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Solid fuels in Chemical-Looping Combustion

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Feeding of fuel and distribution of volatiles

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Abstract

Conventional CO_2 capture processes have large costs and energy penalties associated with gas separation. Chemical-looping combustion (CLC) uses interconnected fluidized beds and a metal oxide to transfer oxygen from air to fuel. Thus, fuel is oxidized without mixing fuel and air and the combustion products, CO_2 and H_2O, are recovered in a separate flow. After H_2O condensation essentially pure CO_2 is obtained, thus avoiding the high costs and penalties of an active gas separation.

CLC of solid fuels has important similarities to well-established combustion in circulating fluidized bed (CFB), and a comparison indicates an added cost of 16-26 €/tonne CO_2. The major cost besides CO_2 compression is oxygen-polishing of the gas from the fuel reactor, indicating that high gas conversion is beneficial.

Today, >2000 h of solid-fuel CLC operation in smaller pilots have been accomplished worldwide. The experiences show that the concept works in practice and that high gas conversion is reached with low-volatile fuels, typically 95%. However, fuels with more volatiles show lower conversion, highlighting the need to feed the fuel in way that provides good contact between volatiles and bed material, i.e. the metal oxide oxygen-carrier.

For a larger size CLC the fuel should be fed in a way that make the volatiles enter the bed in the lower part and well distributed over the horizontal cross-section. Here, a system for distribution of volatiles is presented. It is based on a fundamental principle of fluidization, that a box immersed in a fluidized bed with the opening downward becomes empty. Moreover, if such a box has holes in its sides the bed level inside the box will rise but not above the holes and gas added will exit through these holes. Such a box in the form of a system of arms is proposed to distribute volatiles over the cross-section.

The paper discusses principles and possible design of such a volatiles distributor and how it can be implemented in a large-scale CLC.

Keywords: Chemical-Looping Combustion, solid fuels, fluidized bed, distributor of volatiles

1. Introduction

Chemical-looping combustion (CLC) has emerged as an attractive option for carbon dioxide capture because CO_2 is inherently separated from the other flue gas components, i.e. N_2 and unused O_2, and thus no energy is expended for the gas separation and no gas separation equipment is needed. The CLC system is composed of two interconnected fluidized bed reactors, an air and a fuel reactor. Oxygen carriers in the form of metal oxide particles are used to transfer oxygen transfer between the two reactors. The general principle is shown in Figure 1 and an example of how the process could be designed using the circulating fluidized bed principle for the transfer of particles between the two reactors is shown in Figure 2.

CLC research and development initially had a focus on gaseous fuels, but in the last years important work has been dedicated to adapting the process to solid fuels. Technology overviews are given in a number of reviews, e.g. [1-5].

Chemical-looping combustion of solid fuels could use the general circulating fluidized bed (CFB) concept outlined in Figure 2, but the fuel reactor system needs to be adapted for use of solid fuels.

In the case of gaseous fuels, these are introduced through the bottom plate as fluidizing gas, thus achieving a good distribution over the cross-section. As the gas moves upwards through the bed it is gradually converted and if conditions are suitable the gases are fully oxidized to CO_2 and H_2O as they leave the reactor, as has been shown in pilot testing with gaseous fuels like natural gas [6].

When heated, solid fuels release gaseous combustible compounds (volatiles) that may react with the oxygen carrier to form CO_2 and H_2O. After the volatiles release there is a remaining char that also need to be burnt. The reaction between the oxygen-carrier and the char remaining after volatiles release is not direct, but involves an intermediate gasification step, i.e. $C + H_2O \Rightarrow CO + H_2$, Figure 3.

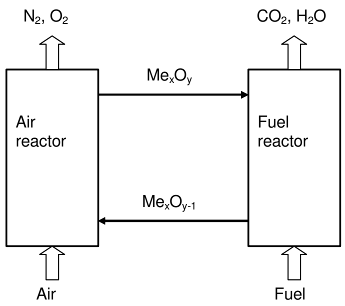

Figure 1. CLC principle. Me_xO_y is the metal oxide circulated.

