A DUAL CIRCULATING FLUIDIZED BED (DCFB) SYSTEM FOR CHEMICAL LOOPING PROCESSES

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Abstract

A fluidized bed system combining two circulating fluidized bed reactors is proposed and investigated for chemical looping combustion using metal oxides as oxygen carriers. The global solids loop starts in one of the two reactors (primary reactor) where solids are entrained, separated from the gas in a cyclone and sent to the other reactor (secondary reactor) via a fluidized loop seal. From the secondary reactor, the solids are flowing back into the primary reactor via a second loop seal connecting the bottom regions of the two reactors. The secondary reactor features a circulation loop in itself (secondary reactor cyclone and loop seal) and may be optimized with respect to good gas-solid contact and low particle attrition. The global circulation rate can be effectively controlled by staged fluidization of the primary reactor. The direct hydraulic communication of the two circulating fluidized bed reactors via the lower loop seal allows stable solids distribution in the system. A 120 kW fuel power laboratory unit has been designed for chemical looping combustion of natural gas. The air reactor, where oxygen carrier particles are oxidized, is designed as the primary reactor. The fuel reactor, where the oxygen carrier serves to oxidize gaseous fuel, is designed as the secondary reactor. The reactor dimensions have been determined considering fast fluidization in the air reactor and turbulent fluidization in the fuel reactor. Experimental results with a NiO-based oxygen carrier show that fuel conversion increases with operating temperature. For the investigated system, the CO_2 yield from CH_4 is 0.94 at 950 °C (1223 K). It is expected that fuel conversion can be further improved by increasing the height of the riser reactors.

Introduction

Carbon capture and storage is the key mid-term strategy to limit the carbon dioxide concentration in the atmosphere [1]. Different approaches are currently discussed in order to capture CO_2 from combustion processes. Most of these approaches require gas separation steps: either CO_2 separation (pre- and post combustion capture) or O_2 separation from air (oxyfuel combustion). Chemical looping combustion (CLC), however, is a way of indirect combustion where fuel and air are never mixed [2]. Metal oxides are used to selectively transport oxygen from air to fuel in the solid phase. If a suitable metal oxide is used as oxygen carrier, the CLC system can be operated in a way that the exhaust gas of the fuel reactor ideally consists of CO_2 and H_2O only and allows for subsequent water condensation, compression, and storage of CO_2. Therefore, CLC is discussed as one of the very energy-efficient approaches towards carbon capture from power production or fuel upgrading.

Chemical looping combustion is a typical dual fluidized bed technology where chemically active bed material, i.e. metal oxide, is circulated between two fluidized bed reactors separated with respect to the gas phase. It has been initially proposed as early as 1954 as a method to produce pure CO_2 from oxidizable carbonaceous material [3]. Then, the concept was studied theoretically as a means to improve the reversibility of combustion [4-6]. More recently CLC has been identified as a promising technology for CO_2 capture from power plants, where 100 % of carbon capture can be

achieved without a significant energy penalty [7-10]. In the so-called fuel reactor (FR), a hydrocarbon fuel is oxidized by oxygen released from the bed material. The global reaction in the FR can be summarized for the case of full oxidation as follows:

$$C_xH_y + \left(2x + \frac{y}{2}\right) MeO_\alpha \rightarrow xCO_2 + \frac{y}{2} H_2O + \left(2x + \frac{y}{2}\right) MeO_{\alpha-1} \quad (1)$$

This step takes place at temperatures between 750 and 1000 °C and is either slightly exothermic or even endothermic depending on the type of fuel and on the oxygen carrier chosen [11]. In the so-called air reactor (AR), the bed material is re-oxidized with air:

$$MeO_{\alpha-1} + \frac{1}{2} O_2 \rightarrow MeO_\alpha \quad (2)$$

This step is always strongly exothermic and the sum of reaction enthalpies of Reactions (1) and (2) is equal to the reaction enthalpy of direct combustion. Heat is withdrawn from the system with the hot exhaust gas streams. For common excess air ratios around 1.2, additional heat must be withdrawn directly from the reactors either by cooling the reactor walls or by cooling the circulating bed material stream. In practice, the extent in which fuel oxidation happens in the fuel reactor depends on the availability of oxygen (sufficient carrier circulation) and on the kinetics of the elementary gas-solid reactions (sufficient gas-solid contact time). If less oxygen is provided than needed for full oxidation, the chemical looping system operates in chemical looping reforming (CLR) mode. In this case the fuel reactor exhaust contains at least the combustible species CO and H_2 besides CO_2 and H_2O and the global heat release is decreased.

