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# CHALLENGES WITH THE COUPLING OF FLUIDIZED BEDS FOR CHEMICAL LOOPING COMBUSTION

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# CHALLENGES WITH THE COUPLING OF FLUIDIZED BEDS FOR CHEMICAL LOOPING COMBUSTION

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## ABSTRACT

In the present work the system of interconnected fluidized bed reactors of a Chemical Looping Combustion (CLC) process is simulated in pilot plant scale and 100 $MW_{th}$ scale. Attrition models, derived from small scale laboratory experiments, are employed to predict the behavior of a large scale CLC process in terms of attrition and oxygen carrier (OC) losses. Realistic circulation mass flows of OC are calculated and the sources of the losses are further investigated. Different arrangements of cyclones are evaluated for their potential to improve the solids recovery. For example the introduction of a second-stage cyclone separation for the air reactor reduces the OC losses significantly.

## INTRODUCTION

Chemical Looping Combustion is an interesting variant for the inherent separation of anthropogenic carbon dioxide inside a power generation process that has recently attracted much attention by numerous research groups. The process consists of two interconnected fluidized bed reactors. In between these two reactors are solids circulated which transport chemically bound oxygen taken up from the air inside the air reactor to the so called fuel reactor. The oxygen carrier particles provide the fossil fuel (i.e. natural gas or coal) with oxygen and will themselves be reduced. Reduced oxygen carrier particles are then cycled back towards the air reactor for re-oxidation. CLC has the advantage that the carbon dioxide of the off-gas will not be diluted by nitrogen. After condensation of water, almost pure carbon dioxide can be derived and transported to its designated storage location.

Like other processes, the feasibility of this process is dependent on the process costs, which will be greatly influenced by the oxygen carriers involved. Thus it is of great importance to reduce the loss of oxygen carrier particles. This means, the particles have to be attrition resistant and the losses through the gas-solids separation devices like cyclones have to be minimized. Oxygen carriers can both be of natural origin (ores etc.) or synthetically manufactured. Synthetic OC particles are usually composed of an inert porous carrier material and a reactive metal oxide.

Their use can be advantageous in respect of both the attrition and reaction rate due to the increased mechanical stability and the increased porosity.

The aim of this investigation is to study the process from the particle technology point of view. Simulations have been carried out to study the circulation mass flow between the interconnected fluidized bed reactors as well as the respective particle size distributions and OC losses through the gas-solids separation devices. The influence of attrition of the OC particles on the process performance is investigated and possible improvements of the solids recovery are studied. Simulations have been carried out in two scales: pilot scale and an upscale to a 100 $MW_{th}$ Chemical Looping Combustion process.

## THEORY

### Process Designs

Chemical looping combustion was studied in different types of unit configurations (1-3) but systems of interconnected fluidized beds dominate the literature due to the implied good gas / solids contact. In 2001 Lyngfelt et al. (3) made a first sketch of a process similar to the one shown in Figure 1. The air reactor is realized as a circulating fluidized bed (CFB) whereas the fuel reactor is a bubbling fluidized bed (BFB). The setup sketched in Figure 1 is chosen as the reference setup of the simulations.

