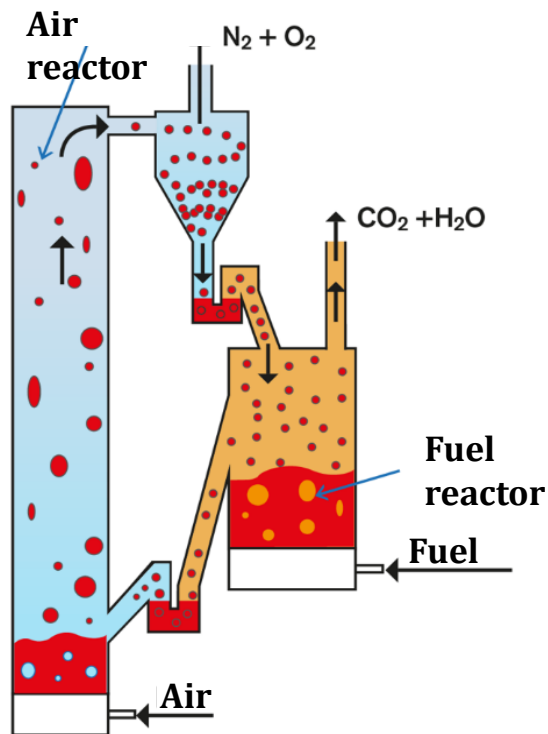


Chemical-Looping Combustion (CLC)

Insights into CLC Reactor Design

Anders Lyngfelt



*Looping Technologies
for Sustainable Power and Hydrogen Production*
Department of Chemical Engineering
National Institute of Technology (NIT), Warangal
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Warangal, India



CONTENT

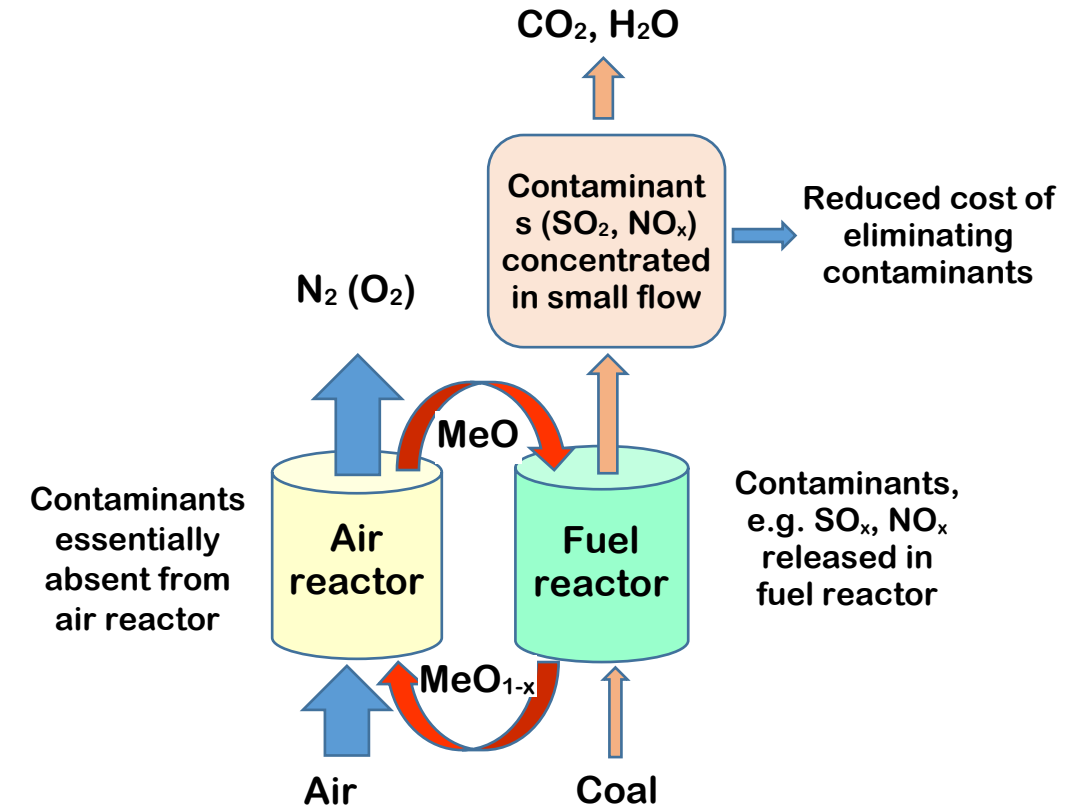
- CLC Applications
 - CLC of coal
 - CLC biomass
 - CLC-SMR for blue hydrogen

Three critical aspects that must work

- Oxygen carriers (brief)
- Circulation
- Downstream treatment

Chemical-looping combustion of coal

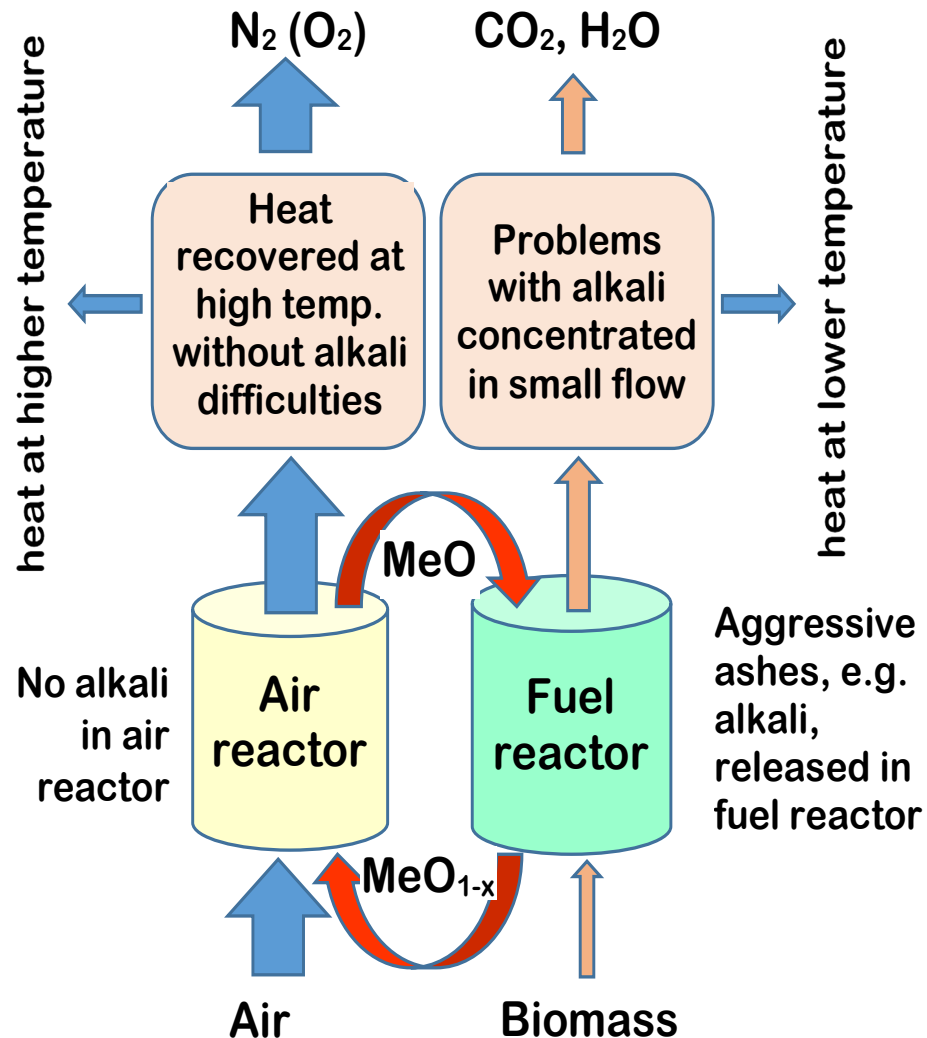
- high similarity to normal circulating fluidized bed technology
- small added cost, low energy penalty
- *unique potential for dramatic reduction in CO₂ capture cost*
- pollutants concentrated in CO₂ could reduce costs of SO_x/NO_x reduction
- large potential market



Chemical looping combustion of biomass

- same advantages as in coal combustion above:
 - similarity to normal circulating fluidized bed technology
 - small added cost, low energy penalty
 - ***unique potential for dramatic reduction in CO₂ capture cost***
 - concentration of pollutants in CO₂
 - large potential market
- in addition potential advantage with respect to alkalis
- using biomass gives **negative emissions**
- to meet climate targets **gigantic negative emissions** are needed

Chemical-looping combustion of biomass



Alkali in biomass gives low ash-melting temperature together with silica (i.e. sand).

With ilmenite oxygen carrier (FeTiO_3) the alkali forms **non-sticky** titanates.

>20,000 h of OCAC (oxygen-carrier aided combustion) in full-scale CFBs with ilmenite

Long-term operation with ilmenite, 300 h, shows alkali penetrates to centre of particles, and only minor loss in reactivity

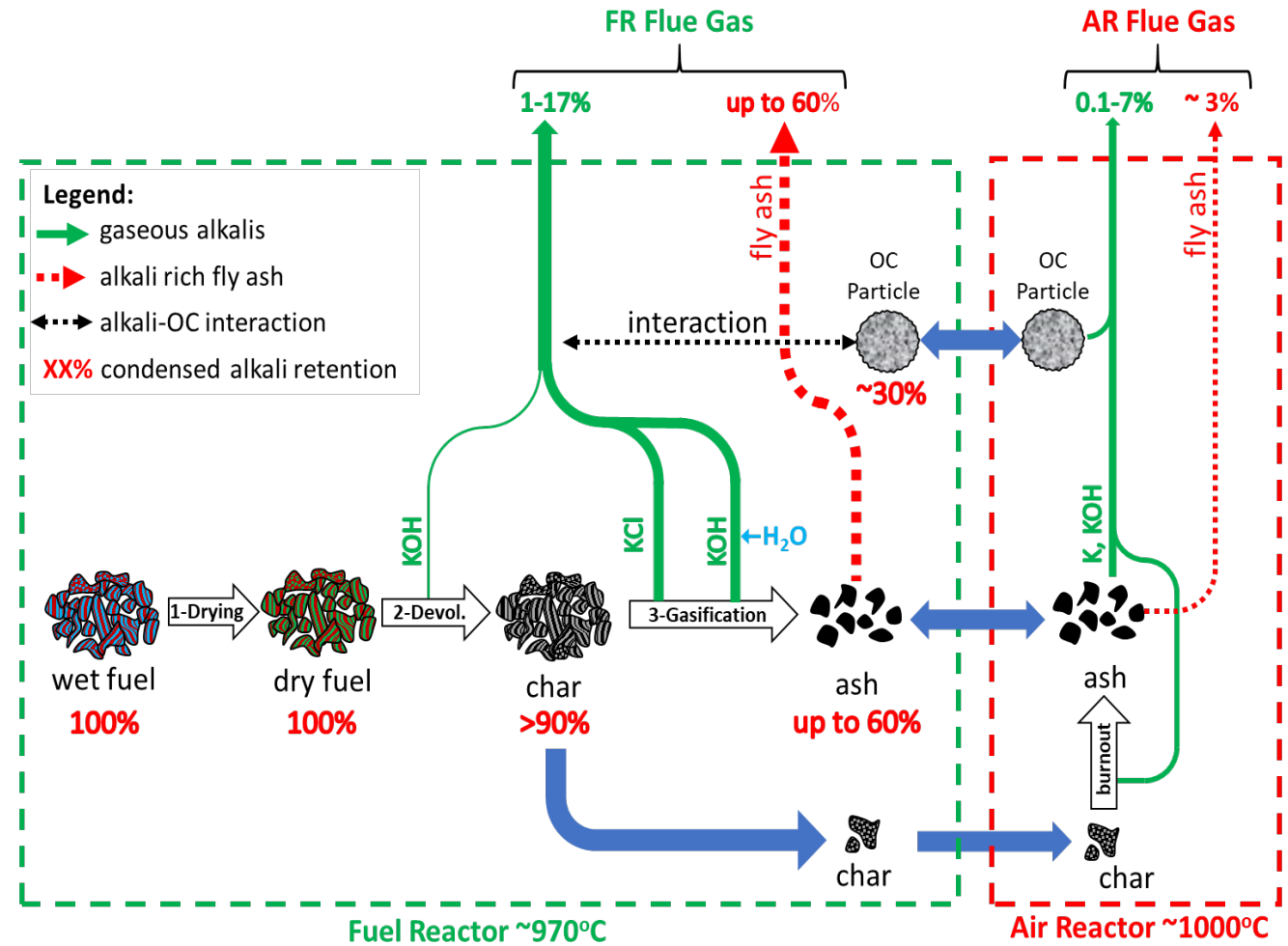
Only small part of alkali released in air reactor

Air reactor essentially free from chlorine

Could range of possible fuels be extended to more difficult fuels? (straw fuels)

Studies of alkali flows in three CLC pilots found:

- majority of alkali retained in oxygen carrier
- majority of alkali in fly ash, from fuel reactor
- ***low fraction of alkali in air reactor outlet***
- ***air reactor will be essentially free of KCl***

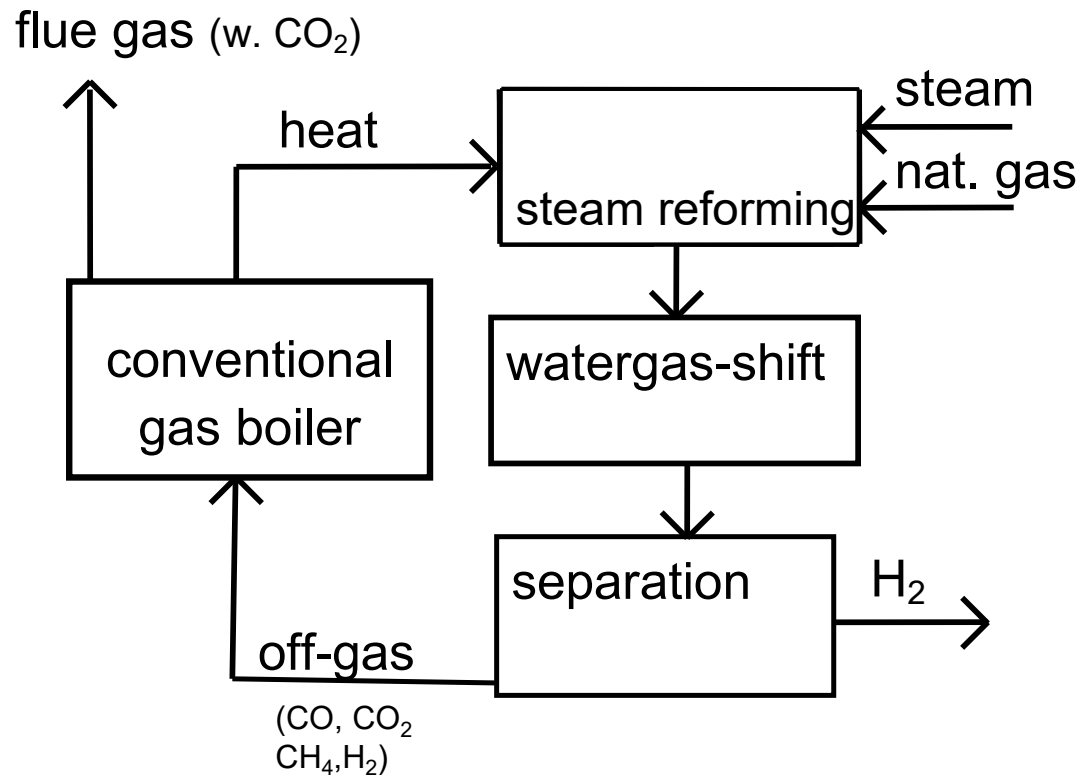


Ivan Gogolev, Amir H. Soleimani Salim, Daofeng Mei and Anders Lyngfelt, Effects of Temperature, Operation Mode, and Steam Concentration on Alkali Release in Chemical Looping Conversion of Biomass – Experimental Investigation in a 10 kWth Pilot, *Energy & Fuels*, 36:17 (2022) 9551–9570