A key-issue for the industrial feasibility of CLC is the availability of oxygen carriers suitable from both the technical and the economical point of view. Therefore, extensive research is performed concerning the preparation and subsequent testing of materials as summarized e.g. by Johansson et al. [12].

The dual circulating fluidized bed (DCFB) system

For chemical looping combustion (CLC) or reforming (CLR) processes with selective oxygen transport by the bed material, the following basic requirements can be stated:

- High global solids circulation is required in order to provide enough oxygen in the fuel reactor and in order to keep the temperature difference between air reactor and fuel reactor low.

- Excellent gas-solids contact is required in both reactors in order to obtain satisfactory gas conversion. This is especially true for the fuel reactor of CLC systems where significant amounts of unconverted fuel will hardly be tolerable in applications.

- Low particle attrition rates are appreciated especially if costly oxygen carriers are to be used.

Therefore, the system investigated in the present study represents a combination of the existing practice in CLC technology, where a bubbling bed fuel reactor is added to the return leg of the solids of a circulating fluidized bed system, with the idea to use two scale-up ready CFBs for both air reactor and fuel reactor. A second aim of the present effort is to propose a robust fluidized bed system which

is most simple with respect to necessary process control devices. In the dual circulating fluidized bed (DCFB) system according to Fig. 1, the two CFB reactors are interconnected via a fluidized loop seal in the bottom region of the reactors (lower loop seal). The entrainment of the left hand side reactor (primary reactor) determines global solids circulation. The solids are separated from the primary reactor exhaust stream in a cyclone separator and pass over through a fluidized loop seal (upper loop seal) into the right hand side reactor (secondary reactor). From there, the global solids loop closes via the lower loop seal. The secondary reactor features a circulation loop in itself (secondary reactor cyclone and internal loop seal) and may be optimized with respect to good gas-solid contact and low particle attrition rates. The global circulation rate can be effectively controlled by staged fluidization of the primary reactor. This is common practice in CFB technology. The direct hydraulic communication of the two CFB reactors allows stable solids distribution in the system as long as the lower loop seal is designed large enough to not significantly hinder solids flow. Imposing moderate pressure differences between the two reactors changes the theoretical solids levels in the system. This can be done by changing the backpressure from the exhaust gas lines and allows active control of the solids hold-up in each reactor.

Apart from CLC, the DCFB system has potential to be applied in other dual bed processes such as carbonate looping for end-of-pipe CO_2 capture [13], dual bed gasification and sorption enhanced reforming [14,15]. The design of the 120 kW fuel power pilot plant for CLC is described in the following.

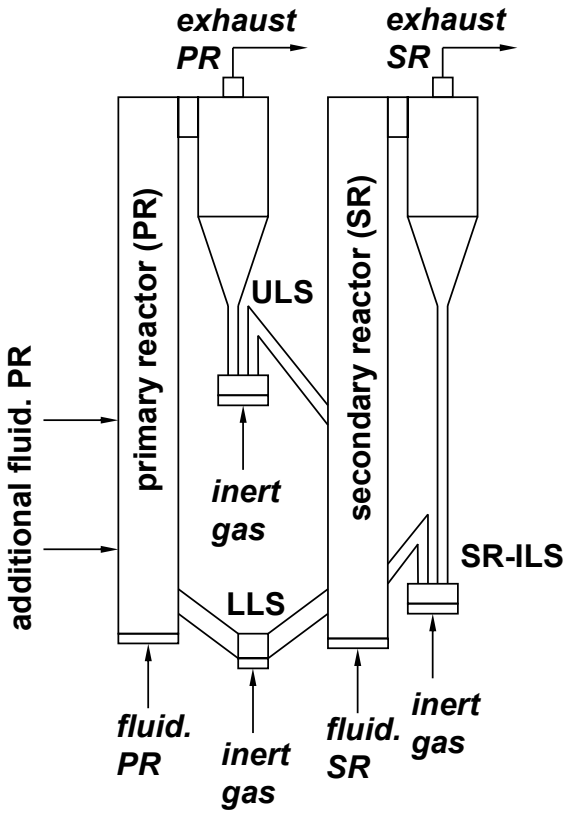

Figure 1. Dual circulating fluidized bed reactor concept (LLS = lower loop seal, ULS = upper loop seal, SR-ILS = secondary reactor internal loop seal)

Design of the 120 kW test rig

A DCFB test rig for CLC of gaseous fuels has been designed and built with the hot commissioning phase completed in early 2008. The air reactor (AR) of the CLC system is designed as the primary reactor in the sense of the DCFB concept described above. The fuel reactor (FR) is the secondary reactor, which may be optimized with respect to gas phase conversion. For means of simplicity at the small scale, the lower loop seal connecting the two reactors represents a continuation of the reactor bodies. The main fluidization nozzles are arranged along the circumference of the cylindrical reactor shells. The bulk geometry of the two reactors and the operating parameters of the design case are reported in Table 1.