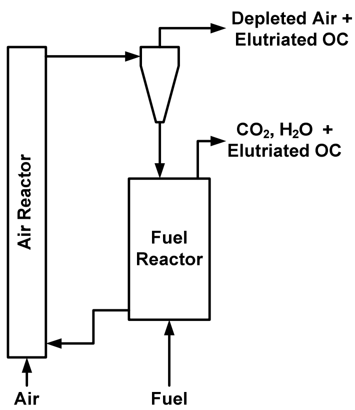


**Figure 1: Initial simulated CLC process setup, according to Lyngfelt et al. (3)**

### Fluid Dynamics in the Fluidized Bed Reactors

The fluidized bed reactors are for the calculations divided into two zones, the bottom zone and the upper dilute zone. The bottom zone is described by a semi-empirical approach, dividing the bottom zone into two phases, the suspension phase and the bubble phase which is assumed to be solids free. The fluid dynamics of the bottom zone are calculated according to the Werther & Wein model (4). The initial bubble size is calculated by the equation proposed by Davidson & Schüler (5). As soon as the boundary of the bed is reached the upper dilute zone begins. This is accompanied with a change in the description. The upper dilute zone is treated as a single phase, where the solids are suspended in the gas flow. To calculate the elutriation from the reactors above the transport disengaging height (TDH), an elutriation constant approach is used. Out of numerous correlations two are chosen for the simulations. The correlation of Colakyan & Levenspiel (6) was validated at superficial gas velocities in the range of 0.9 – 3.7 m/s for particles of the size range 300 - 1000 µm. The second correlation from Tasirin & Geldart (7) was validated at superficial gas velocities in the range of 0.2 - 0.8 m/s for particles of the size range 68 - 124 µm. Assuming a relative velocity of the particles equal to the difference of the superficial gas velocity and the terminal velocity of the particles (8), the solids volume concentration $c_v$ above transport disengaging height (TDH) can be calculated. Between the $c_v$ above TDH and the $c_v$ at the top of the bed, an exponential decay of the solids volume concentration is assumed and calculated according to Kunii & Levenspiel (9).

In case a CFB is to be described, the models stated above are extrapolated to the present gas velocities and the bottom zone is described as a bubbling fluidized bed at high gas velocities.

### Reactions in the Fluidized Beds

Inside the fluidized bed reactors, the heterogeneous reaction between the oxygen carrier particles and the respective gases have to be accounted for. Several investigations (e.g. (10-13) ) have shown a good agreement between shrinking core models (SCM) (9) and measurements of OC conversion by various gaseous reactants.

$$\frac{t}{\tau} = 1-(1-X_s)^{1/3}, \quad \tau = \frac{\rho_m \cdot r}{b \cdot k \cdot C^n} \tag{1}$$

The SCM can both be applied to a description of the entire particle as well as a description of reactive grains on an inert structure. In case a grain description is favored the grain radius is a fitting parameter. In the bottom zone, the reaction is assumed to exclusively take place in the suspension phase. The bubble phase is regarded as solids-free. In dependency of the gaseous reactant, the reactions inside a reactor can lead to changes in the volume flow. The model assumes the excess gas to rise entirely in the bubble phase. In chemical looping combustion the reactions can significantly influence the fluid dynamics of the fluidized beds. For instance full conversion of methane will increase the volume flow by 200 % while the stoichiometric full oxidation of the OC-particles will result in a volume flow decrease of 21 %. Due to the change of volume flow the convective transport of gas between the suspension and bubble phase and the dilution of reactant gases by product gases can not be neglected. In this model the change in volume flow is accounted for according to the approach suggested by Sitzmann et al. (14). Diffusive transport between the suspension and bubble phase is calculated from the correlation of Sit & Grace (15).

### Population Balance Modeling

The focus of this investigation is to simulate the flows as well as the particle size distributions inside this system of interconnected fluidized bed reactors. It is assumed that particles do not break and the dominating attrition mechanism is abrasion, which is a reasonable assumption for catalyst attrition under normal conditions (16). The simulation of the population balances relies on the approach suggested by Werther & Hartge (8). Employing this approach the fate of particles of different size classes is individually followed. Mother particles undergoing abrasion will slightly shrink in size while the produced fines are assumed to be small in size and added to the first size interval. Three sources of attrition are regarded. First, attrition can be caused by the solids movement induced by the bubbles in a fluidized bed. Secondly, the attrition due to gas jets is regarded and the third considered attrition source is the solids recovery in the cyclones. The mass of produced fines inside a bubbling fluidized bed reactor is calculated by the equations given by Merrick & Highley (17) and Reppenhagen & Werther (18). The attrition occurring in the cyclone is calculated according to Reppenhagen & Werther (18). For the attrition calculation one material specific constant for each attrition mechanism is needed ($C_b$, $C_j$, $C_c$). These constants have to be calculated from experimental results.

## Simulation

For the investigation of the CLC process, the flow sheet simulation environment SolidSim (19) has been selected. SolidSim is a commercial software package for the simulation of solids processes and was originally developed at the Institute of Solids Process Engineering and Particle Technology of the Hamburg University of Technology (20). SolidSim employs a sequential modular approach for the simulation of the steady-state behavior of solids processes. Unit operations are calculated in series and loops are solved by fixed-point iteration of the loop unit operations.