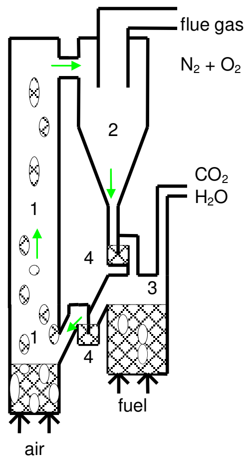

Figure 2. CFB reactor system for gas, 1) air reactor, 2) cyclone, 3) fuel reactor 4) loop seals

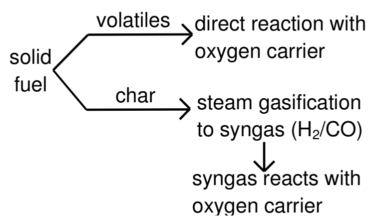

Figure 3. Solid fuel reactions in CLC

Pilot testing with CLC and solid fuels [7, 8], shows high conversion, up to 95%, of the syngas generated when the char is gasified, whereas the conversion of volatiles is considerably lower. Further, pilot testing has also shown that moving the location of fuel introduction from above the bed to a position well below the bed surface, results in a dramatic improvement of gas conversion [9]. This is expected, since fuel feeding above the bed means that most of the volatiles are released above the bed and will have little opportunity to react with the oxygen carrier. The present paper is concerned with options for improving the conversion of volatiles, and more specifically the possibilities to achieve a good distribution of the volatiles in the dense bottom bed of a fuel reactor.

2. Similarity to Circulating Fluidized Bed Combustion

The CLC process has important similarities to normal combustion of solid fuels in circulating fluidized bed (CFB) boilers. Thus, CFB combustion is an integral part of the state of art for CLC. A comparison of technology and costs between a 1000 MW_{th} CFB boiler and a 1000 MW_{th} CLC boiler has been made, [10]. The two boilers are outlined in Figure 4. Important differences and similarities are:

- The horizontal cross-section area is similar, because similar fluidization velocities are used.
- In the case of CLC the combustion chamber is divided in three parts, with one adiabatic fuel reactor in the middle surrounded by two air reactors.
- The same number of cyclones are used but the flows from all the cyclones are led to the fuel reactor. The flows from the four air reactor cyclones are fed into the fuel reactor above the bottom bed, whereas the internally circulating flows of the two fuel reactor cyclones enter in the bottom bed. The latter is motivated to feed recycled char into the bottom bed.
- A duct below the reactors returns the circulated materials from the fuel reactor to the air reactors.
- The fuel reactor has similar height as the FBC boiler in order to maximize char conversion.
- The air reactors are shortened because air reactor height has no benefits as there are no homogeneous gas phase reactions that should be brought to completion. Furthermore a lower air reactor riser has the advantage of giving increased solids circulation.
- The adiabatic fuel reactor will give added costs for insulated walls that are not used for steam generation. On the other hand, the heat transfer in the air reactor is almost doubled because of higher temperature in the air reactor, leading to a significant reduction in heat transfer area.
- Not shown in the figure is the post-oxidation chambers where final oxidation of the gas from the fuel reactor takes place. Oxygen can be added in the cyclone outlets and the ducts leading from the cyclones may serve the purpose of post-oxidation chambers.
- The fuel reactor will have a high bottom bed height in order to achieve both good gas conversion and long residence time of the char particles to be gasified. Lower bed height is needed in the air reactor, but the bed levels will be approximately similar because of the connecting duct. Therefore, the floor of the air reactor is raised as compared to the fuel reactor to avoid unnecessary pressure drop in the air reactor.

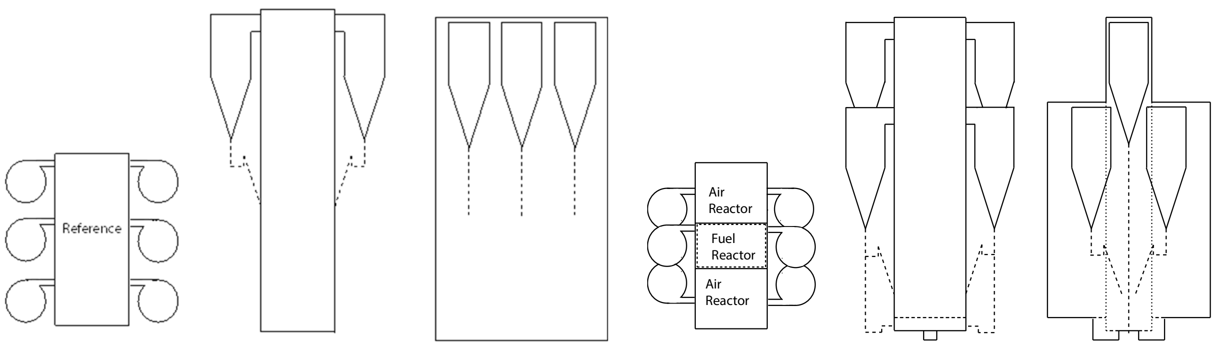

Figure 4. Left: layout of 1000 MWth FBC boiler, Right: Layout of 1000 MWth CLC boiler. From [10].