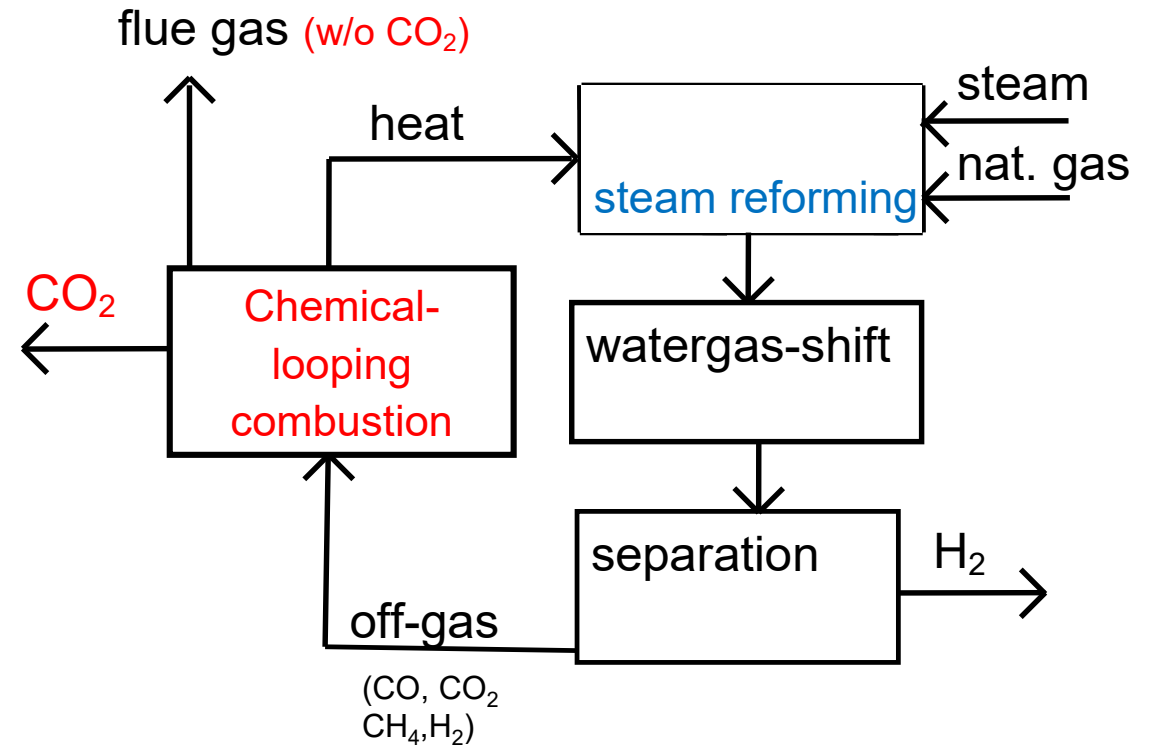
Ivan Gogolev, *The Release, Distribution, and Implications of Alkalis in Chemical Looping Combustion of Biomass*, PhD Thesis, Chalmers University of Technology, Göteborg, Sweden 2022

Blue hydrogen at low cost with CLC-SMR

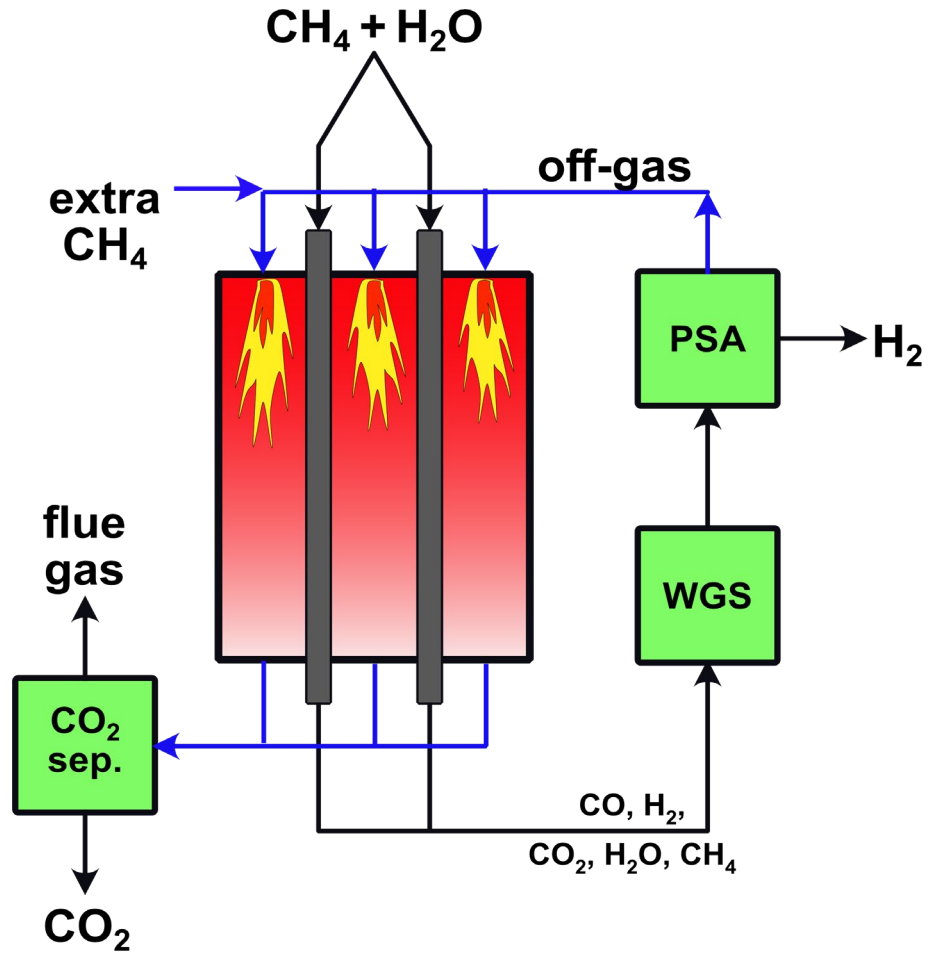
Steam methane reforming (SMR)



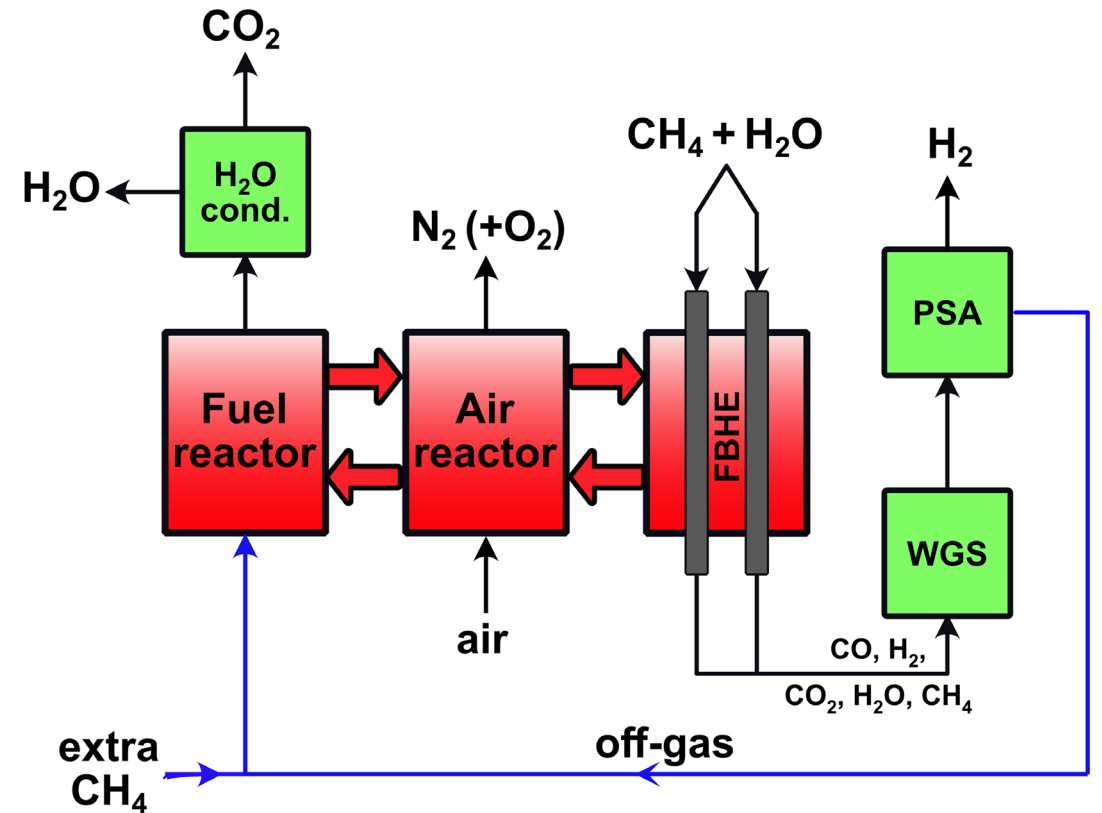
Steam reforming with CLC



Steam Methane Reforming (SMR)



Steam reforming with CLC



Why CLC-SMR?

Capture of CO₂ with no/small energy penalty

Negative energy penalty for process¹ (T outlet reduced from e.g. 1200 – 950°C)

Capture of CO₂ with without high equipment/operational cost for gas separation

More efficient heat transfer and more benign conditions

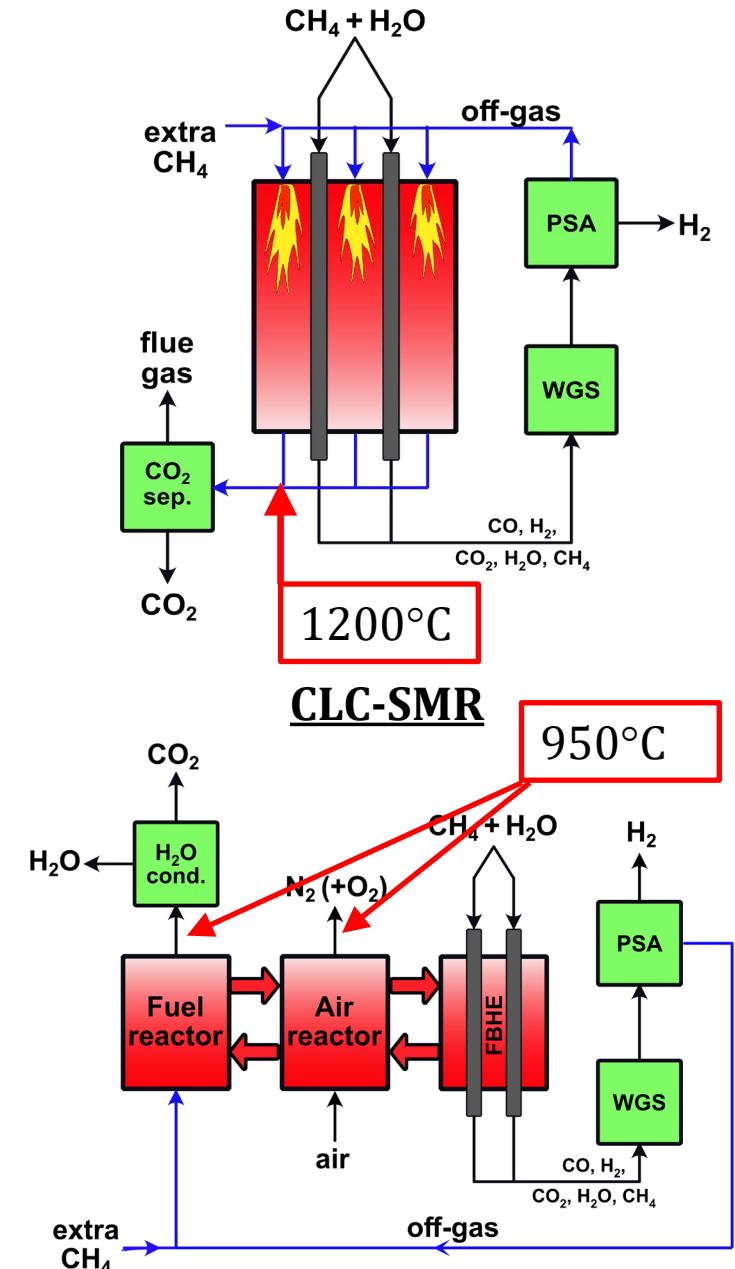
- smaller tube diameter possible in FBHEs (fluidized-bed heat exchangers)
- thus, shorter and thinner tubes (length decrease by factor 3 ?)²
- thus, less catalyst (amount decreased by factor of 3 ?)²
- thus, lower cost of reforming step

In total: Potential for transforming natural gas to CO₂-free H₂ with **negative energy penalty and negative cost penalty** for CO₂ capture. Gigantic potential future market.

1) Stenberg V, Spallina V, Mattisson T, Rydén M. Techno-economic analysis of H₂ production processes using fluidized bed heat exchangers with steam reforming – Part 2: Chemical-looping combustion. *International Journal of Hydrogen Energy* **46** (2021) 25355-25375

2) Pröll, T., and Lyngfelt, A., Steam Methane Reforming with Chemical-Looping Combustion – Scaling of Fluidized Bed-Heated Reformer Tubes, *Energy & Fuels* **36**:17 (2022) 9502–9512

Steam Methane Reforming (SMR)



Commercial CLC plant

–

Three critical aspects that must have adequate solution

- 1) An oxygen carrier that works**
- 2) Adequate circulation**
- 3) Downstream treatment of gas from fuel reactor to achieve a CO₂ that fulfills purity requirements for transportation/ storage**

Oxygen carrier

Solid fuels

- Lifetime limited by ash
- High conversion less critical (oxy-polishing)
- Low-cost ores show high reactivity to gasification gases CO and H₂
- Low-cost natural ores preferred
 - Ilmenite, long experience,
 - >1500 h, (+ OCAC in CFBs >75 MW, >20 000 h¹)
 - Manganese ores, generally more reactive than ilmenite,
 - >1000 h, (20 tested in CLC operation at Chalmers²)

Chemical-looping with Steam-Methane Reforming

- Lifetime not limited by ash
- High conversion more critical
- Low-cost mtrls have low reactivity to CH₄
- Manufactured materials relevant
 - E.g. CaMnO₃
 - Can be manufactured from low-cost limestone and Mn ore
 - Long lifetime in pilot operation
 - Spontaneous release of oxygen / high conversion



¹Moldenhauer, Patrick; Angelica Corcoran; Henrik Thunman and Fredrik Lind, [A Scale-Up Project for Operating a 115 MWth Biomass-Fired CFB boiler with Oxygen Carriers as Bed Material](#), 5th International Conference on Chemical Looping, Park City, Utah, 24-27 September 2018

²Lyngfelt, A., Moldenhauer, P., Biermann, M., Johannsen, K., Wimmer, D., and Hanning, M., Operational experiences of chemical-looping combustion with 18 manganese ores in a 300 W unit, *International Journal of Greenhouse Gas Control*, **127** (2023) 103937

Commercial CLC plant

–

Three critical aspects that must have adequate solution

- 1) An oxygen carrier that works **
- 2) Adequate circulation **
- 3) Downstream treatment of gas from fuel reactor to achieve a CO₂ that fulfills purity requirements for transportation/ storage**

Normally, it is assumed that a CLC boiler can be designed like a circulating fluidized bed (CFB) with the addition of a fuel reactor.

This is also the way essentially all of the 50 CLC pilots are designed. And it works.

But, do we know this works in commercial scale?

Needed circulation is decided by the heat balance.

Reactions in fuel reactor are endothermic.

Thus, for a 100 MW_{th} boiler, appr. 25-30 MW needs to be transferred to the fuel reactor¹

The heat needed in thermal gasification in dual fluidized beds, is about the same (per unit of fuel), but per unit of air added to the air reactor, it is around three times higher.

So thermal gasifier must transfer a lot more heat than CLC.

Successful operation has been reported from dual fluidized-bed thermal biomass gasifiers in the range 8-32 MW.

The largest thermal gasifier corresponds to around 10 MW_{th} if used as CLC.

But what about 100 MW_{th} or more?

¹For dry fuels (Lyngfelt, A., Pallarés, D., Linderholm, C., Lind, F., Thunman, H., and Leckner, B., Achieving Adequate Circulation in Chemical-Looping Combustion – Design Proposal for a 200 MW_{th} CLC Boiler, *Energy & Fuels* 36:17 (2022) 9588–9615)

2) What is the circulation in commercial CFBs ?