## Results and discussion

## Definition of the Test Case

For the simulations the copper based OC Cu10Al-I was selected because of the rich information available in references (21) and (22). Of the fresh feed particles the cumulative distribution is 0.3 % < 45 µm, 1.4 % < 90 µm, 31.4 % < 125 µm, 91.1 % < 180 µm and 100 % < 212 µm. The simulation input parameters are shown in Table 1. The chosen pressure drops equal solid inventories of 47,800 kg OC for the large scale and 17.1 kg for the pilot scale, respectively. The considered reactions are:

$$O_2 + 2Cu \rightarrow 2CuO \tag{2}$$

$$CH_4 + 4CuO \rightarrow 4Cu + CO_2 + 2H_2O \tag{3}$$

According to equation 2 and 3 the stoichiometric coefficient b is 2 for the oxidation and 4 for the reduction of the OC. Information on reaction kinetics was taken from literature (21, 22).

| Parameter | Pilot Scale | 100 $MW_{th}$ scale |
|---|---|---|
| height fuel reactor: | 2 m | 12 m |
| height air reactor: | 10 m | 17 m |
| diameter fuel reactor: | 0.3 m | 10 m |
| diameter air reactor | 0.1 m | 4.2 m |
| $\Delta$p air reactor: | 7000 Pa | 7000 Pa |
| $\Delta$p fuel reactor | 2700 Pa | 2700 Pa |
| $\Delta$p air reactor cyclone | 1200 Pa | 1200 Pa |
| $\Delta$p fuel reactor cyclone (if applicable) | 900 Pa | 900 Pa |
| gas inlet velocity of cyclones | approx. 20 m/s | approx. 20 m/s |
| $CH_4$ feed | 0.0009 kg/s | 1.993 kg/s |
| air feed | 0.0165 kg/s | 36 kg/s |
| gas distributors | porous plate | bubble cap |
| fuel reactor temperature | 850°C | 850°C |
| air reactor temperature | 900°C | 900°C |
| inlet gas pressure | 101325 Pa | 101325 Pa |
| $C_b$ | $3.5 \times 10^{-8}$ 1/m | $3.5 \times 10^{-8}$ 1/m |
| $C_c$ | $4.5 \times 10^{-3}$ $s^2/m^3$ | $4.5 \times 10^{-3}$ $s^2/m^3$ |
| $C_j$ | not applicable | $2.2 \times 10^{-5}$ $s^2/m^3$ |

**Table 1: Simulation input parameters of the test case**

## Simulation results

According to the simulation the 100 $MW_{th}$ scale process reaches at steady-state a circulation mass flow of OC of 627 kg/s while a circulation flow of 0.386 kg/s for the pilot scale is reached. These values lead to specific circulation rates based on the empty cross-section of the air-reactor ($G_s$) of 45.8 kg/m² for the air reactor of the large scale process and 49.6 kg/m²s for the pilot scale. These values are significantly higher compared to regular CFB combustors for coal which are usually expected to operate at roughly 15 kg/m²s (23). Higher $G_s$ values exceeding 100 kg/m²s are known from the operation of Fluid Catalytic Cracking processes which involve fine catalysts (23). Considering these values, the simulated circulation flow rates appear reasonable. The methane conversion reaches 99.4 % in the small scale but only 84.7 % for the large scale. In order to increase the gas conversion of the large scale fuel reactor the hold-up was increased to a pressure drop of 10000 Pa and the gas velocity was decreased from 0.37 m/s to 0.25 m/s. The redesigned fuel reactor has a diameter of 13 m and reaches a gas conversion of 93.1 %. This value is still too low for a technical process and therefore the design of the fuel reactor has to be further optimized by decreasing the bubble sizes which seem to transport too much fuel gas, by-passing the OC. These and other measures to cope with scale-up issues of fluidized bed reactors have for instance been discussed by Werther (24). Nonetheless this improved reactor was employed for all further investigations. The oxygen conversion in the air reactor reaches 82.5 % for the small scale and 78.6 % for the large scale which equals oxygen mole fractions of 5.1 % and 6.2 % in the oxygen depleted off-gas.

## The role of attrition

Simulations have been carried out both with and without regard of particle attrition. Attrition leads to fine particle generation while the mother particles slightly shrink in size. It is difficult to retain the produced fine particles in the system hence the mass loss of OC is increased. The losses have to be made up by a feed of fresh particles which directly influences the operating costs. In Figure 2 the simulation results are shown in terms of OC mass loss related to the amount of thermal energy released. It is observed, that attrition will in fact increase the OC mass losses but also that the pilot scale plant has much lower OC losses compared to the large scale plant. This is mainly due to the lower separation efficiency of large scale cyclones. The separation efficiency of the pilot plant air reactor cyclone reaches almost 100 % while the large scale cyclone reaches 99.976 % with attrition being regarded. For the large scale process without attrition 94 % of the OC losses originate from the overflow of the air reactor cyclone (80 % with attrition regarded). On the other hand for the pilot scale the losses are almost completely originating from elutriation from the fuel reactor.