An analysis of the added costs of the CLC boiler as compared to the CFB boiler, shows that the major added costs are not associated with the boiler, Table 1. The largest cost is CO_2 compression, which is inevitable and common to all CO_2 capture technologies. The second largest cost is air separation for production of oxygen, assuming a gas conversion of 85-95% means that the need for oxygen is in the range 5-15% of that of oxyfuel CO_2 capture. Other added costs are related to oxygen carrier, insulation of fuel reactor, steam fluidization of fuel reactor and coal grinding. The total cost of CO_2 capture is estimated to be 20 €/tonne CO_2 avoided and within the range of 16-26 €/tonne, depending on for instance the gas conversion attained in the fuel reactor and the life of the oxygen-carrier material.

The cost analysis is based on tangible differences between CLC and CFB technologies, which makes the analysis transparent. Should new and better information become available the analysis can be easily updated, consequently providing a platform for further techno-economic analysis of this process.

Table 1. Estimated added costs for CFB-CLC. From [10]

Type of cost	Cost estimate €/tonne CO_2	Cost range €/tonne CO_2	Efficiency penalty, %
CO_2 compression	10	10	3
Oxy-polishing	6.5	4-9	0.5
Boiler cost	1	0.2-2.2	-
Oxygen carrier	2	1.3-4	-
Fuel reactor fluidization	0.8	0.8	0.8
Coal grinding	0.2	0.2	0.1
Lower air ratio	-0.5	-0.5	-0.5
Total	20	16-25.7	3.9

1.1. Fuel size

There are two important differences between normal fluidized bed combustion and chemical-looping combustion. Firstly, the fuel particles need to be small enough in order to be gasified before they reach the air reactor through the normal circulation of particles between the reactors. Secondly, the solid fuel needs to be introduced in the bottom part of the fluidized bed of the fuel reactor to make the reaction of volatile gases with the oxygen carrier possible. The small size of the particles means that they will release volatiles rapidly when introduced in the bed, typically within 1 s. This is also advantageous as it facilitates achieving a release of the volatiles in the bottom of the bed.

3. Fuel feeding and volatiles distribution

Existing pilots for this technology [5, 11-21] use somewhat different approaches to feeding the solid fuels, but they all have in common that the solid fuel is inserted in one point. By different approaches are meant coal screws, pneumatic feeding, and introduction by adding fuel in the particle flow coming from a loop seal. However, all of these units have small cross-sectional areas, with fuel reactor cross-sections less than 0.12 m^2. If this technology is to be built in large scale, the cross-section of the fuel reactor bed would be much larger, e.g. 77 m^2 in the above 1000 MW_{th} design. The consequence of feeding fuel into such a large cross section via one or a few feeding points, considering the rapid devolatilization of the fuel, is that a local plume of volatiles will form at the point of feeding, as illustrated by Figure 5. This plume can be expected to pass through the bed with insufficient contact with the oxygen carrier, thus giving poor conversion of the volatile gas to CO_2 and H_2O.

In order to have a good distribution over the cross-section, the fuel entry points should preferably be close to each other, giving a large number of these. However, it would have significant disadvantages to construct a fluidized-bed with the large number of fuel feeding points needed to properly distribute the volatiles over the cross section, one important being the high cost of fuel feed entries.