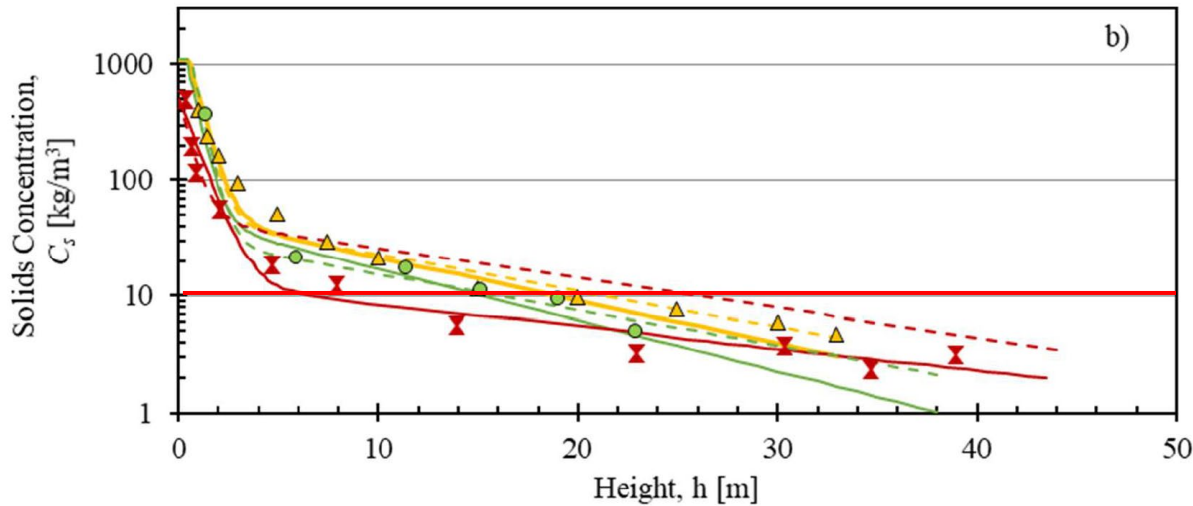
Upwards flow proportional to
solids concentration ρ_s
(kg/m³)

$$G_s = \rho_s (u_0 - u_s)$$

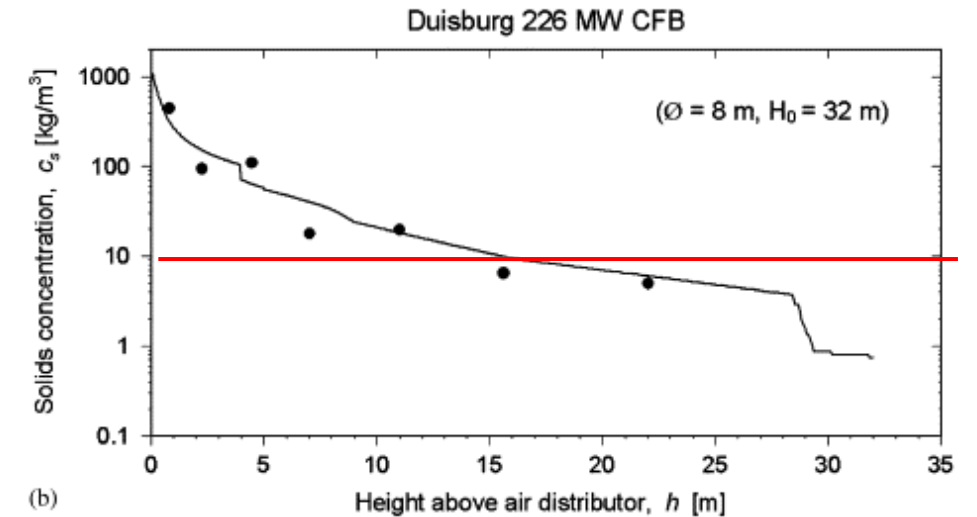
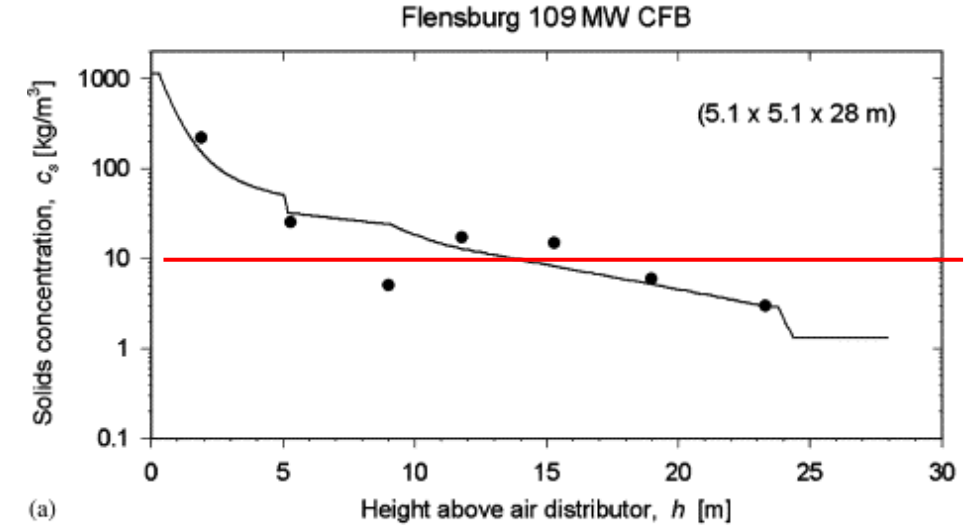
Needed circulation: $G_s > 40 \text{ kg/m}^2\text{s}$, $u_0 < 6 \text{ m/s}$

With $(u_0 - u_s) \approx 4 \text{ m/s}$

$$\rho_s \geq 10 \text{ kg/m}^3$$



Solids concentration versus height for 3 CFB boilers. ▲ Emile Huchet, ● Zibo, ✕ Turow.



Solids concentration versus height.
Data from two CFB boilers

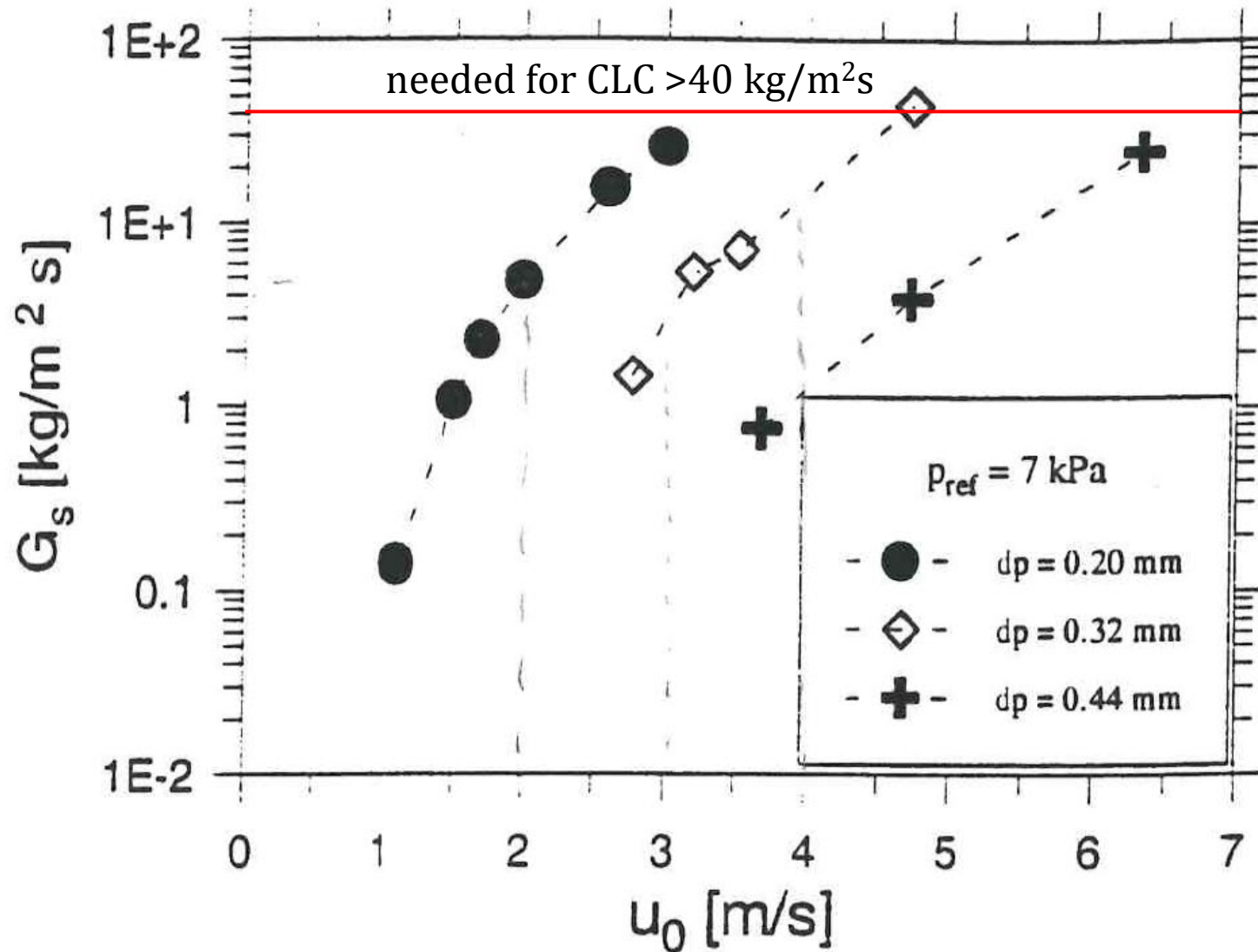
Actual circulation is difficult to measure.

The upwards flow in the top of the riser is *often assumed* to be the actual circulation.

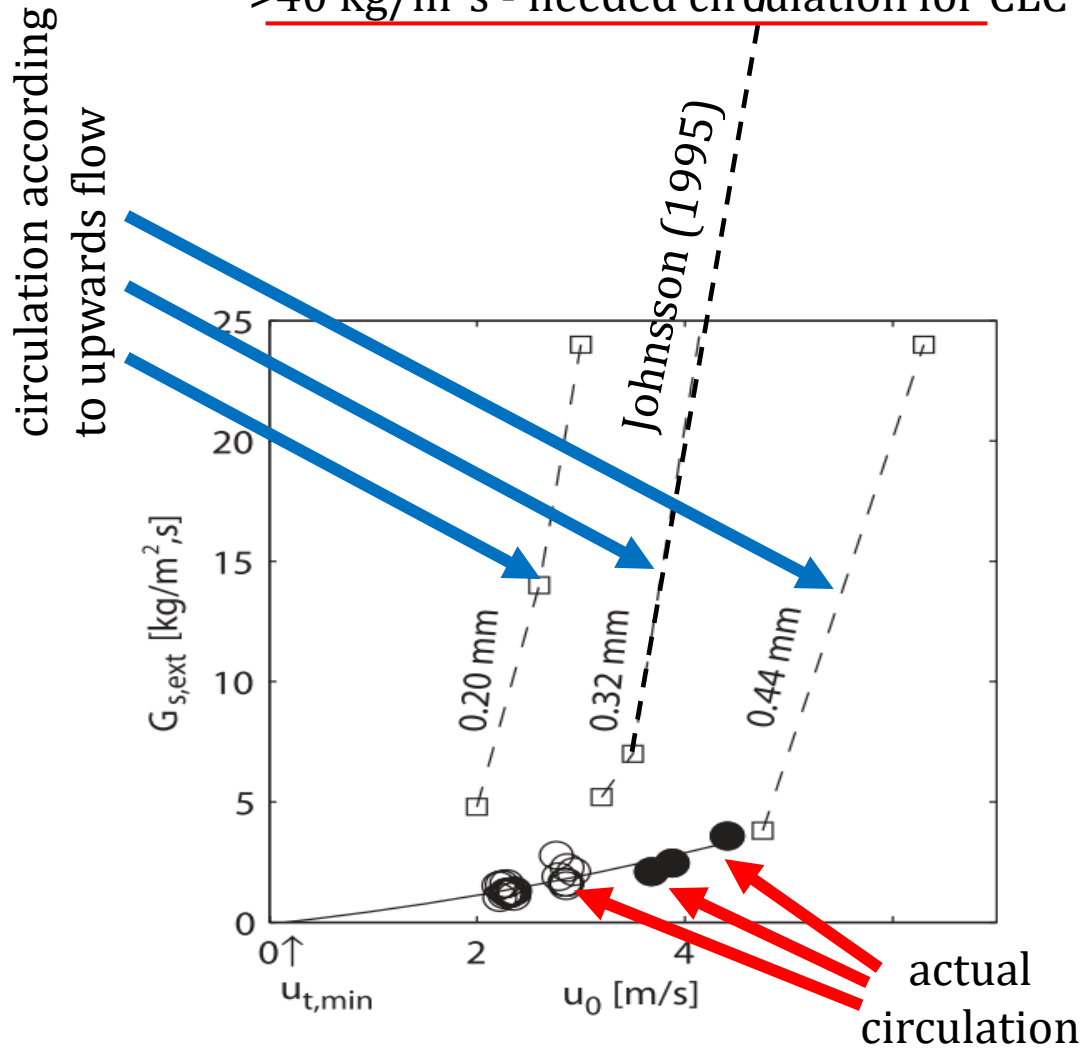
BUT, the upwards flow in the top,
is not necessarily equal to the flow going into
the cyclone

What do we know?

Solids flux in top of a 12 m high 12 MW CFB (Chalmers) (Johnsson 1995)

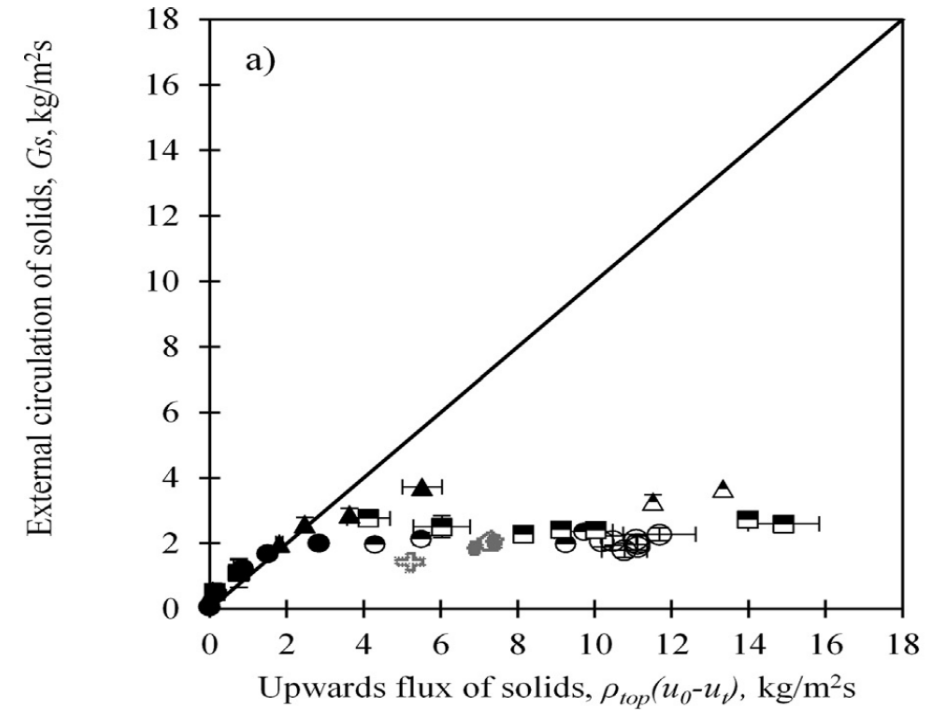


>40 kg/m²s - needed circulation for CLC



External (actual) circulation, measured by heat balance (filled/open **circles**)

Upwards flow from previous slide (boxes/dashed lines)



Measured external circulation versus upwards solids flux in the top of a cold-flow model of a 200 MW_{th} CFB. (Djerf 2021)

Actual circulation:

$$G_s^* = G_{s,top}(1 - k_b)$$

Conclusions

Actual circulation in CFB boilers is 5-50% of what is needed for CLC

Raised gas velocity not an option due to damage to boiler walls.

With smaller particle size, upwards flow can be dramatically increased.
But will the actual circulation also increase ? Increased loss in cyclone?

As noted, upwards flow decreases exponentially with height.