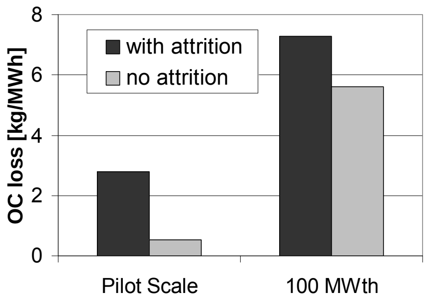


**Figure 2: Influence of attrition on OC mass loss**

### Variation of the solids recovery

The simulation permits now to investigate how the OC loss in the large scale plant can be reduced. The following changes were investigated:

- Introduction of a second-stage air reactor cyclone
- Additional fuel reactor cyclone with a return leg to the fuel reactor entry
- Changes 1 + 2 combined

Figure 3 shows the effect of these changes on the OC loss per MWh of released thermal energy. Improved solids recovery at the air reactor gas exit significantly reduces the OC losses of a large scale CLC process while improvements in the fuel reactor solids recovery do not exert a great influence. Finally the particle size distribution of the circulating OC flow in dependency of the attrition and the different cyclone configurations are investigated. As Figure 4 shows the particle size distribution of the circulating OC flow of the 100 $MW_{th}$ scale preserves its general shape and is shifted towards larger or smaller particles when the effect of attrition is considered and when the solids recovery rate is increased.

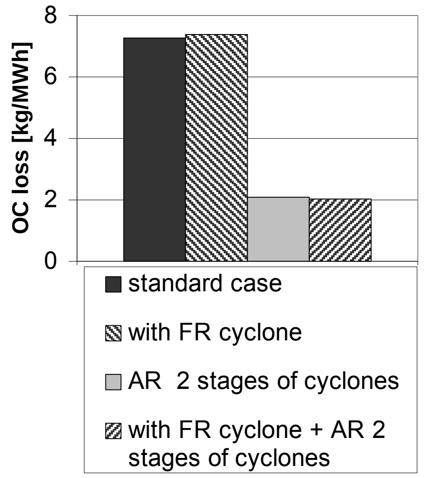


**Figure 4: Influences of variations in the solids recovery system on the OC mass loss related to the produced thermal energy**

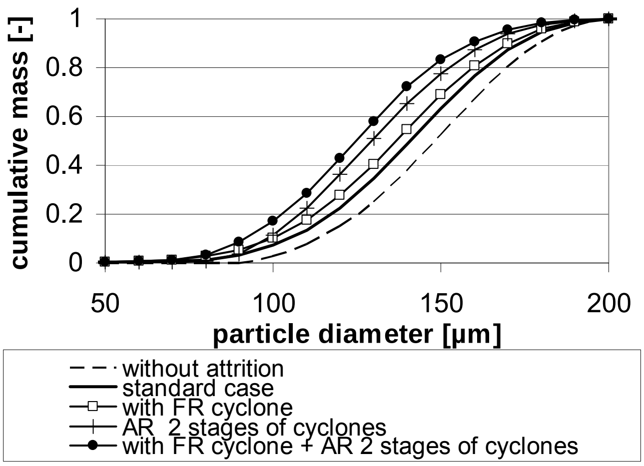


**Figure 3: Cumulative mass distributions for the 100 $MW_{th}$ scale and different simulations**

### CONCLUSION

In the present work a system of interconnected fluidized bed reactors was simulated in two different scales. Based on laboratory attrition investigations the behavior of a large scale Chemical Looping Combustion process was predicted. Realistic circulation mass flows of oxygen carrier particles were obtained. With the help of these simulations the individual sources of OC losses can be evaluated. Possibilities to decrease the OC losses have been investigated. For example the introduction of a second-stage cyclone separation for the air reactor reduces the OC losses significantly.

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## NOTATION

| | | | |
|---|---|---|---|
| b | stoichiometric factor [-] | k | chemical reaction rate constant [$mol^{1-n}$ $m^{3n-2}$ $s^{-1}$] |
| $C$ | local reactant concentration [mol/m³] | n | reaction order [-] |
| $C_b$ | constant for bubble induced attrition [1/m] | r | radius of the spherical grains (or particle radius) [m] |
| $C_c$ | constant for cyclone induced attrition [s²/m³] | $\tau$ | time necessary for full particle conversion[s] |
| $C_j$ | constant for gas jet induced attrition [s²/m³] | $\rho_m$ | molar density of the solid reactant [mol/m³] |

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