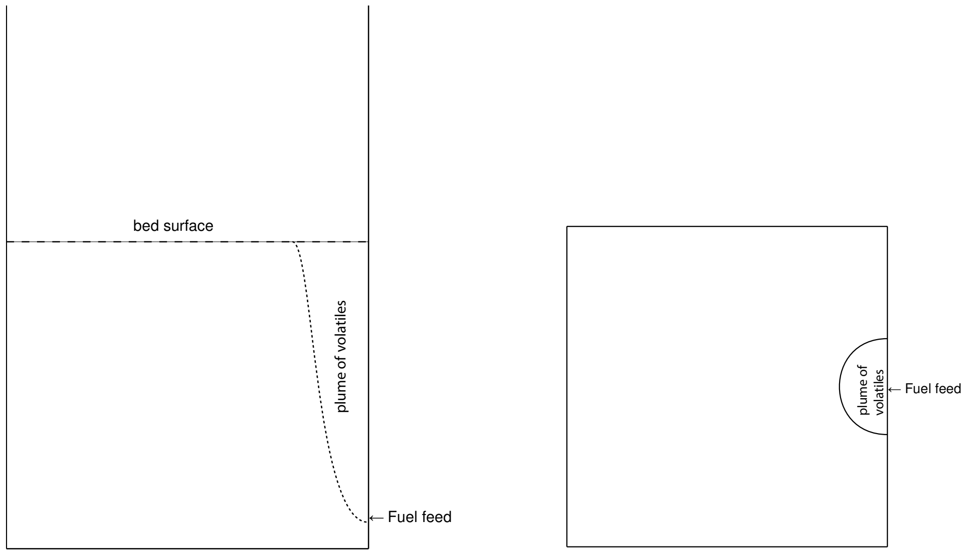

Figure 5. Volatile plume from a fuel feed point.

4. The volatiles distributor

Fluidized beds have properties that resemble liquids and the bed levels of two interconnected beds will be similar if the pressure is the same, but if the pressures above the beds are different the bed levels will adjust. Furthermore, if a box with the opening downwards is immersed in a fluidized bed the pressure inside the box will equal that of the bed at the lower edge. Thus, the bed level inside the box adjusts to the lower edges of the box, Figure 6, meaning that the box becomes empty. If a gas flow is taken out from the box, lowering the pressure inside the bed level will adjust and rise to the level determined by the pressure. A film showing this can be found at [22].

Moreover, if gas is inserted in the box it will leave the box below the lower edge of the box as illustrated by Figure 7. Thus, if the box is elongated to form a long arm it can be used to distribute gas in the surrounding bed. In order to accomplish the distribution of gas over a large cross-section, such a box, or system of boxes, would need to be organized with many arms.

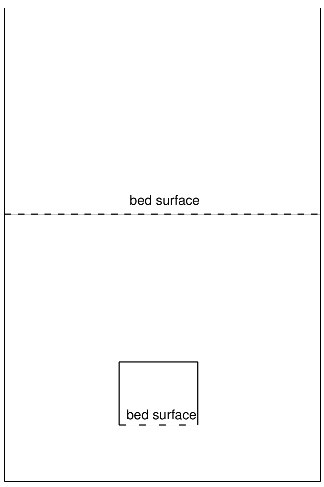

Figure 6. Box with downward opening in fluidized bed

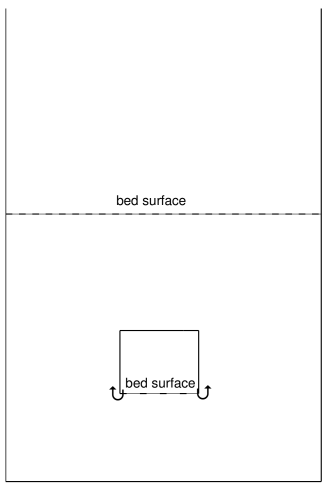

Figure 7. Box with gas added

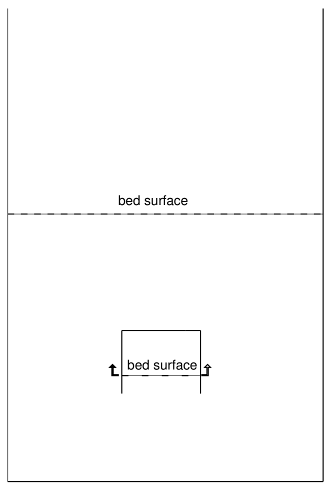

Figure 8. Box with holes on the sides

However, it can be expected that it would be difficult to achieve a uniform distribution of gas if it is distributed along the lower edge, as pressure fluctuations in the surrounding bed can be expected to lead to local discharges of gas, contributing to local formation of large bubbles.

Therefore, if such a box would be used for the distribution of gas in a bed it would be beneficial to fit the distributor with holes on the sides through which gas can be released in the surrounding bed. Such holes would lower the pressure inside the distributor causing the bed level to rise inside the distributor, as illustrated in Figure 8.

The holes may be circular or elongated, and may not necessarily all be on the same height, as illustrated by Figure 9.

