NEXT SCALE CHEMICAL LOOPING COMBUSTION: 
FLUIDIZED BED SYSTEM DESIGN FOR DEMONSTRATION UNIT

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Abstract: The chemical looping combustion process of gaseous fuels is a promising carbon capture and storage technology with respect to energy penalty owing to CO₂ separation. After a successful demonstration at pilot scale, the next logical step in process evolution should be the demonstration of the technology at an industrial scale, e.g. with 10 MW fuel power input. The design of such a unit is evaluated based on the dual circulating fluidized bed (DCFB) system, which has been intensively studied in recent years and successfully tested at a 140 kW pilot scale at the Vienna University of Technology. A heat integration setup is included, and respective fluidized bed dimensions are determined. The proposal focuses on the use of commercially used technologies in industrial and large scale circulating fluidized bed boiler units in order to reduce up-scaling related risks.

Keywords: chemical looping, DCFB, reactor, design

INTRODUCTION

The emission of greenhouse gases from combustion processes is considered one of the most significant contributors to the anthropogenic-caused part of the greenhouse gas effect. Mitigation of these is the key midterm strategy; namely the reduction of carbon dioxide emissions. Combustion of either fossil or fossil-derived fuels in industrial or energy production processes plays a major role when it comes to CO₂ emissions. Different approaches are discussed concerning carbon capture and storage (CCS), aimed at separating the CO₂ and transporting it to suitable storage. Chemical looping combustion is a second generation CCS technology and is discussed as a potential breakthrough technology with respect to CO₂ avoidance costs.

In chemical looping, the combustion of the fuel takes place in two separate reaction zones; an air reactor (AR) and a fuel reactor (FR). A schematic drawing of the chemical looping combustion process is shown in Fig. 1. A metallic oxygen carrier is continuously cycled between these reactors, which is used for selective oxygen transfer from combustion air to the fuel. While the oxidation of the oxygen carrier takes place in the air reactor, the oxidized oxygen carrier is reduced within the fuel reactor vessel. Thus the gas leaving the air reactor is simply oxygen depleted air which can be released to the ambient without major concern. The exhaust gas of the fuel reactor ideally only contains CO₂ and water vapour, and a concentrated CO₂ stream is obtained after condensation of the water.

The advantage of chemical looping combustion compared to other CCS technologies is that gas-gas separation is avoided, which typically is the most energy intense process-step in any other CCS technology. This is why CO₂ avoidance costs are considerably lower in CLC in the range of roughly 2/3 than the typical first generation CCS processes such as oxyfuel or amine post combustion flue gas scrubbing.

The potential of chemical looping combustion for gaseous fuels has been successfully demonstrated in the past in numerous laboratory batch and continuous test facilities, at scales of up to 140 kW fuel input power (Hossain and de Lasa et al., 2008). By the middle of 2010, more than 4000h of experience in
continuous CLC operation had already been collected within the scientific community, including at least eleven chemical looping units (Lyngfelt, 2011). A variety of different oxygen carriers have been tested (Lyngfelt et al., 2008) with nickel based ones being the most intensively studied with more than 1500h of continuous chemical looping combustion operation (Linderholm et al., 2009; Kolbitsch et al., 2009).

For this reason, the logical next step in the process evolution is the demonstration of the technology at an industrial scale to gain sufficient confidence in chemical looping for further up-scaling. This will require an integration of the process into a power or heat generation system. Application of such a unit can involve small scale electrical energy production (Marx et al., 2011a) as well as the production of industrial steam in, e.g., the pulp and paper industry or heavy oil extraction from oil sands using SAGD technology (Marx et al., 2011b). In this work, the design of such a next scale chemical looping combustion demonstration plant using natural gas as the fuel is evaluated considering fuel input loads of up to 10 MW. Up-scaling by a similar factor from 100 kW to 8 MW was successfully accomplished in 2002 at the combined heat and power biomass gasification plant located in Güssing, Austria, using dual fluidized bed technology (Hofbauer et al., 2002). Since then, this demonstration plant has been a great success story, with more than 58 000 cumulative operating hours (Hofbauer, 2011; Pfeifer et al., 2011). Experience in CLC operation from a 140 kW pilot unit with natural gas and higher hydrocarbons is considered in the design of the unit which further increases the confidence in the up-scaling process.