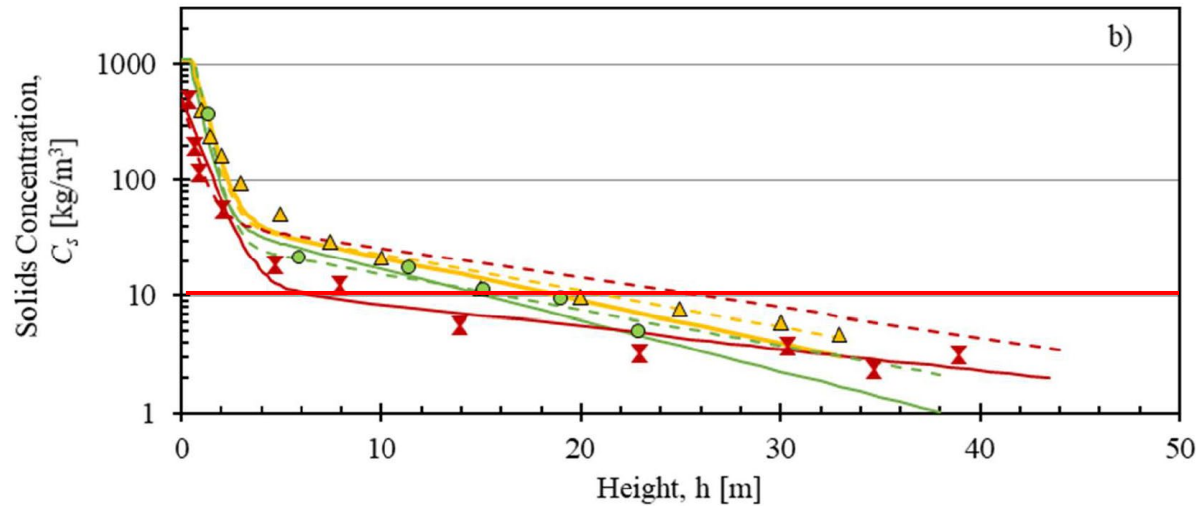
However, ***collection of down-flow along the walls, would be sufficient.***

2) But upwards flow in lower part is sufficient

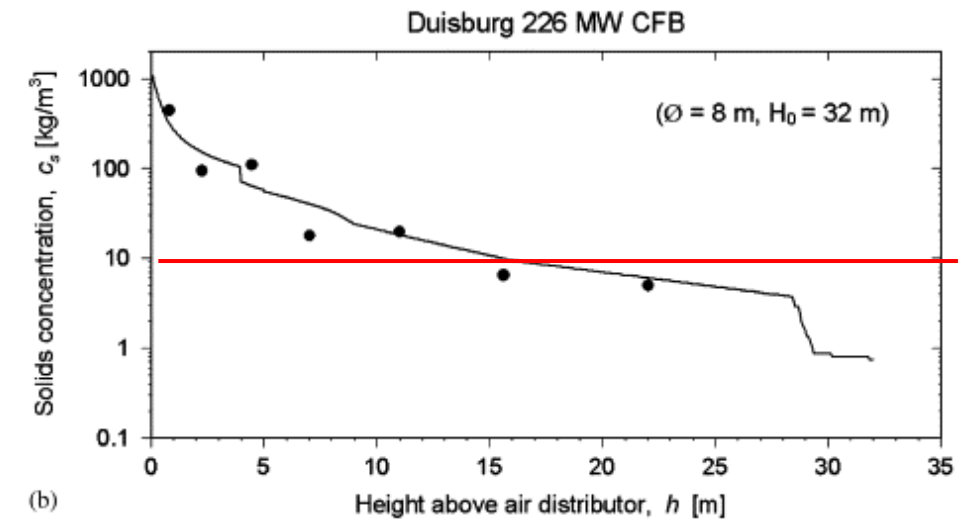
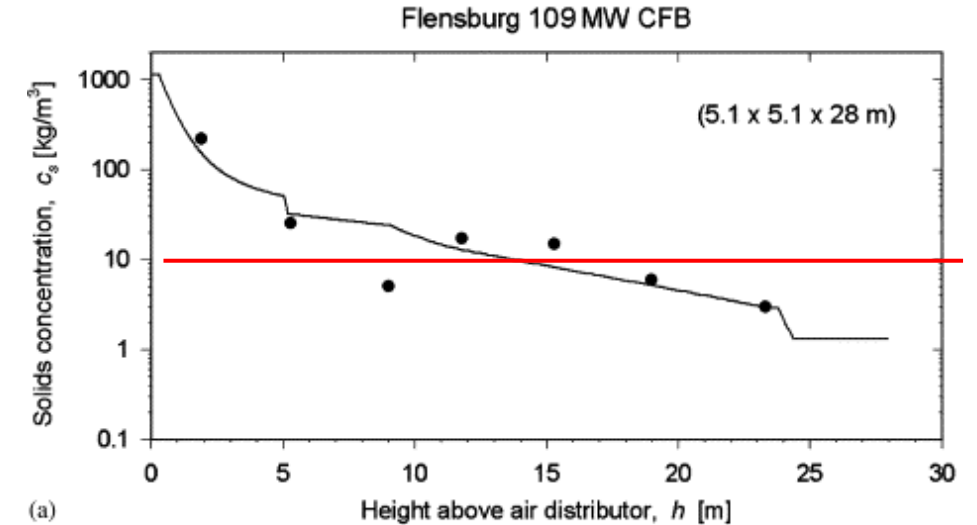
Upwards flow proportional to
solids concentration
(kg/m³)

$$G_s = \rho_s(u_0 - u_s)$$

Needed circulation: $\rho_s \geq 10 \text{ kg/m}^3$

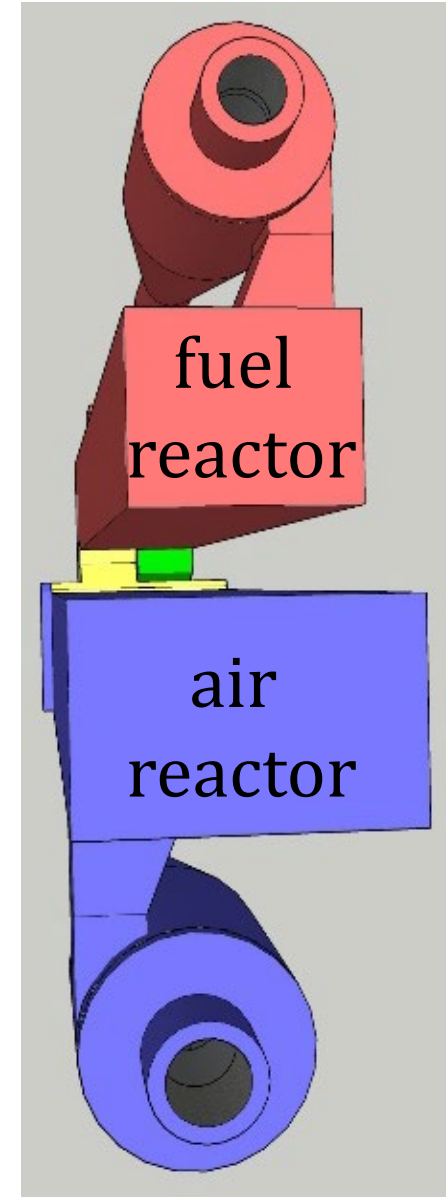
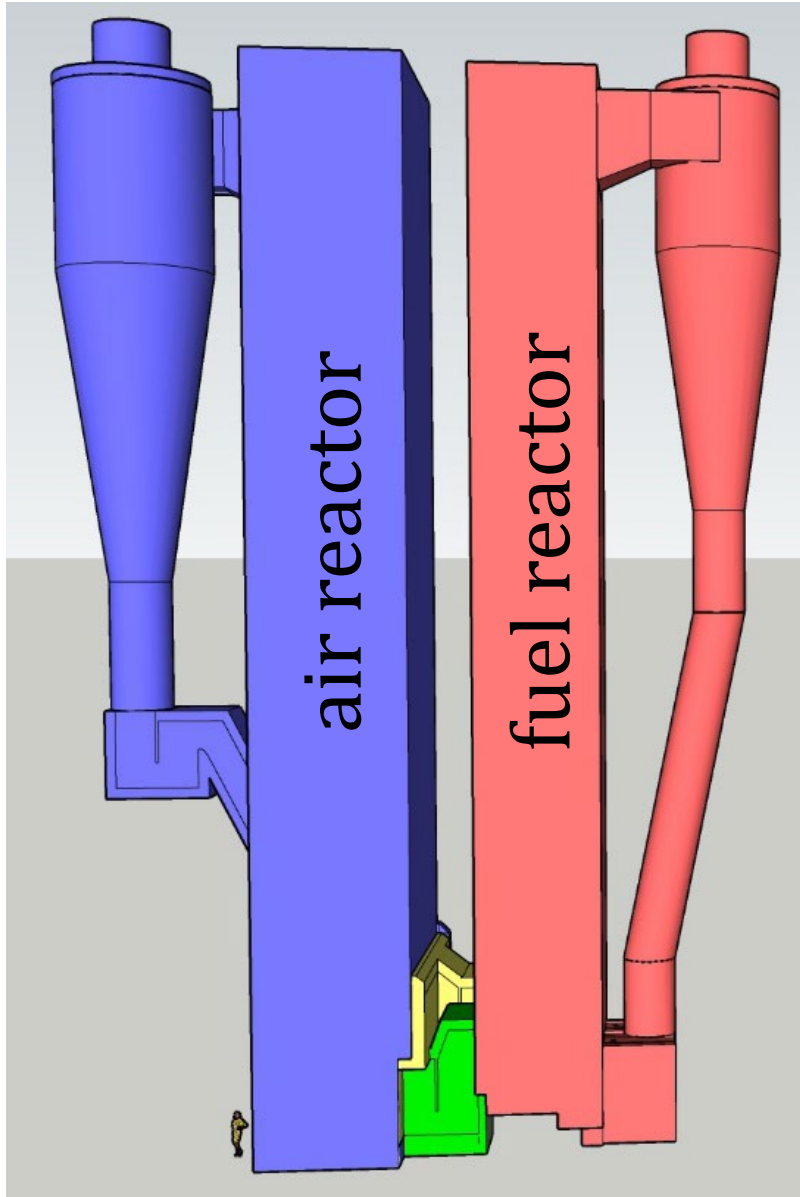


Solids concentration versus height for 3 CFB boilers. \blacktriangle Emile Huchet, \bullet Zibo, \times Turow.

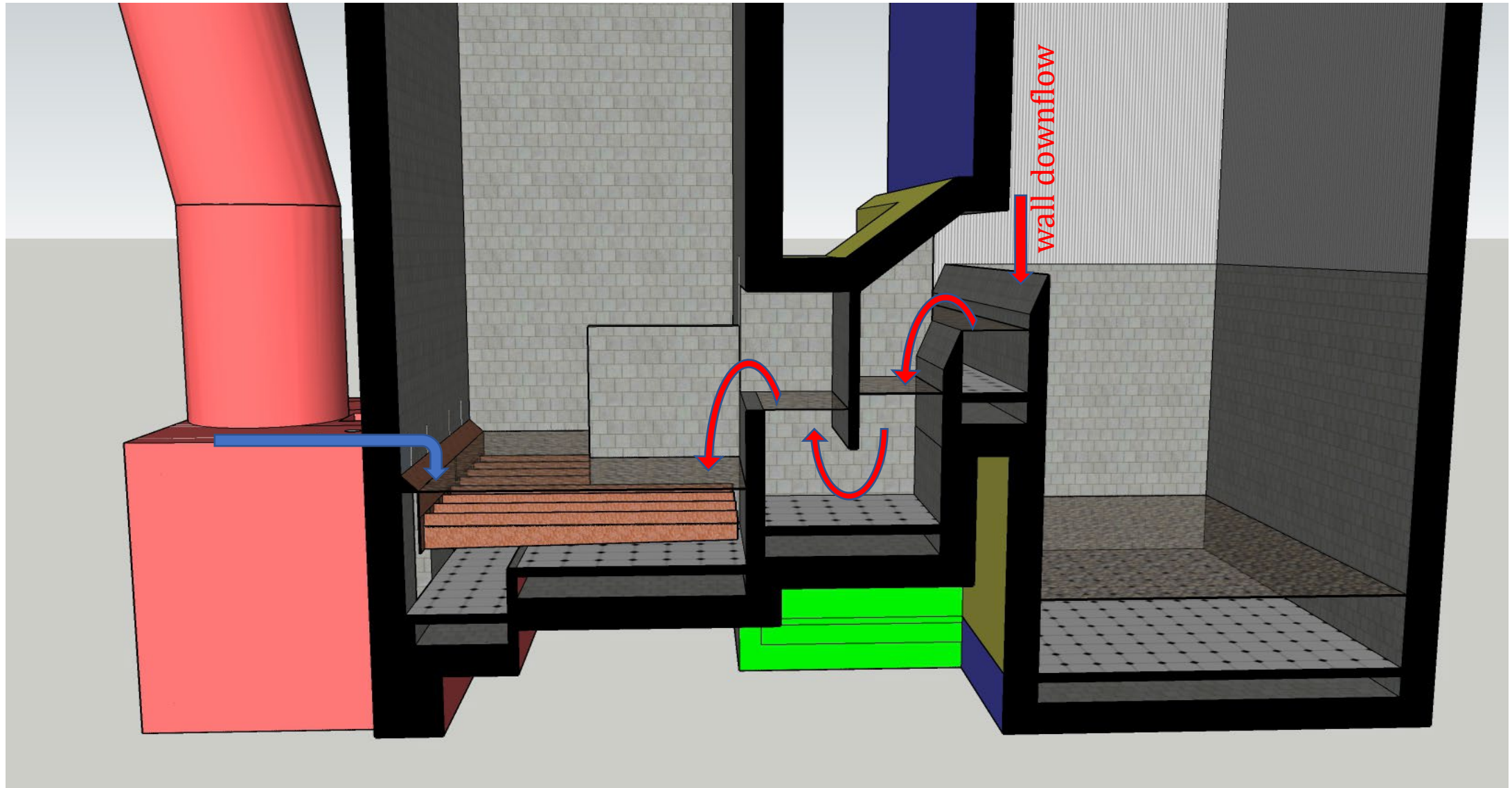


We can collect the downflow along the walls, in the lower part!