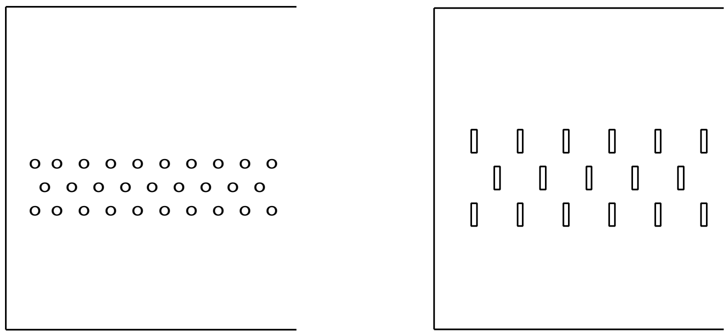

Figure 9. Examples of holes or slits in side of box

If fuel in the form of fine particles is fed into such a box, it will rapidly devolatilize and the volatiles will be released into the gas volume of the box, Figure 10. Thus, such a box can be used to distribute volatiles from a solid fuel. The box can be connected to an incoming flow of solids coming from a cyclone downcomer and the fuel can be added to this flow, Figure 11. This has the advantage of promoting the transport of the remaining char into the fluidized bed. Furthermore, it is not necessary that the fuel is fed directly into the distributor, as long as the volatiles released are transferred into the distributor, as illustrated by Figure 12.

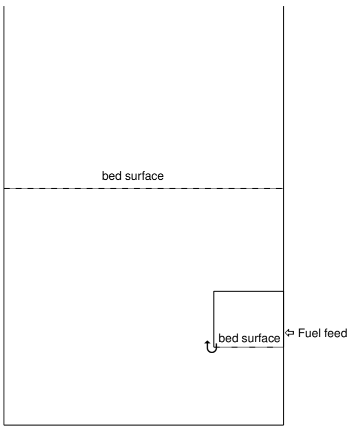

Figure 10. Fuel addition directly in a box

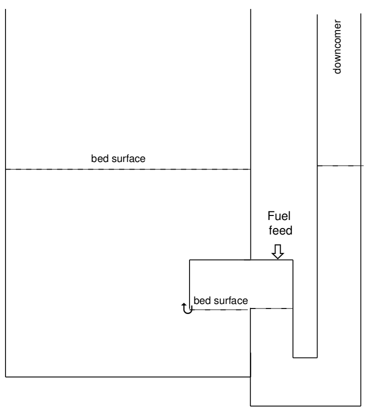

Figure 11. Fuel fed into box together with particle flow.

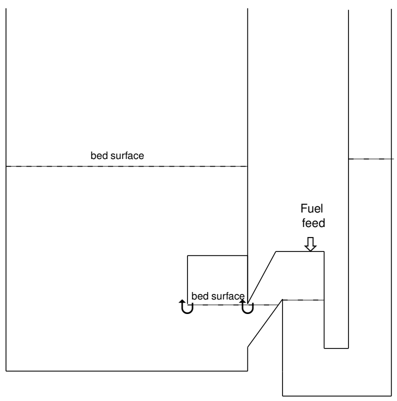

Figure 12. Fuel addition in freeboard from which gas is led into the box.

A preliminary design of a volatiles distributor immersed in a fuel reactor bed is shown in the following figures. Figure 13 shows a side view with the flow directions of the solids indicated by arrows. Solids from the air reactor enter along the right-hand side wall, whereas the flow from the fuel reactor cyclone returns via the downcomer and the loop seal. Fuel is added to this flow as it comes up from the loop seal, and releases its volatiles when meeting this flow. The volatiles collect in the distributor box and are distributed via a number of arms, which can be seen in Figure 14 and Figure 15. The fuel reactor seen in these figures represents the right-hand lower half of the 1000 MW_{th} fuel reactor shown in the top view of Figure 4. Not shown in the figures are the legs needed to support the volatiles distributor.

The char formed during volatiles release will mix into bed material and follow the flow directions indicated by the arrows in Figure 13. The finer char may follow the gas stream and leave the distributor via the holes. Some char may temporarily “float” on the bed surface which would be advantageous as it will give increased residence time for gasification.