THEORETICAL BACKGROUND

Chemical looping combustion system design

Apart from the oxygen carrier material, the reactor system design is a key issue in chemical looping applications. Typically, the reaction intensity, which is in other terms the gas conversion, is dependent on the heterogeneous gas-solids reaction. Improvement of the gas-solid contact time is a key challenge for efficient CLC operation. Fluidized beds are well known for their excellent gas-solid mixing potential and, thus, are expected to be ideal for CLC. Different types of fluidized bed operating conditions are known, and the adoption of the right regime within the reactor system is crucial. Sufficiently high solids circulation from the air reactor to the fuel reactor is needed for oxygen and heat transport. Consequently at least one reactor (e.g., the air reactor) has to be designed in transporting regime which is either fast fluidization or pneumatic conveying in terms of fluidized bed regimes. The required solids circulation rate is mainly determined by the oxygen carrier oxygen transport capacity. Typical solids entrainment rates observed in high velocity turbulent or fast fluidized bed regimes are satisfactory for almost all of the oxygen carriers developed.

Compared to the air reactor, the reaction rate in the fuel reactor is an order of magnitude slower than in the air reactor. Therefore, the gas-solids contact is significantly more important in this reactor. Bubbling fluidized bed fuel reactors suffer from the risk of gas bypass through the bubble phase, which can be minimised by low fluidization numbers and deep beds. Very deep bubbling beds suffer from operational constraints as the bed pressure in the lower bed regions is far different than that in the upper bed, which runs the risk of de-fluidized dead zones at the bottom of the bed or slugging in the upper region in the bed. However, low numbers of fluidization will result in large fuel reactor cross-sectional areas, high solids inventories and large bed pressure drops. Additionally, most of the reactor volume will be lost because no relevant reaction can be expected in the practical particle free freeboard of the bed. Turbulent fluidized bed or fast fluidized bed regimes allow gas-solids contact over the whole height of the reactor and permits operation with lower solids inventories, which is particularly important for increased plant capacity. However, finding the optimum solution between reduced gas residence time at increased gas velocity and less intensive solids distribution over the reactor is a major challenge in the design of a chemical looping reactor unit. In addition to the fluid dynamics, the reactor system has to be simple in operation to avoid the occurrence of uncontrollable conditions.

In summary, the reactor system has to fulfil the following requirements:

- optimal gas-solids contact in both reactor zones,
- high global solids circulation for sufficient oxygen transport,
- low reactor footprint for scale-up, and
- simple operation.

For this reason, the dual circulating fluidized bed (DCFB) reactor concept for chemical looping applications has been developed at the Vienna University of Technology (Kolbitsch et al., 2009; Pröll et al., 2009). It is composed of two interconnected circulating fluidized bed reactors. The design focuses on scale-up related issues such as low solids inventories and low reactor footprint, while maintaining the focus on high gas-solids contact. The principle is shown in Fig. 2. The DCFB concept involves two solids loops; the global and the internal loop. The solids entrained from the air reactor are separated by a cyclone and sent to the upper loop seal. The upper loop seal, fluidized by steam, provides a proper sealing between the reactors to avoid gas leakage. The entrained solids are then transported back to the air reactor by the lower loop seal, closing the global solids loop. The fuel reactor includes an internal solids loop, which is closed by the fuel reactor cyclone, and the internal loop seal. A key feature of the DCFB concept is the lower loop seal. Solids are inherently stabilised by the lower loop seal which acts as a hydraulic link. Solids accumulation in any part of the system is avoided as long as proper fluidization is provided to the loop seal. One feature of the DCFB concept with the lower loop seal is that the two solids loops are largely independent of each other, and as such the fuel reactor can be operated with respect to maximum fuel conversion.

**Figure 2.** Principle setup of the dual circulating fluidized bed reactor system, with the global solids loop indicated by the dotted line and the internal solids loop indicated by the dash-dotted line. AR – air reactor, FR – fuel reactor, LLS – lower loop seal, ULS – upper loop seal, ILS – internal loop seal.

### Heat integration

In chemical looping systems the temperature is limited by the specific properties of the oxygen carrier such as, e.g., material melting point and agglomeration tendency. Typical maximal operating temperatures range from 800 to 1000°C, while the adiabatic combustion temperature is in the range of 1900°C at an air/fuel ratio of 1.1. This energy difference has to be withdrawn from the reactor system, which in addition is dependent on the completeness of the combustion, described by the combustion efficiency $\eta_c$ (Fig. 3). Depending on the selected air/fuel ratio, a great percentage of the total heat release has to be extracted directly from the reactor system. This can be done by direct cooling of the reactor vessels or by cooling the bed material in an external heat exchanger. At typical chemical looping operating conditions (air/fuel ratio=1.1–1.2 and $\eta_c$=90–100%), this means that around ±50% of the heat input has to be extracted from the reactor system itself.