200 MW_{th} CLC-CFB boiler, 40 m high



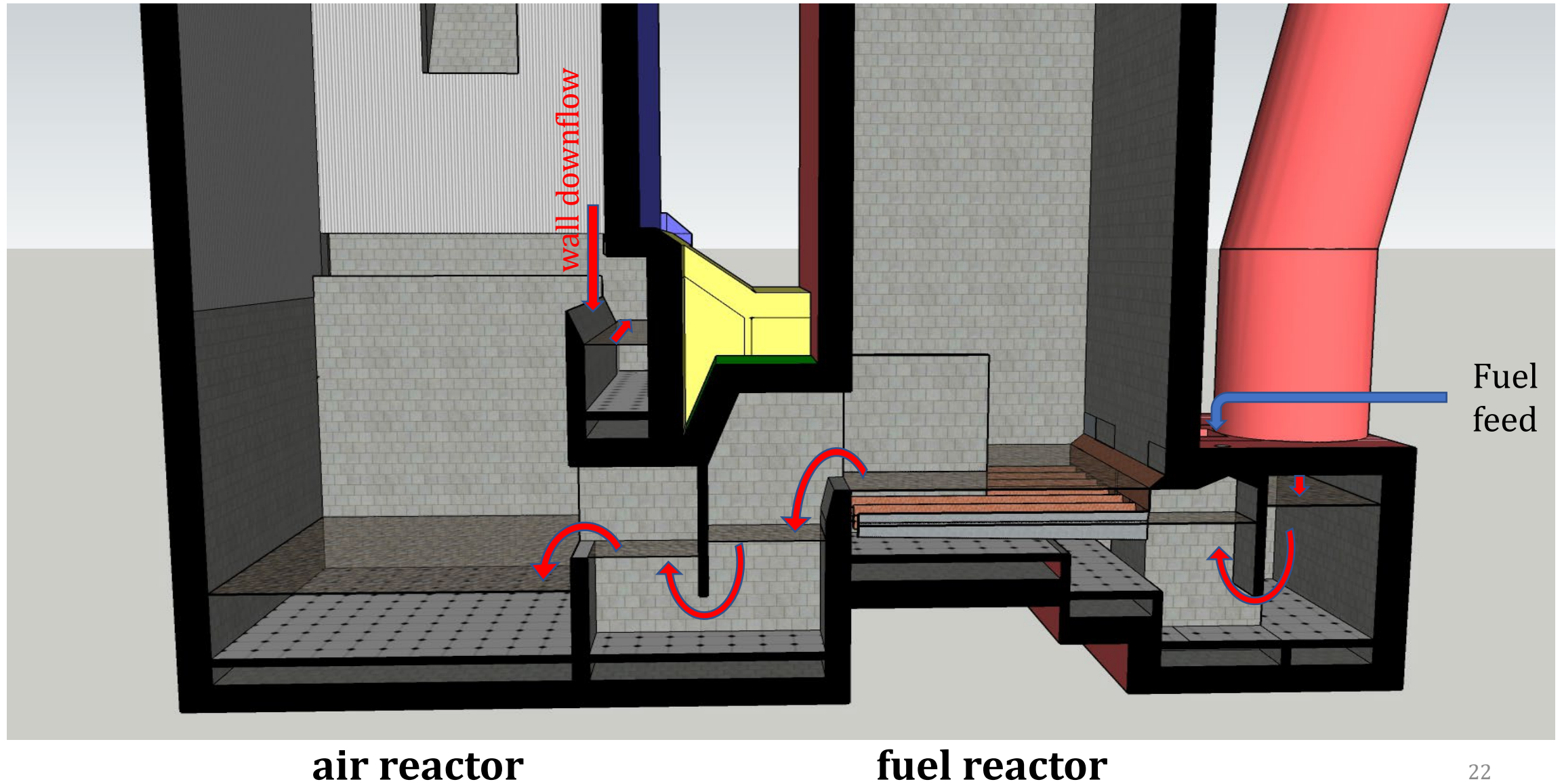
Loopseal leading from air reactor to fuel reactor

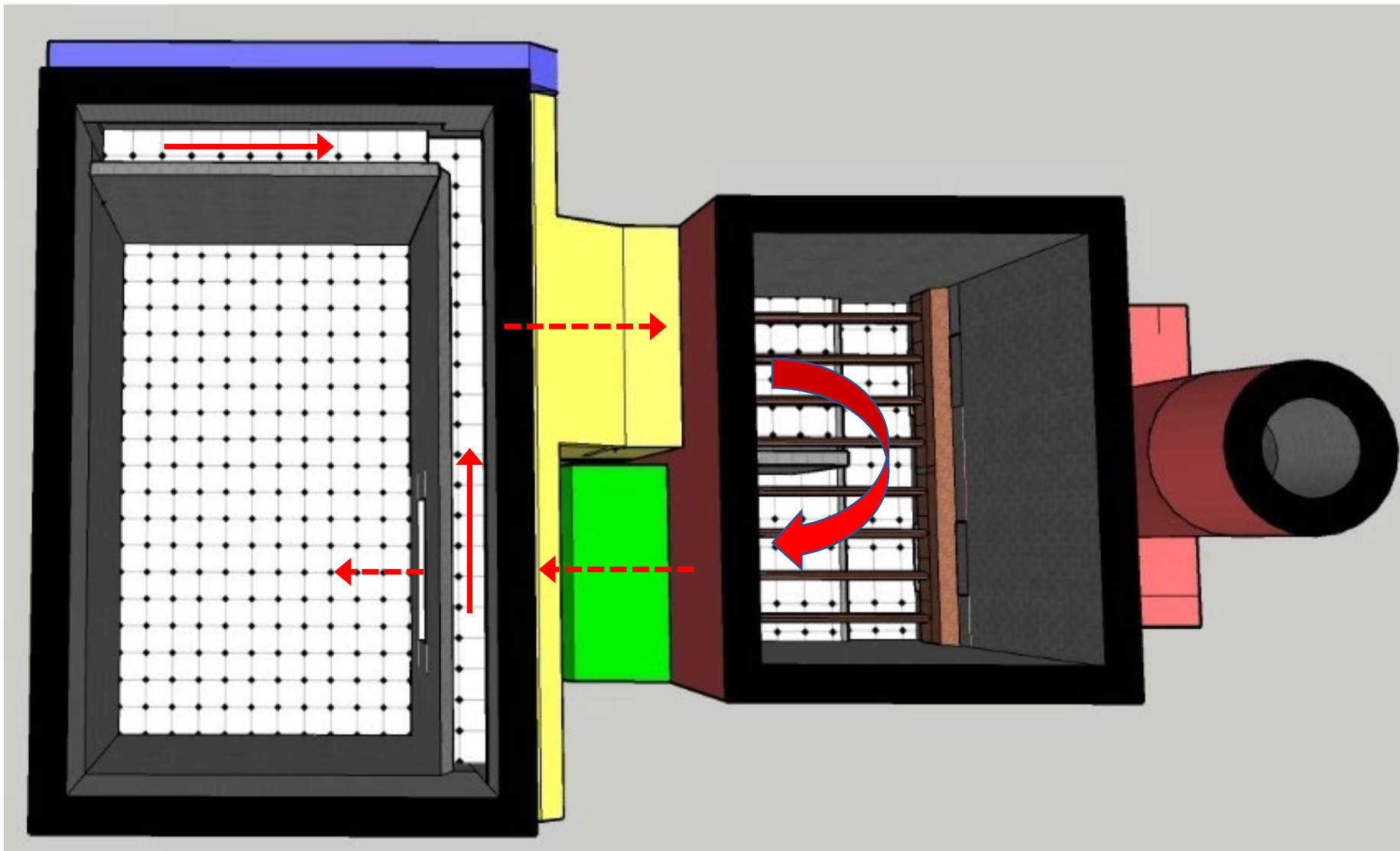


fuel reactor

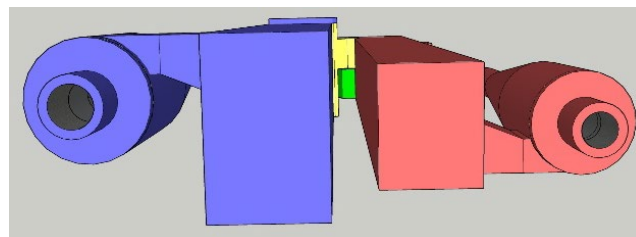
air reactor

Loopseal leading back from fuel reactor to airfuel reactor



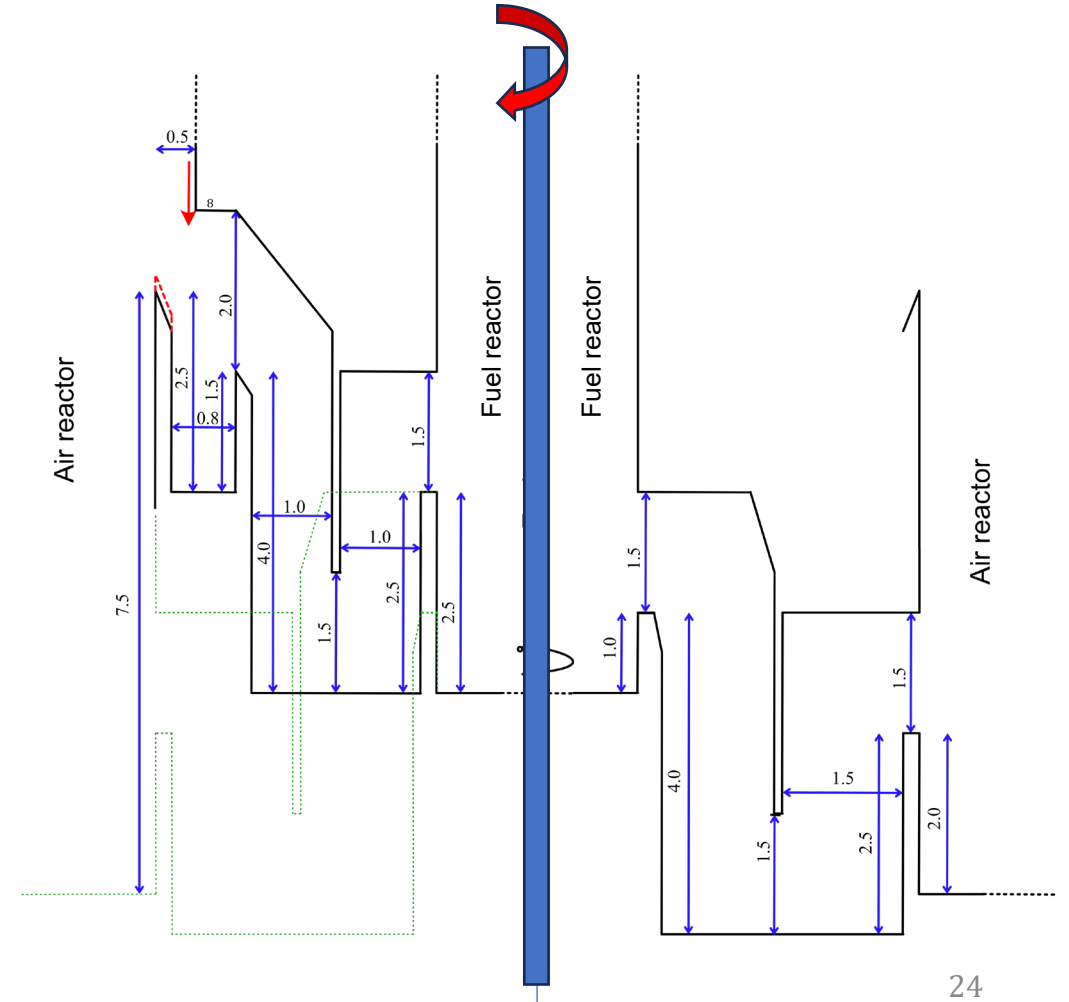


air
reactor

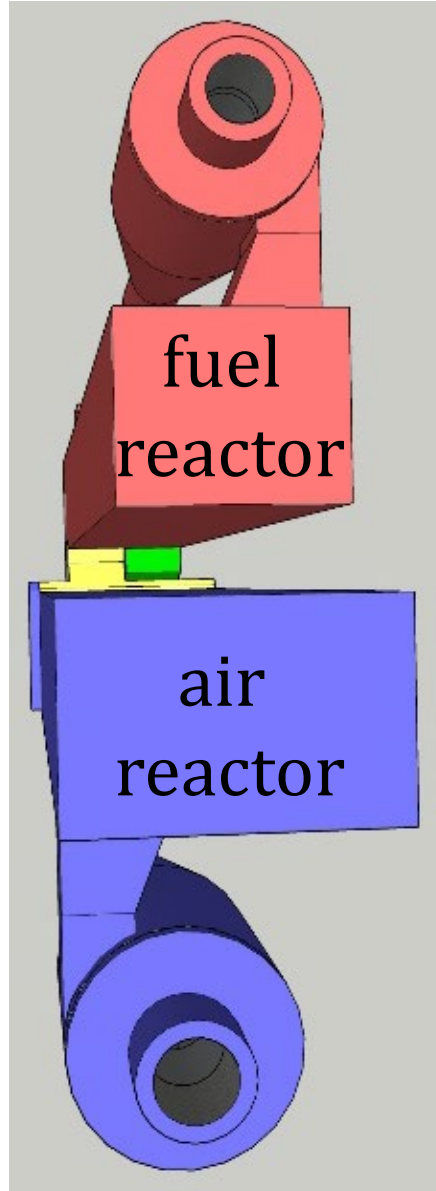
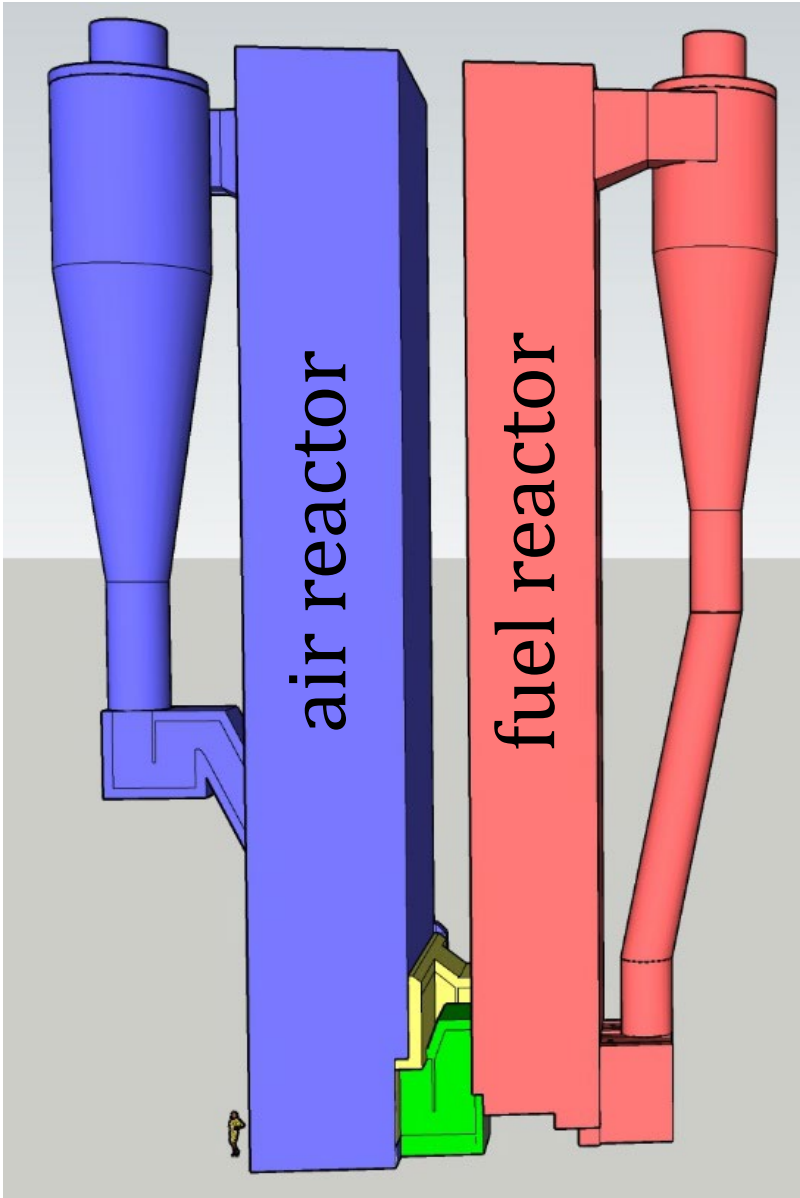


fuel
reactor

- Wall downfall collected on three walls
- Higher drop in loop-seals
- Higher vertical cross-section in loop-seals



200 MW CLC-CFB boiler, 40 m high

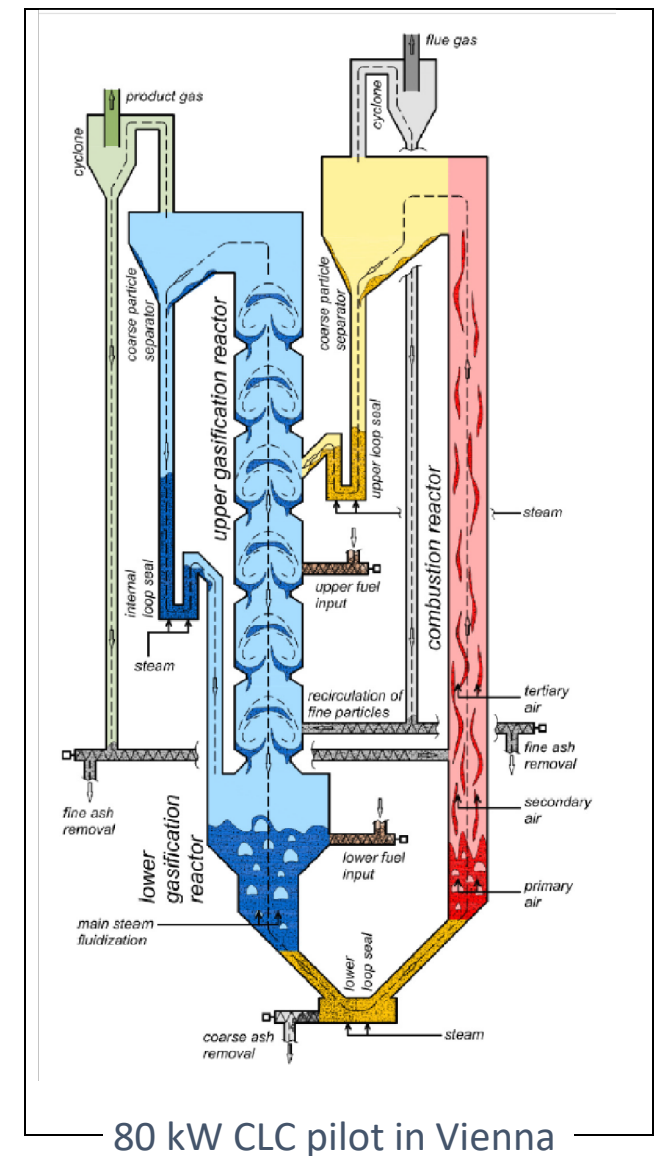


Combined CLC-CFB

- Air reactor can be used as CFB boiler
- Moderate added investment to make new CFB boiler "CLC-ready"
- Seamless shift between CFB and CLC operation
- Start-up as CFB, gradual shifting of fuel addition from air reactor to fuel reactor