In order to remove the heat released from combustion and to control the system temperature independently of the global air ratio, the air reactor shell is equipped with cooling jackets. These cooling jackets are operated either with boiling water or gaseous cooling media. The cyclone separators are designed according to Hugi [16]. The loop seals are fluidized with steam in nominal operation and may be switched to air fluidization during start-up and shut-down. The exhaust gas streams of the two reactors are cooled separately to about 573 K and analyzed on-line to evaluate the conversion of the fuel as well as the leakages of the loop seals. The cooled exhaust gas streams pass valves. These allow for imposing defined backpressure on each reactor. The exhaust gas streams are then mixed and sent to a natural gas fired post combustion unit, cooled again, filtered and sent to the chimney. Solids sampling is possible out of the upper and the lower loop seal during operation. This allows accurate interpretation of experimental results (carrier oxidation states and solids circulation rate).

Table 1. Basic geometry and design case operating parameters of the 120 kW CLC test rig.

Parameter	Unit	Air reactor	Fuel reactor
riser reactor free height	m	4.1	3.0
riser reactor inner diameter	mm	150	159
inlet gas flow	Nm^3/h	138.0	12.0
outlet gas flow	Nm^3/h	113.9	35.9
temperature in reactor	K	1213	1123
design fluid for calculation		depleted air	H_2O/CO_2 = 2/1
particle size	mm	0.12	
particle apparent density	kg/m^3	3200	
particle sphericity	-	0.99	
Archimedes number		7.55	9.13
superficial velocity	m/s	7.32	2.08
ratio U/U_{mf}	-	1280.4	315.4
ratio U/U_t	-	15.5	3.8
fuel power (natural gas)	kW	120	
lower heating value of fuel	MJ/kg	48.8	
design air/fuel ratio	-	1.2	

First operating results

Operation at chemical looping conditions started in January 2008 with natural ilmenite ($FeTiO_3$) as bed material. These tests, where hydrodynamics and syngas conversion have been studied, paved the way for operation with the designed NiO-based oxygen carrier which has been produced under the supervision of Chalmers University of Technology in Gothenburg/Sweden [17]. The first results for ilmenite as oxygen carrier in the 120 kW test rig has been recently reported elsewhere [18]. Here, in the context of the particularities of the DCFB reactor system, results from operation with NiO-based particles will be presented. Apart from steam for loop seal fluidization no steam or nitrogen is added to the fuel reactor.

Figure 2 shows the pressure profile in the reactor system for 150 kW fuel power with natural gas as fuel and at a global air ratio of 1.1. The primary reactor side (air reactor) shows a very distinctive exponential decay of solids with height. The solids profile in the secondary reactor (fuel reactor) show a steep decay of pressure in the lower part of the reactor. This indicates that the solids are concentrated in the dense zone at the bottom and the upper part of the fuel reactor is still relatively lean. The pressure differences in the loop seals represent pressure losses due to the flowing solids. From this point of view, the flow via the internal loop seal (i.e. the fuel reactor solids entrainment) is expected to be small compared to the global solids circulation between air reactor and fuel reactor.

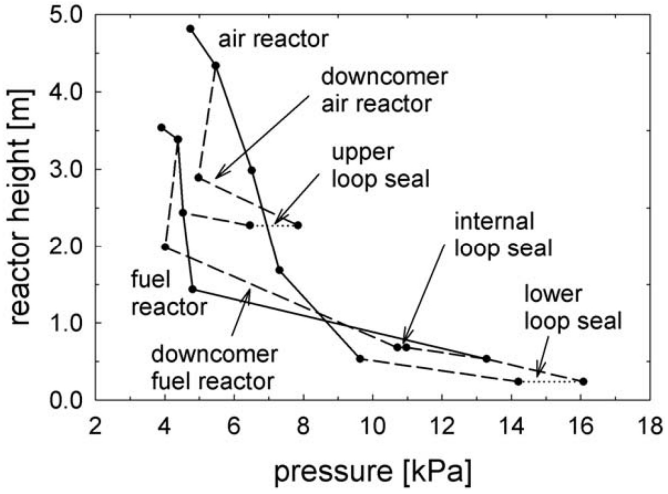

Figure 2. Pressure profile in the test rig at 150 kW fuel power and an air ratio of 1.1.