While direct heat extraction from the reactor system is not limited with respect to net plant efficiency, the air/fuel ratio has to be selected considering specific oxygen carrier requirements and to reduce stack losses. In fluidized bed applications, the vessel can be cooled by using evaporative water walls. The heat extraction ratio varies with vessel temperature and solids-wall contact behaviour (Hamdan and Al-qaq et al., 2008), and thus cannot be significantly influenced by the operator. For this reason, stable off-design load operation is difficult to obtain when only water walls are used. Therefore, there is a strong demand for a controllable heat extraction device for off-design load operation. Typically in CFB applications this is obtained by using external fluidized bed heat exchangers, where the flow of solids to the heat exchanger is controlled, e.g., by a solids flow control valve (Basu and Fraser et al., 1991). In order to keep the size of this heat exchanger within reasonable limits, a combination of both equipments
is assumed to be the most effective.

![Graph showing heat extraction efficiency vs air/fuel ratio](image)

Figure 3. Required cooling of the reactor system dependent on the global air/fuel ratio and the combustion efficiency $\eta_c$ based on lower heating values and a fuel reactor temperature of 900°C.

![Diagram of proposed reactor system](image)

Figure 4. Proposed reactor system arrangement based on the dual circulating fluidized bed concept. Locations where fluidization is applied are indicated by arrows. AR - air reactor, FR - fuel reactor, LLS - lower loop seal, ULS - upper loop seal, ILS - internal loop seal, BMC - bed material cooler, WW - water walls, SCV - solids flow control valve.

In general, both reactors can be equipped with water walls. However, in chemical looping the reactions within the air reactor are always strongly exothermal while the fuel reactor reactions can be, depending on the oxygen carrier used, either slightly exothermal or endothermal. For this reason, a setup where only the air reactor is equipped with water walls is chosen.

The proposed reactor system heat exchanger arrangement is shown in Fig. 4. It includes an external fluidized bed heat exchanger, the bed material cooler, and water walls in the air reactor. The bed material cooler is placed in a return loop of the air reactor where only part of the air reactor entrained solids are directed to the bed material cooler controlled by a solids flow control valve.

The advantage of this arrangement is that:

- part load operation is possible,
- only a small fraction of the air reactor solids entrainment has to pass the bed material cooler, thus only a minor loss of global solids circulation is expected,
- the function of the bed material cooler only has a minor effect on the fuel reactor operation,
- the bed material cooler can be fluidized by air, and as a result
- bed material cooler fluidization air takes part in the air reactor oxidation reaction, and thus
- no additional supplementary air is needed for bed material cooler fluidization.

**FLUIDIZED BED REACTOR DESIGN**

**Design parameters and boundary conditions**

The design is based on the dual circulating fluidized bed concept for chemical looping systems. The main
design parameters are shown in Table 1. Air is used in the air reactor as the fluidization agent while the fuel reactor is fluidized by gaseous fuel. To avoid fuel reactor exhaust gas dilution by, e.g., nitrogen, the loop seals are fluidized by superheated steam. Air staging in the air reactor riser is used to control the global solids circulation rate. The air and fuel reactor gas-solids cyclone separators are designed according to Hugi, 1997. With the selected arrangement depending on the global solids circulation rate and the selected air/fuel ratio the solids flow to the bed material cooler is chosen.

<table>
<thead>
<tr>
<th>Item</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>fuel input power (methane)</td>
<td>$P_{\text{fuel}}$</td>
<td>10</td>
<td>MW</td>
</tr>
<tr>
<td>lower heating value of the fuel</td>
<td>LHV</td>
<td>50</td>
<td>MJ/kg</td>
</tr>
<tr>
<td>stoichiometric combustion oxygen demand</td>
<td>$O_{\text{min}}$</td>
<td>4.1</td>
<td>kg/kg</td>
</tr>
<tr>
<td>stoichiometric combustion air demand</td>
<td>$I_{\text{min}}$</td>
<td>17.4</td>
<td>kg/kg</td>
</tr>
<tr>
<td>design air/fuel ratio</td>
<td>$\lambda$</td>
<td>1.1</td>
<td>-</td>
</tr>
<tr>
<td>design fuel reactor temperature</td>
<td>$\theta_{\text{FR}}$</td>
<td>900</td>
<td>°C</td>
</tr>
<tr>
<td>design air reactor temperature</td>
<td>$\theta_{\text{AR}}$</td>
<td>960</td>
<td>°C</td>
</tr>
</tbody>
</table>

| Oxygen carrier                               |        |      |      |
| active material                              |        | Ni/NIO | -    |
| active Ni content                            |        | 40    | wt%  |
| oxygen transport capacity                    | $R_0$  | 0.084 | kg/kg|
| mean particle size                           | $d_p$  | 200   | μm   |
| particle apparent density                    | $p_p$  | 3425  | kg/m³|
| Sphericity                                   | $\psi$ | 0.9   | -    |

**Air reactor**

The air reactor is designed based on two requirements:
- oxidation of the reduced oxygen carrier coming from the fuel reactor, and
- sufficient oxygen carrier entrainment for oxygen transport.