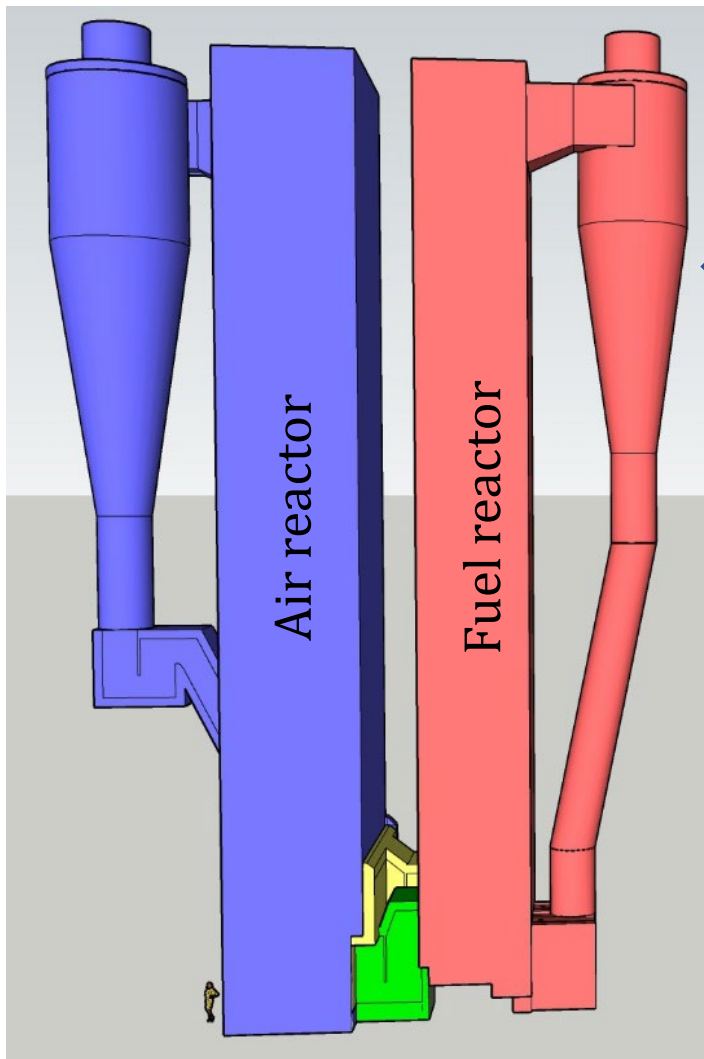
Design aspects

- Wall downflow should not be cooled by walls
 - All, or part of, walls in air reactor not cooled
 - Well known: Andritz CFB waste boilers only have external cooling
- Fuel reactor is not cooled
 - Could be used as CFB if equipped with external cooling
- Fuel reactor should be designed for high pressure drop in riser, to assure high gas conversion
 - Could contractions of the path work in large scale
- Optimal temperature of CLC higher than CFB
 - Design for up to 1100 C recommended¹
- Use of a volatiles distributor to enhance contact?



¹Best operational results with ilmenite and biomass, 80 kW pilot in Vienna, at 1057-1060 C (FR) and 1087-1088 C (AR)

Fleiß B, Fuchs J, Müller S, and Hofbauer H. *Chemical Looping for efficient biomass utilization*. Second interim report, Project Bio-Loop, Technical University of Vienna, Date accessed, 2022; Available from: <https://repositum.tuwien.at/handle/20.500.12708/139514>.



200 MW CLC-CFB, added cost of Fuel Reactor:
 1500 m² insulated wall
 at
 2000 €/m²

>>> 3 M€

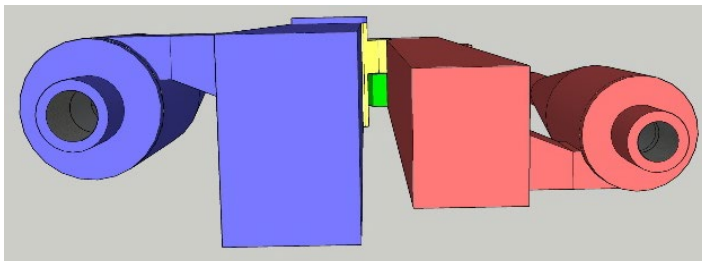
or

0.3 M€/year

capture: 0.4 Mt CO₂/year

cost of fuel reactor : **0.75 €/t CO₂**

Cost of post-combustion CO₂ capture:
 100 €/t CO₂ ?



Type of cost	estimation, €/tonne CO ₂	range, €/tonne CO ₂	Efficiency penalty, %
CO ₂ compression	10	10	3
Oxy-polishing	6.5	4-9	0.5
Boiler cost	1	0.1-2.3	-
Oxygen carrier	2	1.3-4	-
Steam and hot CO ₂ fluidization	0.8	0.8	0.8
Fuel grinding	0.2	0.2	0.1
Lower air ratio	-0.5	-0.5	-0.5
<u>Total</u>	<u>20</u>	<u>15.9-25.8</u>	3.9

big cost

small cost

Comparison

Aker Energi, offers CO₂ capture at fixed price: 40-90 €/tonne (depending on energy cost)

3) Purification of CO₂ stream

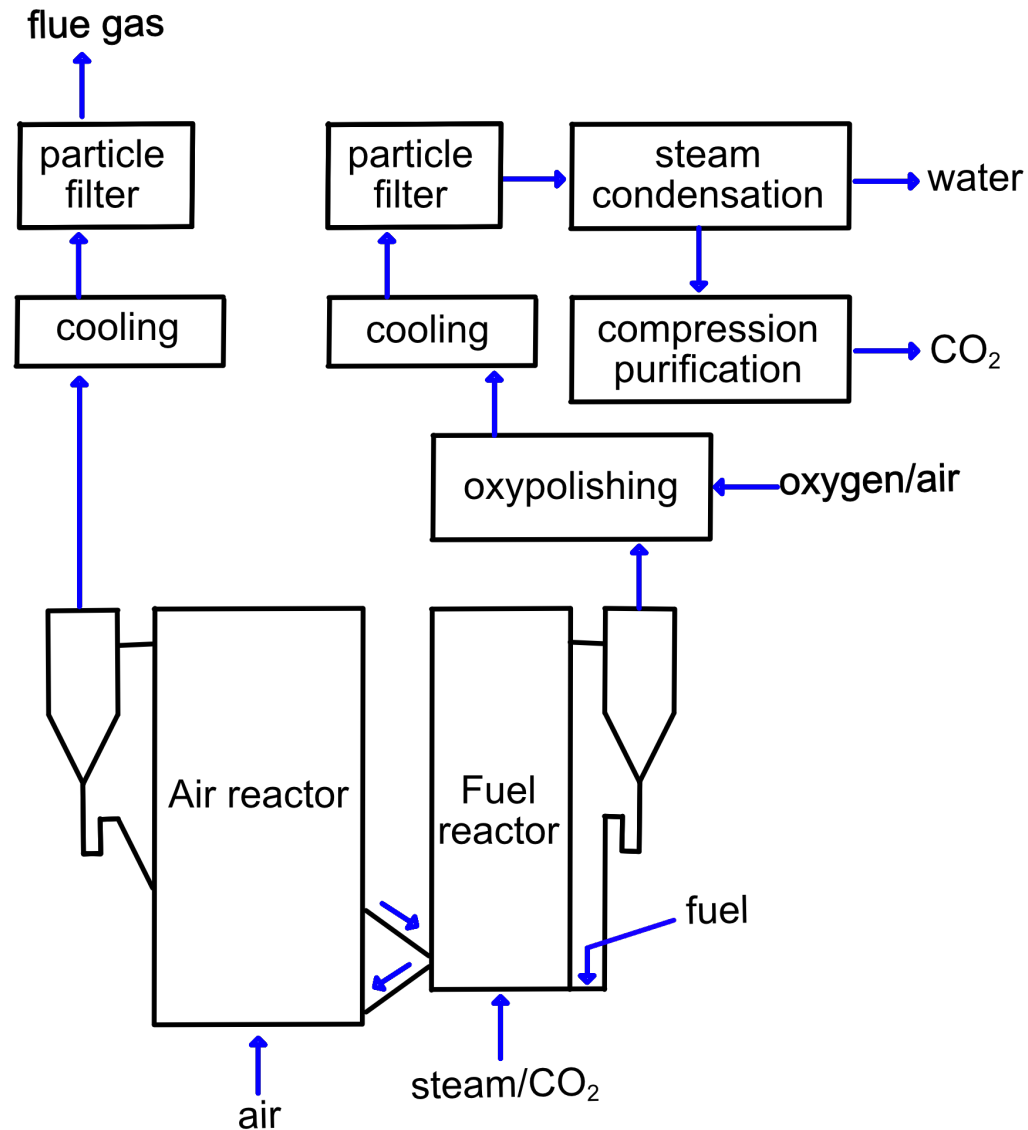


Table 2. Required purity of CO₂. [69, 70]

Component	ppm
Water, H ₂ O	≤30
Oxygen, O ₂	≤10
Sulphur oxides, SO _x	≤10
Nitric oxide/nitrogen dioxide, NO _x	≤10
Hydrogen sulphide, H ₂ S	≤9
Carbon monoxide, CO	≤100
Amine	≤10
Ammonia, NH ₃	≤10
Hydrogen, H ₂	≤50
Formaldehyde	≤20
Acetaldehyde	≤20
Mercury	≤0.03
Cadmium + Thallium (sum)	≤0.03

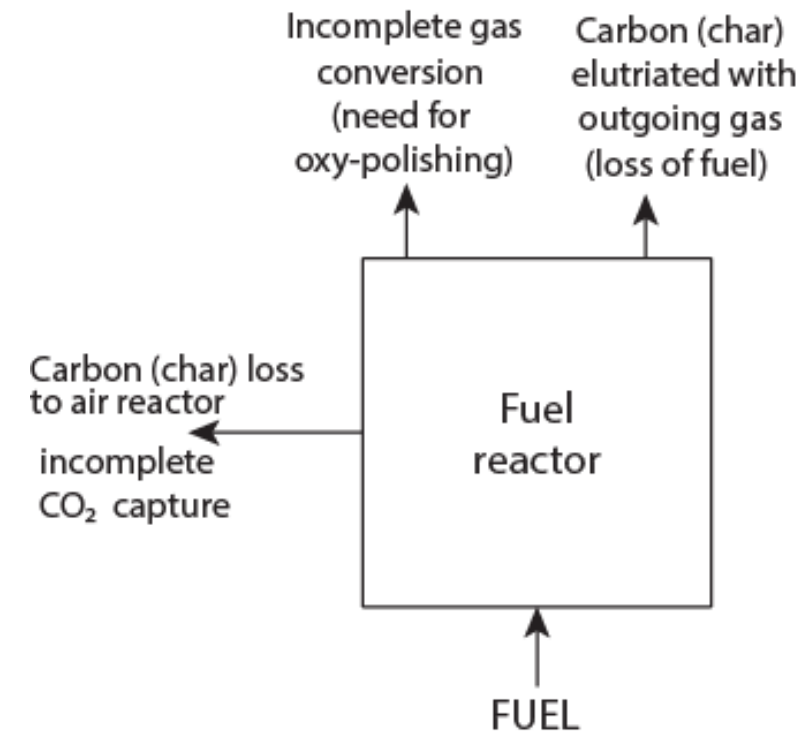
Performance criteria

Operation with solid fuels – 3 aspects of incomplete fuel conversion

1. Gas not fully oxidized to $\text{CO}_2/\text{H}_2\text{O}$
 - oxygen needs to be added after fuel reactor
2. Fine char particles lost from fuel reactor
 - added cost of fuel, increased waste disposal.
3. Char follows particle flow to air reactor.
 - CO_2 capture not complete.

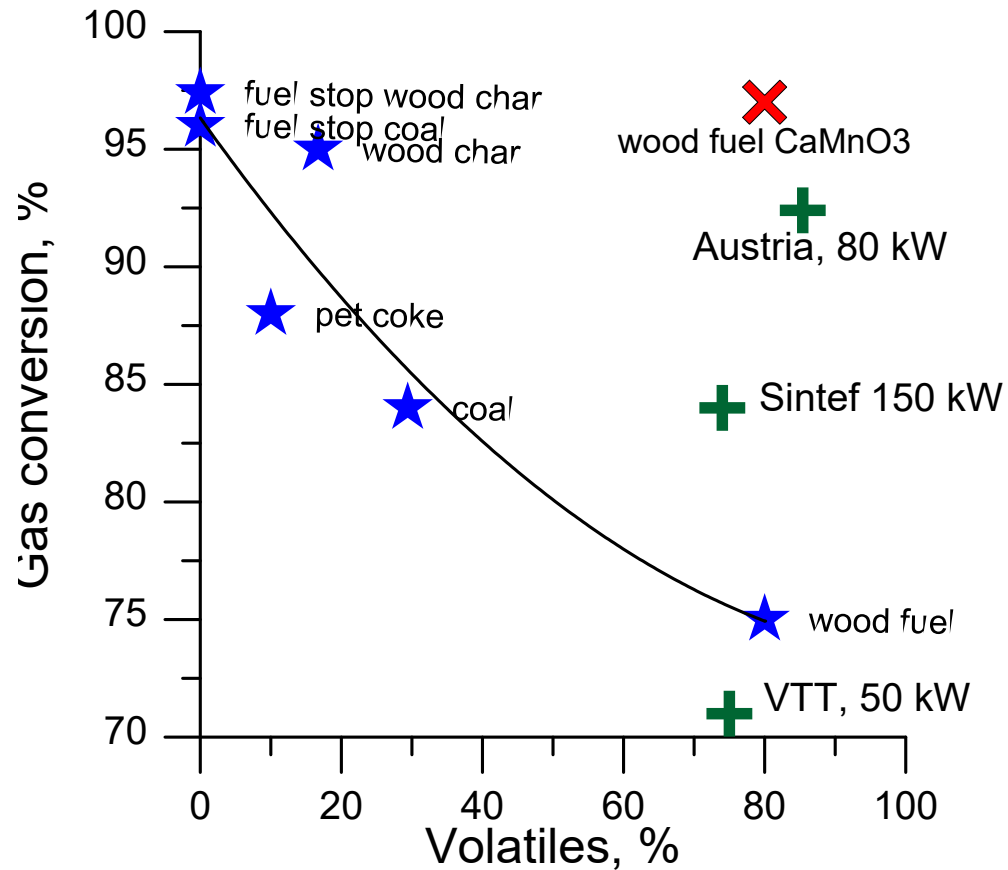
⇒ 3 performance criteria:
⇒ 1) oxygen demand
⇒ 2) carbon loss
⇒ 3) CO_2 capture

2) and 3) no issue with biomass



Gas conversion and volatiles content

Comparison Chalmers 100 kW
and 3 other CLC pilots



Austria 80 kW

- Oxygen demand <10%
- Riser pressure drop of 2 kPa
 - corresponds to 10 kPa in full scale or 100 kg/MW

- 1) Oxygen demand
 - Reactivity of oxygen carrier
 - Temperature
 - Gas-solids contact
 - High for gas from gasification, fuel particles mix with oxygen carrier
 - Poor for volatiles *in bubbling bed operation (by-pass)*
 - ***Solids inventory***, if bubbling bed, increased height doesn't help much
 - ***Riser pressure drop***: high velocity and height

2) Carbon loss (coal)

- Char reactivity
 - Choice of fuel
- H₂O concentration
 - Fluidization of fuel reactor with CO₂ + H₂O, or H₂O only
- **Temperature**
 - Very strong temperature dependence
- Residence time
 - Cyclone efficiency for recirculation of char fines
 - **Riser height**, significant difference between 4 m pilot and 50 m full scale
- Fuel size
 - **Avoid fines**, e.g. pulverized coal
 - *100-300 μm coal likely optimal*

3) CO₂ capture (coal)

- As with carbon loss:
 - Oxygen carrier reactivity
 - H₂O concentration
 - Temperature
- Residence time (different from carbon loss)
 - Solids inventory
 - Carbon stripper
- Fuel size
 - **Avoid large particles**
 - **0.1-0.3 mm coal** likely optimal (cf. carbon loss)

Selective Non-Catalytic Reduction of NO Needed ??

