Chemical-Looping Combustion without the Costly and Energy-demanding Gas Separation

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Meeting with BASF

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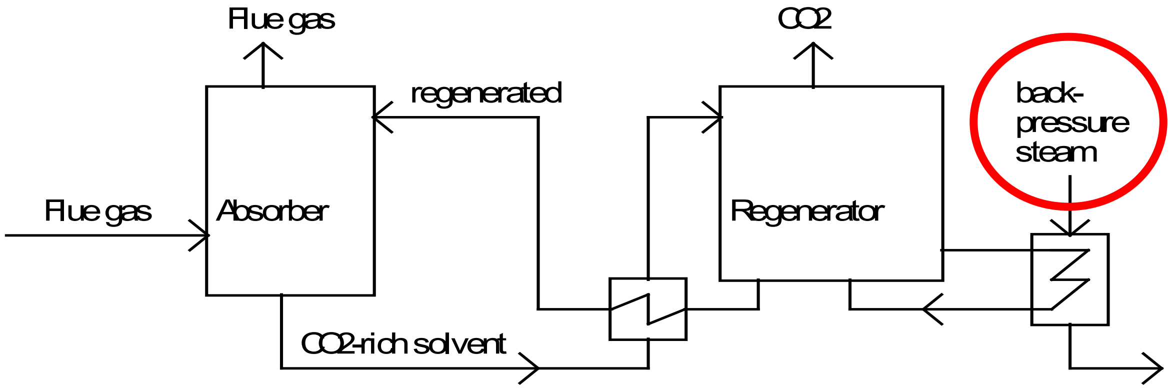
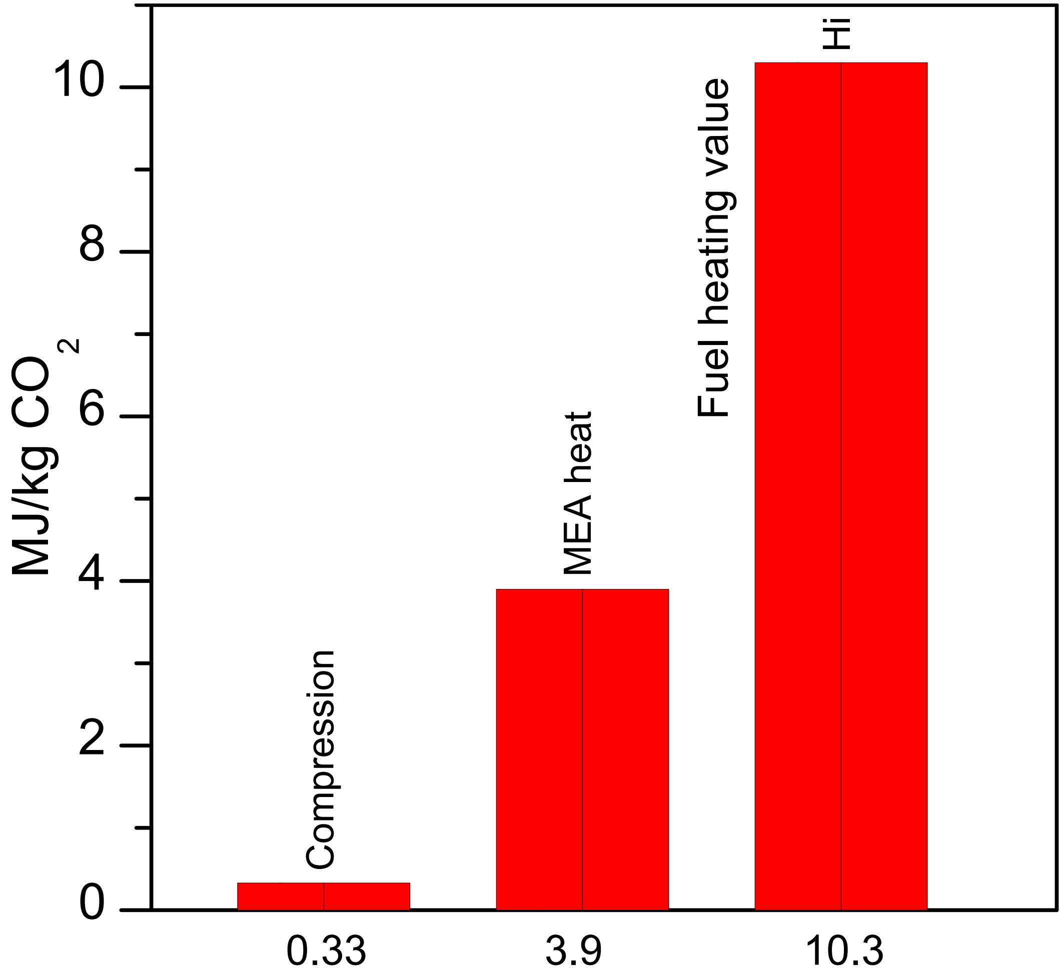
CHALMERS