Therefore the air reactor is designed as a fast fluidized bed. The onset of fast fluidization is described as the regime where significant solids entrainment from a lower dense section of the fluidized bed is observed. Bi and Grace, 1995 addressed this limit as the superficial velocity $U_{se}$ which is calculated with the corresponding Reynolds number, $Re_{se}$, as:

$$Re_{se} = 1.53 \cdot Ar^{0.50} \quad (2 < Ar < 4 \cdot 10^6)$$

(1.)

For proper operation the air reactor superficial gas velocity range is:

$$U_{AR} = 7 - 8 \frac{m}{s}$$

(2.)

This value corresponds to approximately 1.2 times $U_{se}$ for the chosen OC. Then an air reactor cross-sectional area of 1.44 m² is needed. If required, the air/fuel ratio can be increased in part load operation to maintain sufficient solids circulation.

**Fuel reactor**

The main design criterion of the fuel reactor is to maximise the gas-solids contact while keeping the solids inventory low. Turbulent fluidized beds are characterised by bubble break-up instead of bubble growth as in bubbling fluidized beds. Small voids and particle clusters dart to and from the indistinct top surface of the bed. Thus, potential gas-slip through the bubble phase is minimised, while gas-solids contact is expected to increase. The onset of the turbulent regime is defined by the critical velocity $U_c$ where the standard deviation of the pressure fluctuation reaches a maximum. It is believed that this point reflects a dynamic balance between bubble coalescence and break-up. The turbulent regime according to Bi and Grace, 1995 is defined by the velocity range $U_c$ to $U_{se}$, with $U_c$ calculated from:

$$Re_{c} = 1.24 \cdot Ar^{0.45} \quad (2 < Ar < 1 \cdot 10^8)$$

(3.)
The fuel reactor design superficial gas velocity is chosen to be in the middle of the turbulent regime. Thus, the fuel reactor superficial gas velocity range is:

$$U_{FR} = 5.25 - 5.75 \frac{m}{s}$$  \hspace{1cm} (4.)

This value corresponds to approximately 4 times $U_c$ and is about 70% of $U_{se}$ under design operating conditions. The required fuel reactor cross-sectional area then is 0.64 m$^2$.

The operating points at nominal load of air and the fuel reactor are shown in the flow regime map suggested by Bi and Grace, 1995 in Fig. 5.

![Flow regime map](image)

**Figure 5.** Fluidization regime of the air and fuel reactor in the flow regime map as suggested by Bi and Grace (Bi and Grace, 1995). The fuel reactor is operated in turbulent mode and the air reactor in fast fluidization regime.

**Loop seals**

The loop seals are non-mechanical devices that allow the flow of solids from the entrance to the outlet. For proper operation, fluidization has to be applied to the loop seal to produce a friction force provoking the motion of the solids. Different types of loop seal are used in CFB applications, with loop seals of L-, and J-types being the most commonly used. A rectangular shaped J-type loop seal is applied to the design of the upper and internal loop seal, while a modified V-shaped version of a J-type loop seal is used in the lower loop seal section. The pressure balance and typical vertical and horizontal solids velocities are considered with the minimum free cross-section, and are determined by an average solids flux of

$$G_s = 300 \frac{kg}{m^2 s}$$  \hspace{1cm} (5.)

Such, and even higher, values have been measured in the 140 kW pilot and are in the range proposed by Basu and Fraser et al., 1991.

**Bed material cooler**

The bed material cooler is an external fluidized bed containing heat transfer surfaces. Typically low velocity bubbling fluidized beds are used where the heat transfer coefficients are very high. This device can therefore be relatively compact with respect to the heat transfer rate. Compared to heat exchanger surfaces placed in the CFB riser, the heat transfer rate in the bed material cooler can be controlled easily.
This helps meet the varying fuel load conditions and thus increases the load control capability of the unit. The heat transfer rate can basically be influenced by the fluidization conditions and by the solids flow to the bed material cooler chamber, which is obtained by a mechanical solids flow control valve between the upper loop seal and the inlet to the bed material cooler.

