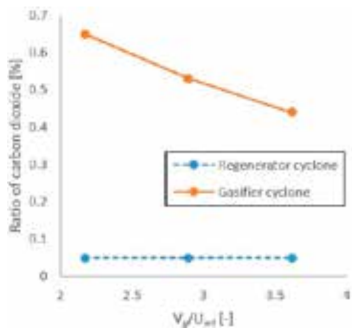


Fig.9. Gas leakage test from gasifier to storage silo

CONCLUSION

The several hydrodynamic experiments for compact bed system have been done in this paper with cold flow model. Experiment results for pressure drop, solid circulation rate, mass distribution and gas leakage were presented. The pressure profiles prove that the design of compact bed, i.e. an upper riser above a gasifier, can operate stably under standard operating conditions with globally solid circulation. The pressure drop against superficial velocity in upper riser was obtained and gas flow rate in gasifier has more impact on it. The superficial velocity in regenerator has more influences on solid circulation rate comparing to the effect of the superficial velocity in gasifier. The gas tightness from gasifier to storage silo (viz. standpipe of upper loop seal) has been proven good. Steady-state global solid circulation was achieved in this system with a constant pressure drop, reflecting the stable operation probability in the current configuration.

NOTATION

$\rho_{s,real}$	true density, kg/m^3
d_p	average particle diameter, μm
t	time, s
U_t	terminal velocity, m/s
U_{mf}	critical fluidization velocity, m/s
H	stack height, m
G_s	solid circulation rate, kg/(m^2•s)
ρ_{bulk}	bulk density, kg/m^3
F	air flow rate, m^3/h
S	sectional area, m^2
v	superficial velocity, m/s
M	mass, kg
V_{ur}	superficial velocity in upper riser, m/s
V_r	superficial velocity in regenerator, m/s
V_g	superficial velocity in gasifier, m/s
Fr	Freud number, [-]
Re_p	Reynolds number of particles, [-]
L	length, m
D	diameter, m
φ	sphericity, [-]
PSD	particle size distribution, [-]
h_m	materials height, m
FR	fuel reactor, [-]
AR	air reactor, [-]
TSI	total solid inventory, kg
CFM	cold flow model, [-]

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