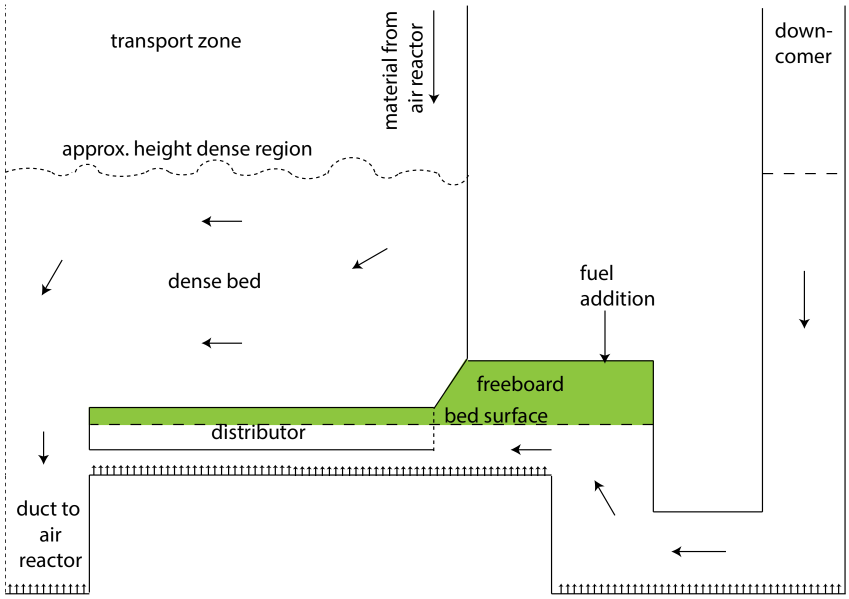

Figure 13. Volatiles distributor in bed. Side view.

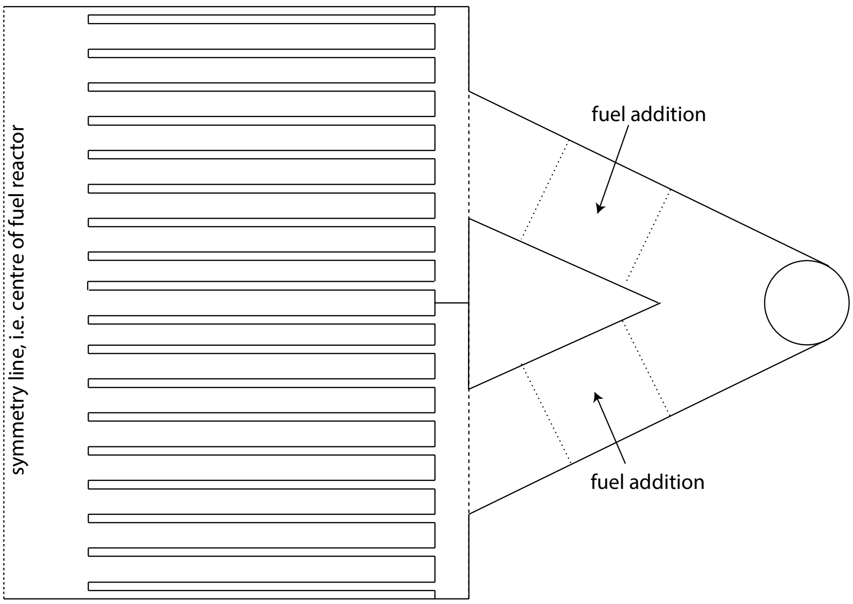

Figure 14.Volatiles distributor, top view.

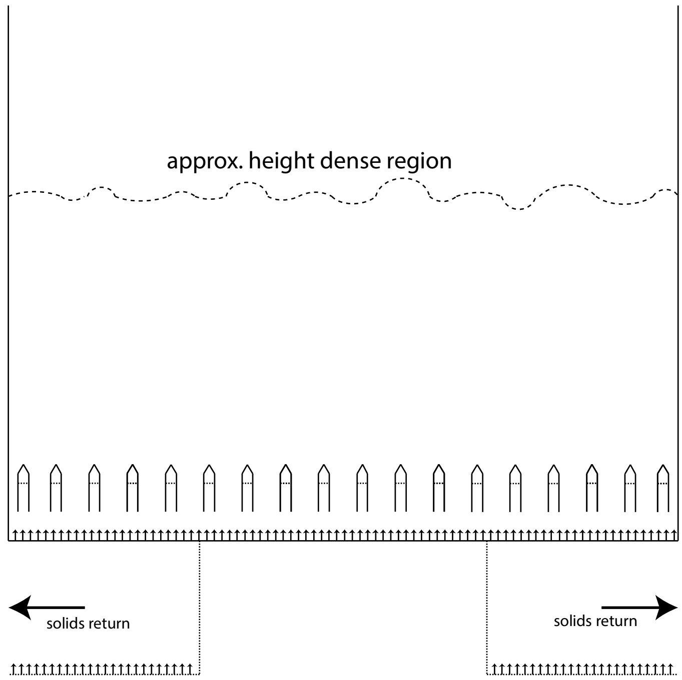

Figure 15. Volatiles distributor, other side view.