Summary of results

Bulk dimensions and important design parameters of the 10 MW next larger scale chemical looping combustion plant are summarised in Table 2. Expectable solids fluxes are determined according to Kolbitsch et al., 2009 and from experiments at the 140 kW chemical looping pilot at the Vienna University of Technology, and also from experience at the 8 MW dual fluidized bed biomass gasification plant in Güssing, Austria.

<table>
<thead>
<tr>
<th>Item</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>total air flow rate</td>
<td>13820</td>
<td>kg/h</td>
</tr>
<tr>
<td>total fuel flow rate</td>
<td>720</td>
<td>kg/h</td>
</tr>
<tr>
<td>superficial gas velocity in the air reactor</td>
<td>7-8</td>
<td>m/s</td>
</tr>
<tr>
<td>superficial gas velocity in the fuel reactor</td>
<td>5.25-5.75</td>
<td>m/s</td>
</tr>
<tr>
<td>air reactor cross-section area</td>
<td>1.44</td>
<td>m²</td>
</tr>
<tr>
<td>fuel reactor cross-section area</td>
<td>0.64</td>
<td>m²</td>
</tr>
<tr>
<td>upper loop seal downcomer cross-section area</td>
<td>0.28</td>
<td>m²</td>
</tr>
<tr>
<td>internal loop seal downcomer cross-section area</td>
<td>0.07</td>
<td>m²</td>
</tr>
<tr>
<td>lower loop seal downcomer cross-section area</td>
<td>0.33</td>
<td>m²</td>
</tr>
<tr>
<td>air and fuel reactor riser height</td>
<td>15</td>
<td>m</td>
</tr>
<tr>
<td>air reactor solids flux</td>
<td>70</td>
<td>kg/m²s</td>
</tr>
<tr>
<td>fuel reactor solids flux</td>
<td>25</td>
<td>kg/m²s</td>
</tr>
<tr>
<td>upper loop seal solids flux</td>
<td>350</td>
<td>kg/m²s</td>
</tr>
<tr>
<td>internal loop seal solids flux</td>
<td>90</td>
<td>kg/m²s</td>
</tr>
<tr>
<td>lower loop seal solids flux</td>
<td>325</td>
<td>kg/m²s</td>
</tr>
</tbody>
</table>

CONCLUSION

The dual circulating fluidized bed reactor system concept has been applied to the design of a 10 MW_{th} next scale chemical looping combustion plant using gaseous fuels. A heat exchanger arrangement focusing on high flexibility in operation is proposed. The setup includes a combination of water walls in the air reactor riser and an external fluidized heat exchanger, the bed material cooler, in the air reactor return loop. This allows:

- part load operation,
- only a small fraction of the air reactor solids entrainment has to pass the bed material cooler, thus only a minor loss of global solids circulation is expected,
- the function of the bed material cooler only has a minor effect on the fuel reactor operation,
- the bed material cooler can be fluidized by air, and as a result,
- bed material cooler fluidization air takes part in the air reactor oxidation reaction, and thus,
- no additional supplementary air is needed for bed material cooler fluidization.

Bulk dimensions of the fluidized beds are determined considering a fast fluidized bed air reactor and a high velocity turbulent bed fuel reactor. Further steps will include the erection of a cold flow model considering scaling laws to confirm the fluidized bed concept.

ACKNOWLEDGEMENT

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NOTATION

Symbols

$\alpha_r$ archimedes number
$d_p$ mean particle size $\mu$m
$G_s$ solids flux $\text{kg/m}^2\cdot\text{s}$
$LHV$ lower heating value of the fuel MJ/kg
$I_{\text{min}}$ stoichiometric combustion air demand kg/kg
$O_{\text{min}}$ stoichiometric combustion oxygen demand kg/kg
$P_{\text{fuel}}$ fuel input power MW
$Re$ reynolds number -
$r_{o}$ oxygen transport capacity kg/kg
$U_i$ superficial gas velocity m/s

Greek letters

$\eta_c$ combustion efficiency %
$\theta_{\text{AR}}$ air reactor temperature $^\circ\text{C}$
$
\theta_{\text{FR}}$ fuel reactor temperature $^\circ\text{C}$
$\lambda$ air/fuel ratio -
$\rho_p$ particle apparent density $\text{kg/m}^3$
$\psi$ sphericity -

Abbreviations

AR air reactor
BMC bed material cooler
CCS carbon capture and storage
CFB circulating fluidized bed
DCFB dual circulating fluidized bed
FR fuel reactor
ILS internal loop seal
LLS lower loop seal
MeO metal oxide
SCV solids flow control valve
ULS upper loop seal
WW water walls

REFERENCES