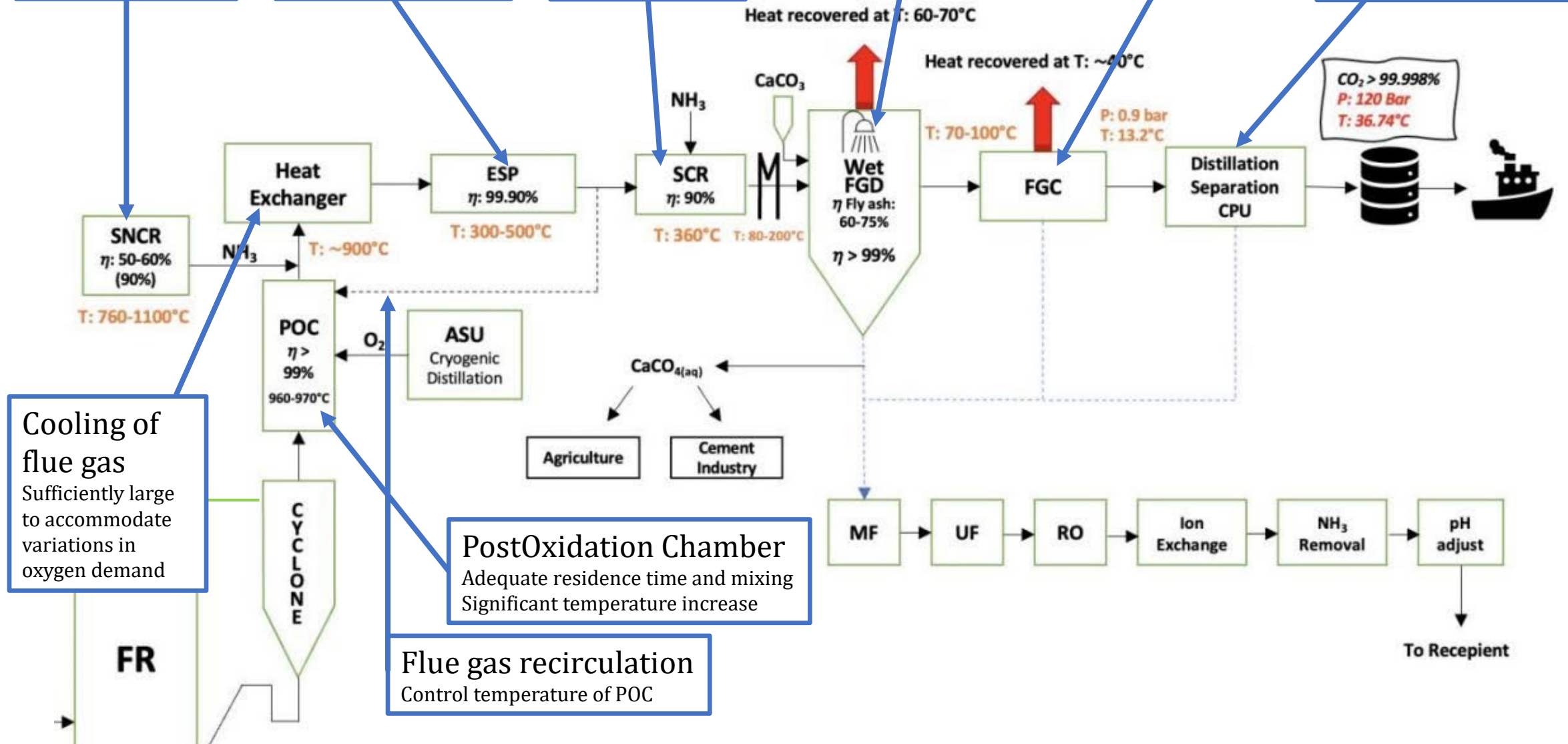
Electrostatic Precipitator or bag filters to remove particles

Selective Catalytic Reduction of NO Needed ?

Flue Gas Desulfurization Needed for coal But biomass ??

Flue Gas Condensor High content of H₂O to remove

Compression and distillation to reach ppm levels of contaminants



Postoxidation chamber

Oxygen added in small excess

combustibles oxidized to H_2O and CO_2

any reduced N and S compounds (NH_3 , HCN , H_2S) oxidized to NO/N_2 and SO_2

Mixing and residence time important

Temperature increase, downstream system should be designed to accommodate for variations

Essentially no N_2 , so no thermal NO_x , but formation of NO if NH_3 present

Cost for oxygen production, i.e. gas separation.

If oxygen demand 5, 10 or 20%, need for gas separation is still reduced by a factor of 20, 10 or 5

Measures for purification

1) Elimination of in-leakage

Downstream costs for removal of air ingress are very high.

Should not be a major technical issue to assure no, or very low, air ingress.

- Construction measures to assure no inleakage
 - Moving joints can use bellow seals and barrier gas (CO_2)
 - Measures to seal discharge of fly-ashes
- Strict protocols for avoiding mistakes leading to air ingress
- Careful monitoring of gas purity, to detect and address any inleakage

2) Removal of SO_2

Any SO_2 present must be removed by wet flue gas desulphurization. Can be done in connection with water removal. Concentrated stream lowers costs, whereas need for high purity increases costs.

3) Removal of NO_x

Perhaps not needed ?

- Partly reduced oxygen carrier ilmenite is efficient in reducing NO to N₂ and oxidizing NH₃ to NO
- Only way of NO formation in FR is by oxidation fuel nitrogen by oxygen carrier.
- Equilibrium NO concentration in fuel reactor below 0.001 ppm

If needed:

- Conventional Selective Catalytic NO_x Reduction.
 - High reduction not possible
 - Incoming NO needs to be low
- Co-removal of NO and SO₂, at pressure, e.g. 30 bar.
 - Oxygen must be present
 - Deep reduction not possible, incoming NO must be low
 - Not commercial technology
- Addition of Cl₂O, to the co-removal system
 - Deeper reduction possible
 - Not commercial technology
- Distillation of CO₂

Addition of 10 000 ppm of NO or NH₃ to the inlet stream (fuel/inert) of a 300 W CLC pilot with ilmenite shows:

In presence of fuel,

NO is completely reduced to N₂

No NH₃ is oxidized to NO

With no fuel and fully oxidized oxygen carrier:

NO is not reduced

Some NH₃ is oxidized to NO

With no fuel and partly reduced oxygen carrier:

NO is completely reduced to N₂ (NO below detection limit, <10 ppm)

No NH₃ is oxidized to NO (NO below detection limit, <10 ppm)

=> *There is good reason to assume that in a high riser, any NO formed would be reduced.*

CLC pilot data shows: 0-2000 ppm for coal

Reference	Size, kW	Oxygen carrier	Temp, °C	Fuel	Inlet N fraction	NO _x ppm, (normalized)	N-conversion to NO _x %
Song et al. ⁵⁷	1	NiO	850-950	Bitum. coal	1.03% ad ^b	400-630	
Song et al. ⁵⁷	1	NiO	850-950	Anthracite	1.39% ad ^b	1-20	
Song et al. ⁵⁸	1	Fe ₂ O ₃	970	Bitum. coal	1.03 % ad ^b	0	0
Song et al. ⁵⁸	1	Fe ₂ O ₃	970	Anthracite	1.39 % ad ^b	0	0
Markström et al. ⁵⁹	100	Ilmenite	960	Bitum. coal	1.65 % daf ^a	1000-2000	10-20
Linderholm et al. ⁶⁰	100	Ilmenite	950-970	Wood char	0.4% daf ^a	500, (850)	7-32
Mendiara et al. ⁶⁵	0.5	Ilmenite	875/930	Lignite	0.6%	20	1
Gu et al. ⁶⁷	1	Fe ₂ O ₃	880-980	Bitum. coal	1.03% ad ^b	24-68	0.5-0.8
Ohlemüller et al. ⁶⁹	1000	Ilmenite, Iron ore		Coal, coal + biomass	1.81%, 0.17%	0, 20, 8	

One work in 100 kW with biomass shows 20-70 ppm

100 kW work also shows significant amounts of NH₃
This is (partly) oxidized to NO in postoxidation chamber

But, in commercial scale, with a high riser ???

Conclusion

Large uncertainty with respect to presence of NO_x

4) Removal of O₂

Catalytic combustion

- at high temperature with CH₄
- at lower temperature with H₂

5a) Compression with single flash separation

With flash separation compounds of low solubility, e.g. N₂, NO, O₂, can be partly removed, depending on pressure.

Could be sufficient, if concentrations of gases that need deep reduction is low enough.

Power need 2.9 - 3.8% of fuel heating value (coal),

5b) Compression with cryogenic distillation

Remove gases with low solubility in CO₂ to ppm levels.

Removal steps 3) NO and 4) O₂ not needed.

Power need 7% of fuel heating value (coal)

Necessary if NO cannot be lowered enough in 3)

6) Drying of CO₂

Water can be removed using molecular sieves or a dessicant, e.g. triethylene glycol

Commercial CLC plant

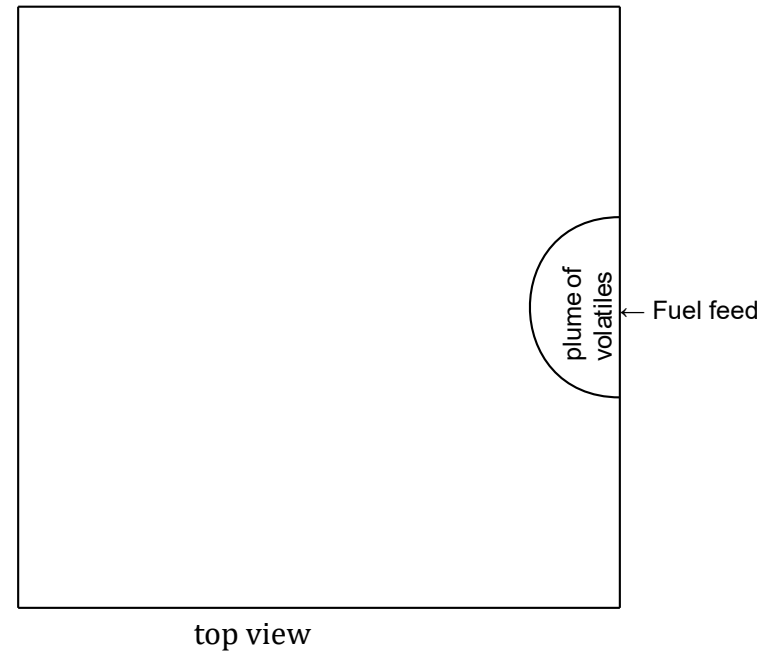
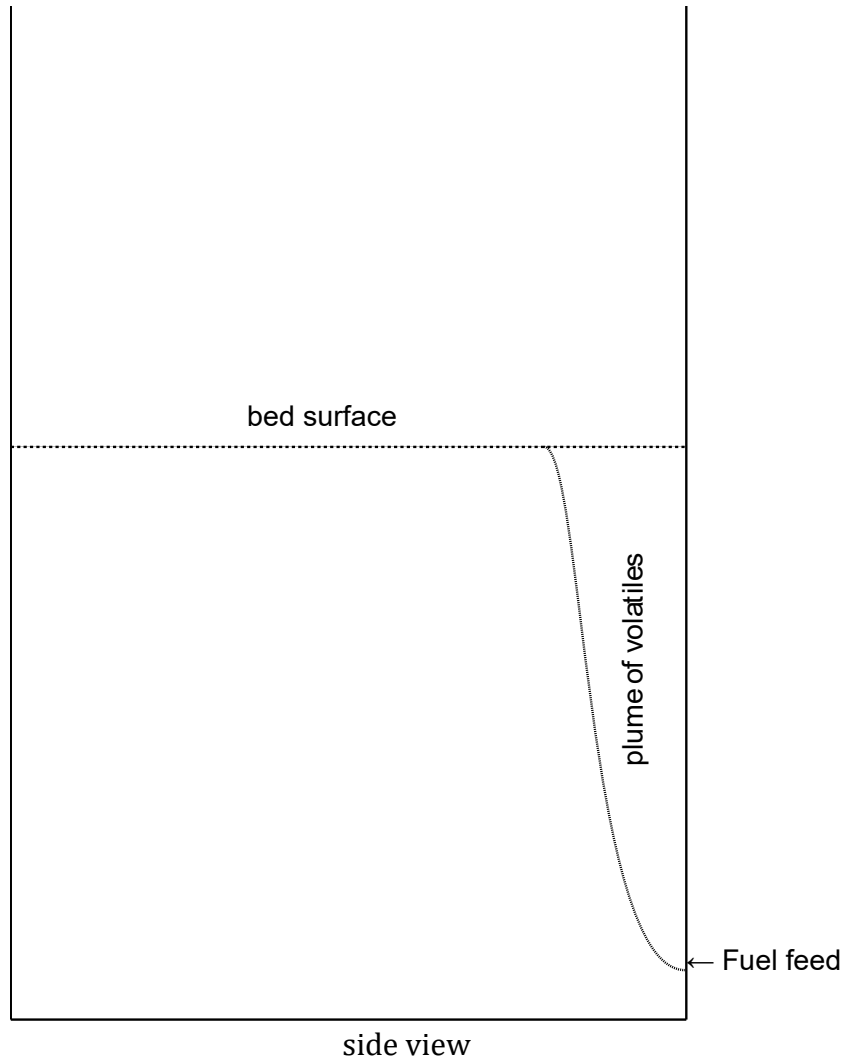
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Three critical aspects that must have adequate solution

- 1) An oxygen carrier that works ☒**
- 2) Adequate circulation ☒**
- 3) Downstream treatment of gas from fuel reactor to achieve a CO₂ that fulfills purity requirements for transportation/ storage ☒**

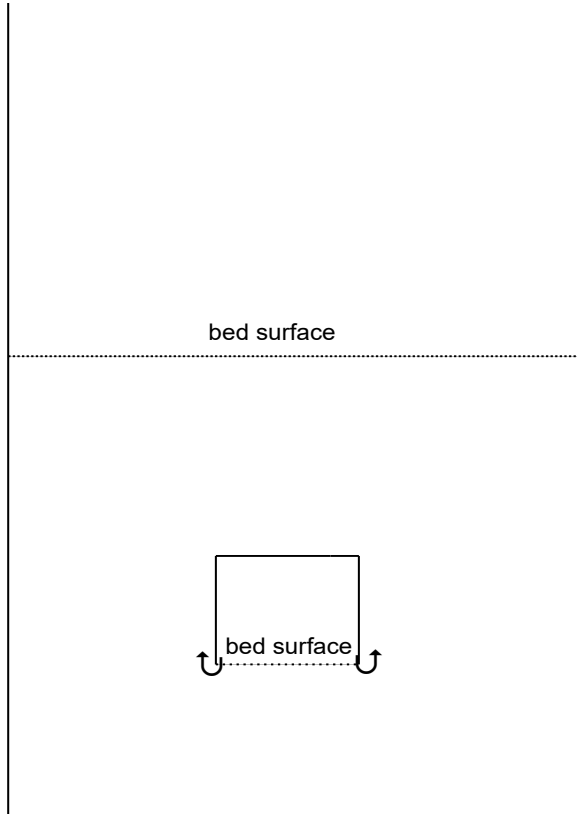
Conversion of volatiles

A local plume of volatiles in the bottom part reduces contact

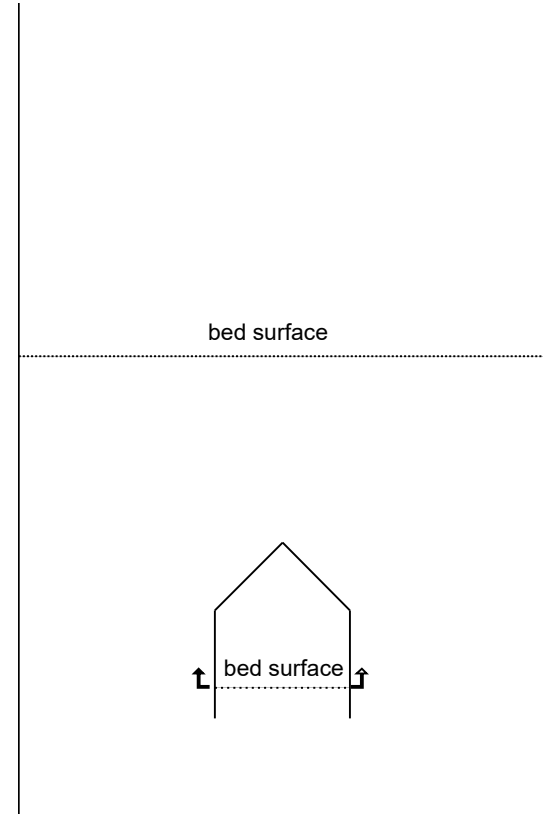


A box placed with the opening downwards in a fluidized bed will become empty and have a bed surface in the bottom.