4.1. Dimensions of distributor

In order to assure a reasonably uniform distribution of gas and minimize the risk of gas slipping out below the lower edge the distributor is designed as follows: The height is 0.5 m high and the holes in the side are approximately 0.1 m from the top. The size and spacing of the holes is chosen to give a pressure drop through the holes of 2 kPa, which means that the bed level would be at a height approximately 0.1 m below the holes, and that the bed level inside the distributor is approximately 0.3 m above the lower edge, cf. Figure 13 and 15.

The flow of volatiles going through the distributor is estimated to 22 m^3_n/s, or 100 m^3/s, which, with 36 arms and a free cross-section of 0.0225 m^2 in the upper part of the arms, gives an average velocity in the first part of the arms of 124 m/s. The arms are 4 m and the pressure drop over the arm length is estimated to be of the order of 0.1 kPa, which is small compared to the pressure drop over the holes. If needed, it would be possible to compensate for the pressure drop along the length of the arms by slight differences in hole spacing or hole size between the front and end of the arm.

The spacing and sizing of the holes could also be used to optimize the distribution if anything else than an even distribution would be advantageous. For instance, it could be an advantage to distribute more volatiles to locations where release of syngas from char is lower, or where the oxygen carrier from the air reactor enters.

4.2 Estimation of size and number of holes.

For the gas velocity through a grid hole the following equation can be used, [23].

$$v = C_d \sqrt{\frac{2\Delta P}{\rho}} \qquad \textbf{(1)}$$

where v is the velocity, ΔP the pressure drop, ρ the gas density and C_d is the orifice discharge coefficient. For a sharp-edged orifice C_d is 0.6, whereas a typical value of C_d for a grid hole is 0.8, [23]. Kunii and Levenspiel propose values for C_d of 0.6-0.7 depending on the Reynolds number for the total flow in the channel leading to the orifice, [24]. Similar results are obtained from adding pressure drops for inlets and outlets, [25], thus the pressure drop for an inlet or outlet is given by

$$\Delta \boldsymbol{P} = \boldsymbol{\zeta_E} \frac{\boldsymbol{\rho v^2}}{\boldsymbol{2}} \quad \textbf{(2)}$$

where ζ_E is 1 for an outlet and around 0.5 for an inlet, thus giving a total of around 1.5 for inlet and outlet. Comparing equations (1) and (2) shows that

$$C_d = \frac{1}{\sqrt{\zeta_E}} \quad (3)$$

and inserting ζ_E = 1.5 in equation (3) yields C_d = 0.82.

Here a value of 0.8 is used, giving a velocity through the holes of 162 m/s with an assumed density of the volatiles of 0.098 kg/m^3. The total side of the 36 arms is 288 m and assuming circular holes with a diameter of 0.012 m, the distance between the holes would be 0.05 m.

4.3. Model validation

Further studies in cold-flow models and mathematical models, e.g. CFD, would be needed to validate the detailed design. Furthermore, testing in larger pilots would be needed.

4.4. Cost

The distributor would be made in expensive high temperature steel and be subject to severe conditions limiting its life. Nevertheless, an estimation of material cost for such a distributor suggests a low cost, around 0.03 €/tonne of CO_2 captured, whereas an improved gas conversion of for instance 6% would reduce costs for oxygen production by around 3 €/tonne of CO_2, [10]. Thus, a well-designed distributor would likely give significant reductions in overall costs.

4. Conclusions

A distributor of volatiles has been proposed to attain a more uniform distribution of volatiles over the bottom bed cross-section of a fuel reactor in a boiler for chemical-looping combustion. The cost of such a distributor is very likely small in comparison to the gains of the expected improvement in gas conversion. Further studies using both cold-flow and mathematical models, as well as testing in pilots, would be needed to validate the detailed design.

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