The most important performance criterion of CLC systems is the degree of fuel conversion in the fuel reactor. The critical output parameters methane conversion

$$X_{CH_4} = 1 - \frac{y_{CH_4}}{y_{CH_4} + y_{CO} + y_{CO_2}}, \tag{3}$$

and CO_2 yield

$$\gamma_{CO_2} = \frac{y_{CO_2}}{y_{CH_4} + y_{CO} + y_{CO_2}} \tag{4}$$

are shown Figure 3. The active solids mass in each reactor is obtained from pressure differences. It turns out that the CO_2 yield of the investigated oxygen carrier and plant design is strongly dependent

on operating temperature. At lower temperatures the slip of unconverted fuel as CO and H_2 out of the fuel reactor is increased while the (primary) conversion of CH_4 seems to be less dependent on temperature. There is much room for further research especially with respect to the reaction mechanism and chemical kinetics of the fuel reactor. The CO_2 yield for propane operation also reported in Figure 3 indicates that the presence of higher hydrocarbons is not a problem in CLC. Contrarily, the CO_2 yield for C_3H_8 is even higher than for natural gas (CH_4). It must be realized that scaling up the results for the current pilot plant to larger scale conversion level will benefit from increasing reactor height from 3 m to e.g. 12-18 m typical for circulating fluidized beds.

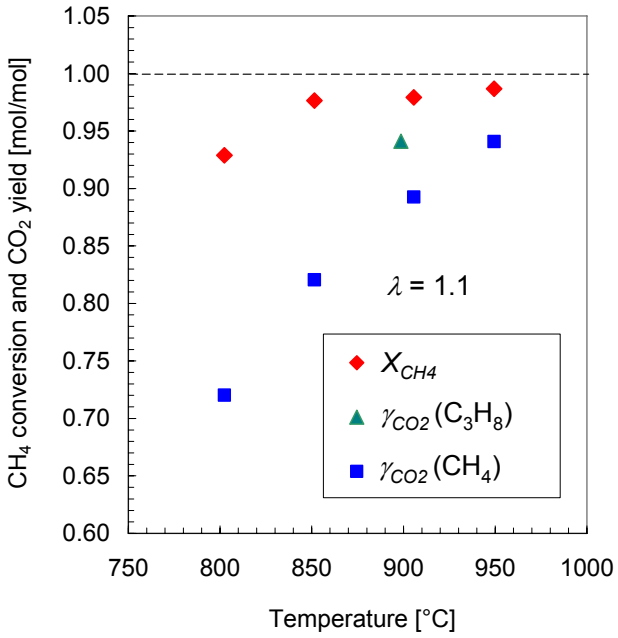

Figure 3. CH_4 conversion and CO_2 yield at the test rig as a function of fuel reactor operating temperature (global air ratio $\lambda = 1.1$, natural gas fuel power 145 kW, C_3H_8 fuel power 127 kW).

Conclusions

A system consisting of two circulating fluidized beds reactors hydraulically coupled by a loop seal in the bottom region of the two reactors is presented and investigated for chemical looping combustion using metal oxides for selective transport of oxygen. The proposed system is seen as scale-up ready candidate for large scale chemical looping application. The main characteristics are:

- high solids circulation rate
- low specific solids inventory
- stable solids distribution because of hydraulic connection between the two reactors
- secondary reactor flow regime can be optimized with respect to gas phase conversion
- global solids circulation can be controlled by staged fluidization of the primary reactor or by controlling the flow resistance in the lower loop seal
- solids hold up can be shifted between the reactors by imposing moderate backpressure from the exhaust gas lines

High solids circulation and low solids hold up result in a relatively narrow particle age distribution in each reactor.

The measured pressure profile indicates for the test rig that the circulating fluidized bed regime in the primary reactor is well developed with particles distributed along the whole height. On the secondary reactor side, however, the particles are concentrated in the bottom region and only a low particle flow is indicated for the secondary reactor's internal loop.

The fuel conversion has been found to be well above 90 % for the NiO-based oxygen carrier. For the investigated system, a temperature dependency of CO_2 yield has been found. A design with higher riser reactors is expected to significantly improve global fuel conversion in the dual circulating fluidized bed system for CLC.

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Notation

Ar	Archimedes number	-
T	Temperature	K
U	superficial gas velocity	$m \cdot s^{-1}$
X_{CH4}	conversion of methane	$mol \cdot mol^{-1}$
y	gas phase mole fraction	$mol \cdot mol^{-1}$
γ_{CO2}	CO_2 yield based on carbon supplied	$mol \cdot mol^{-1}$

Super-/Subscripts

AR	air reactor
FR	fuel reactor
i	reference to gas species
mf	minimum fluidization velocity
t	terminal velocity for single particle

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