(If you doubt this see: <http://www.entek.chalmers.se/lyngfelt/co2/Box.htm>)

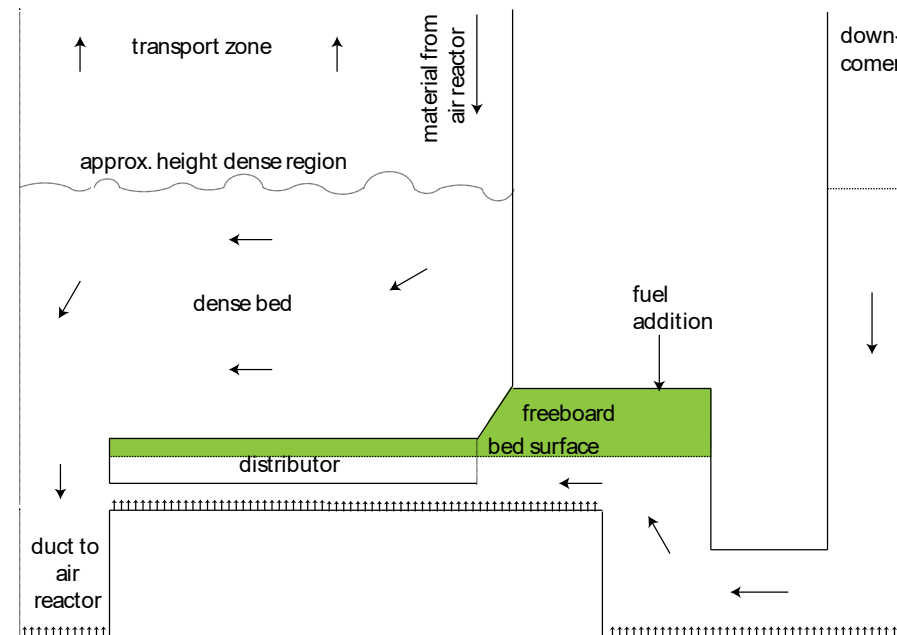
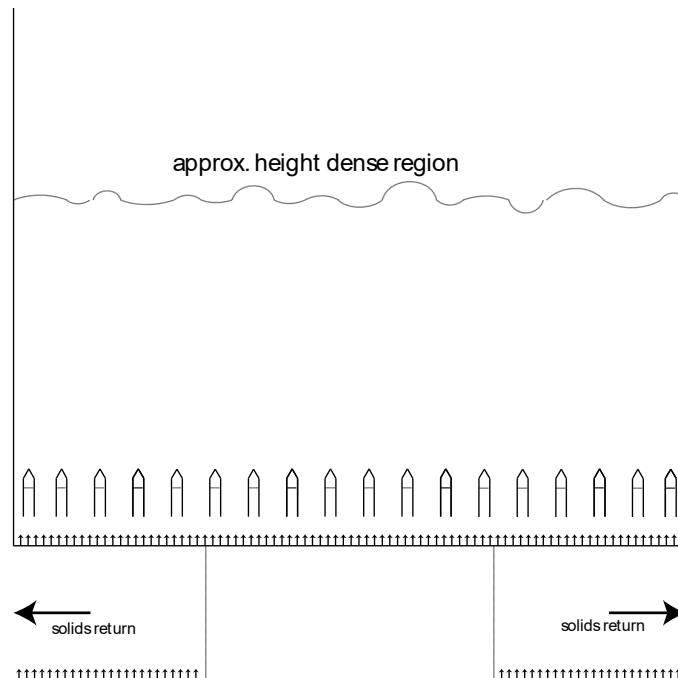
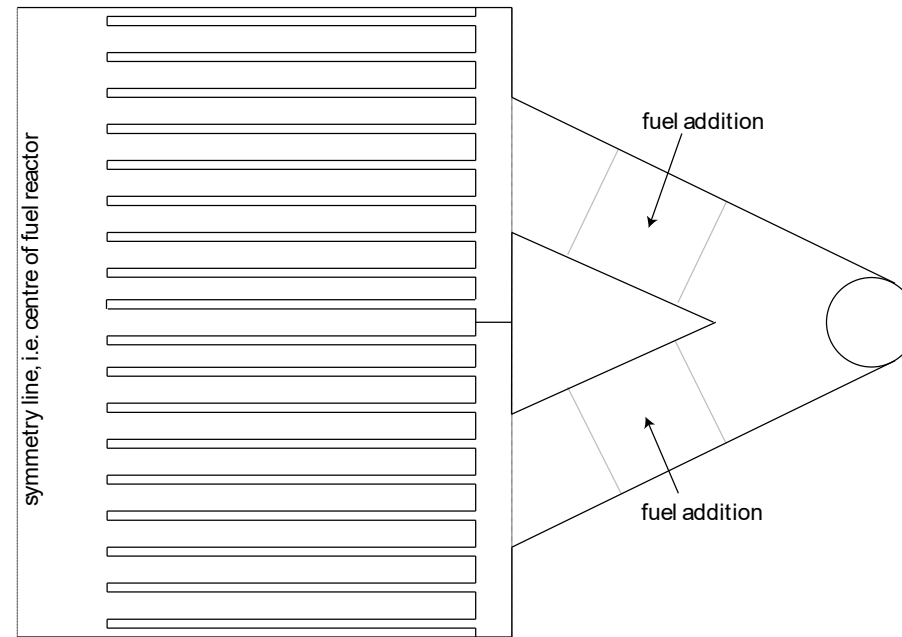
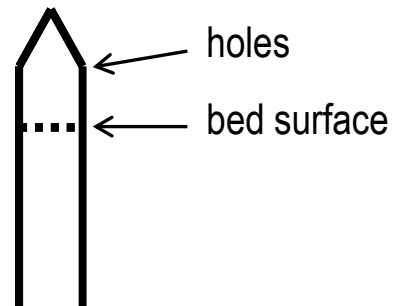


If gas is injected in the box, it will be released at the sides.



If there are holes in the side of the box, the bed level will rise up to these holes.

- Such a "box" can have any form, e.g. long arms, and be used to distribute volatiles.



More on the volatiles distributor

Li, Xiaoyun; Lyngfelt, Anders; Pallares, David; Linderholm, Carl; and Mattisson, Tobias, Investigation on the performance of volatiles distributors with different configurations under different fluidization regimes, *Energy & Fuels*, 36:17 (2022) 9571–9587 <https://pubs.acs.org/doi/pdf/10.1021/acs.energyfuels.1c04159>

Xiaoyun Li, [Experimental study of a Volatiles Distributor for Improving the Cross-sectional Gas Distribution in Fluidized Beds](#), Licentiate Thesis, Dept. of Energy and Environment, Division of Energy Technology, Chalmers University of Technology, Göteborg, Sweden 2022.

Lyngfelt, A., Pallarés, D., Linderholm, C., Rydén, M., Mattisson, T., "Fördelare av gaser i fluidiserad bädd" ("Distributor of volatile gases in the bottom part of a fluidized bed"), [Swedish patent application No. 1400085-5](#), 2014-02-17

Lyngfelt, A., [Solid fuels in Chemical-Looping Combustion – Feeding of fuel and distribution of volatiles](#), *22nd International Conference on Fluidized Bed Conversion*, June 14-17, 2015
Turku, Finland

Chemical Looping combustion (CLC)

CLC boiler very similar to CFB boiler (=circulating fluidized-bed boiler)

Highly concentrated CO₂ stream can be obtained at small added cost

Cost: 25-50% of competing technologies for solid fuels

- Eliminate/reduce emissions of SO₂ (coal)
- Eliminate/reduce emissions of NO_x (coal and biomass)
- Eliminate/reduce problems with alkali ash components (biomass)

Steam Methane Reforming with CLC

- Potential for lower cost than conventional SMR without CO₂ capture, i.e. ***negative*** capture cost



Thank you!

Presentations at:

<https://www.entek.chalmers.se/lyngfelt/presentations/presentations.html>

CLC publications at:

<https://www.entek.chalmers.se/lyngfelt/co2/co2publ.htm>

Removal of CO₂ from the atmosphere = Negative Emissions

Bio-CCS

Growing trees/plants remove CO₂ from the atmosphere.

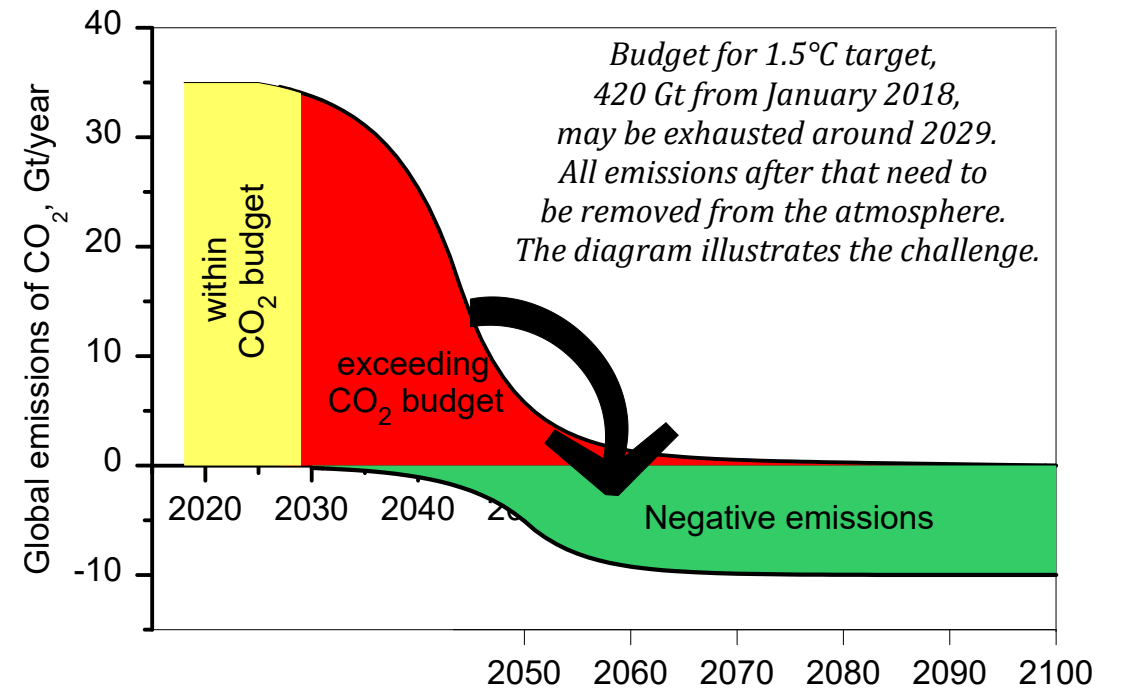
BUT, the CO₂ can be prevented from returning:

Capture and storage of CO₂ from combustion of biomass/biowaste

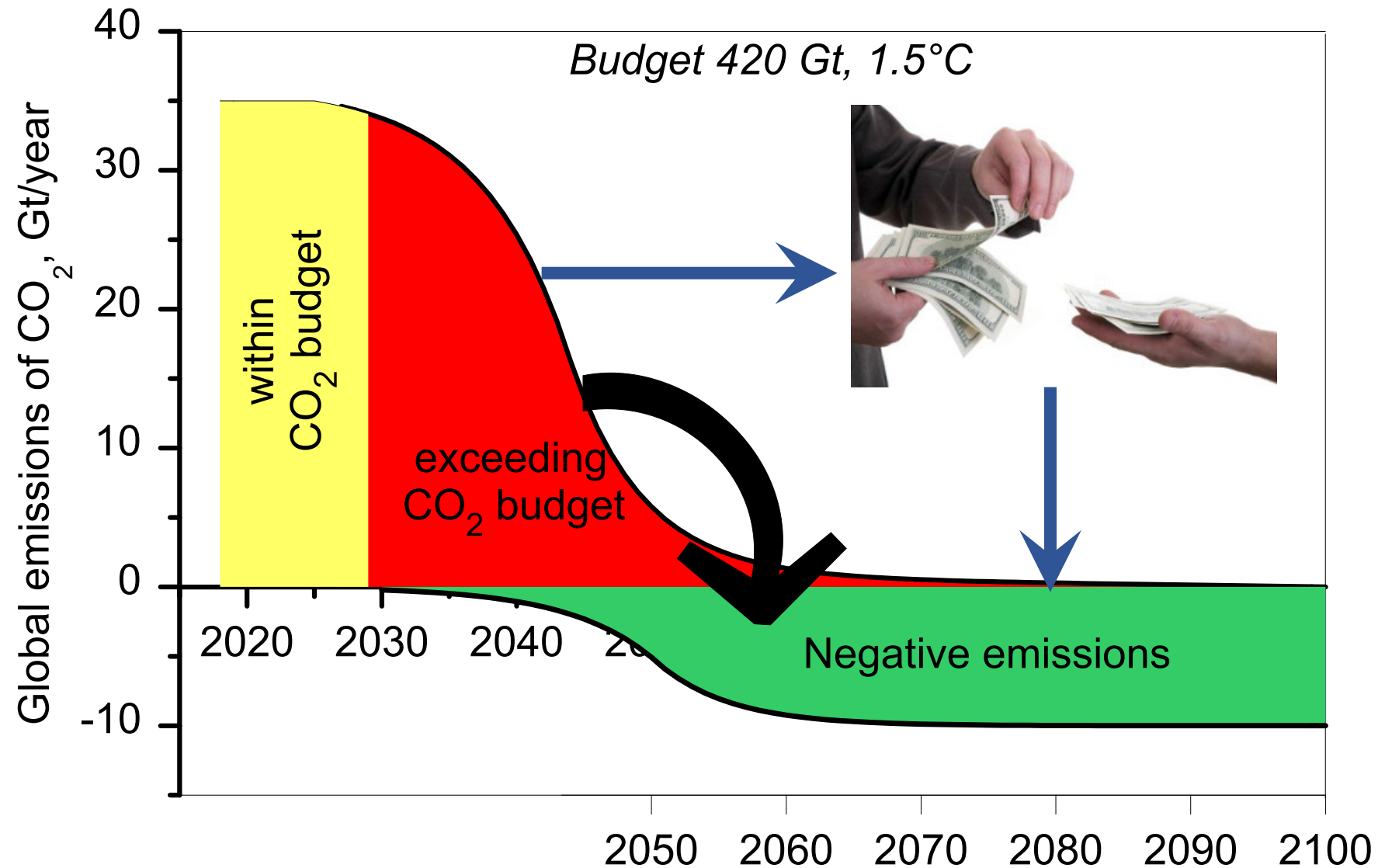
Bio-CCS (BECCS)
(BioEnergy Carbon Capture and Storage)



- Global carbon budget for +1.5°C likely spent around 2029
- Emission reductions cannot be made fast enough to meet the target
- To meet max 1.5°C, all CO₂ emissions after 2029 must be removed from the atmosphere.
- Enormous negative emissions needed to meet max 1.5°C,
- **No realistic mechanism for financing of future negative emissions in place.**



Proposal: Make emitters responsible for, i.e. pay for, removing emitted CO₂ from atmosphere



Atmospheric CO₂ Removal Deposits (ACORDs)