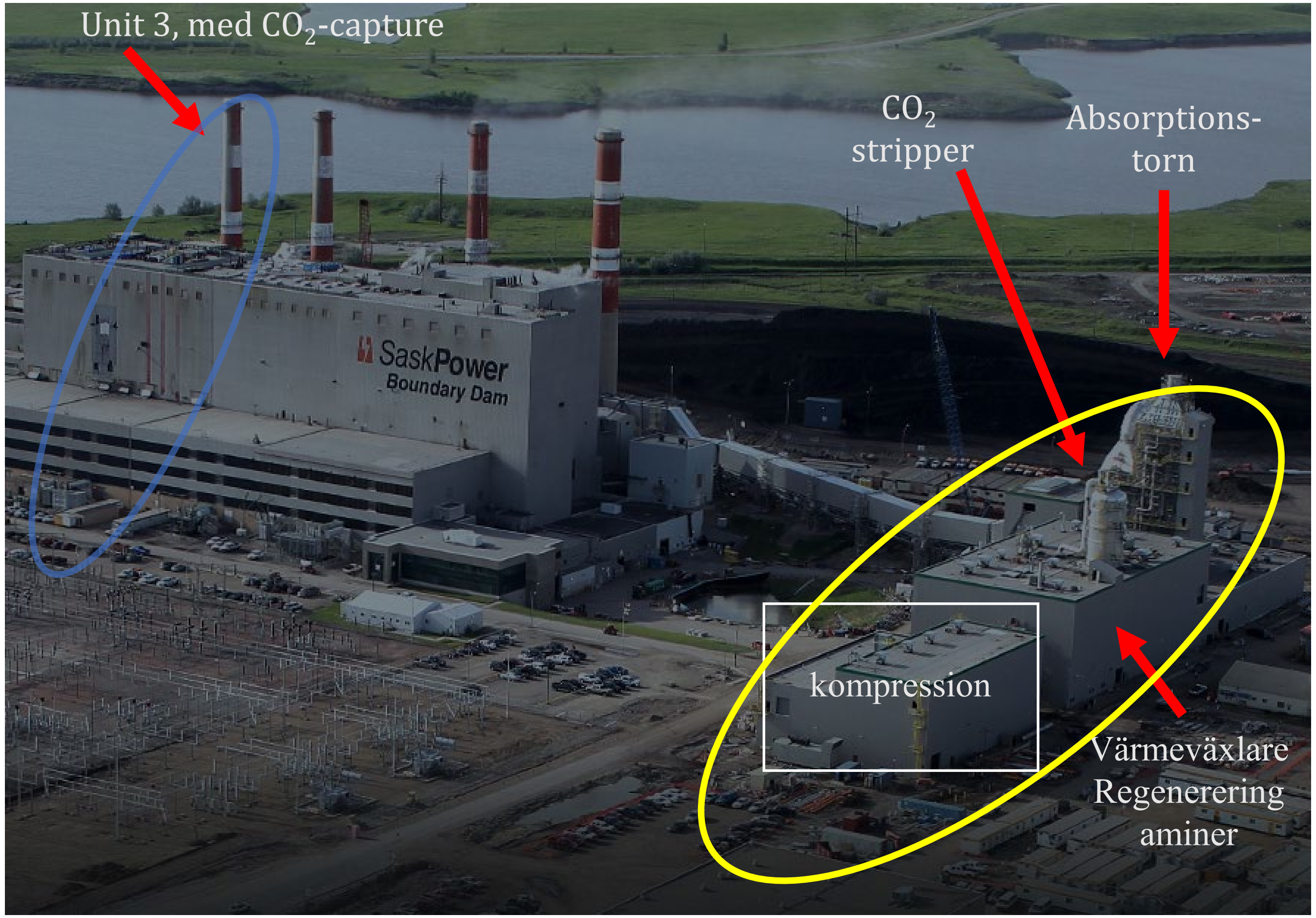
Absorption of CO_2 med monoethanolamine (MEA)





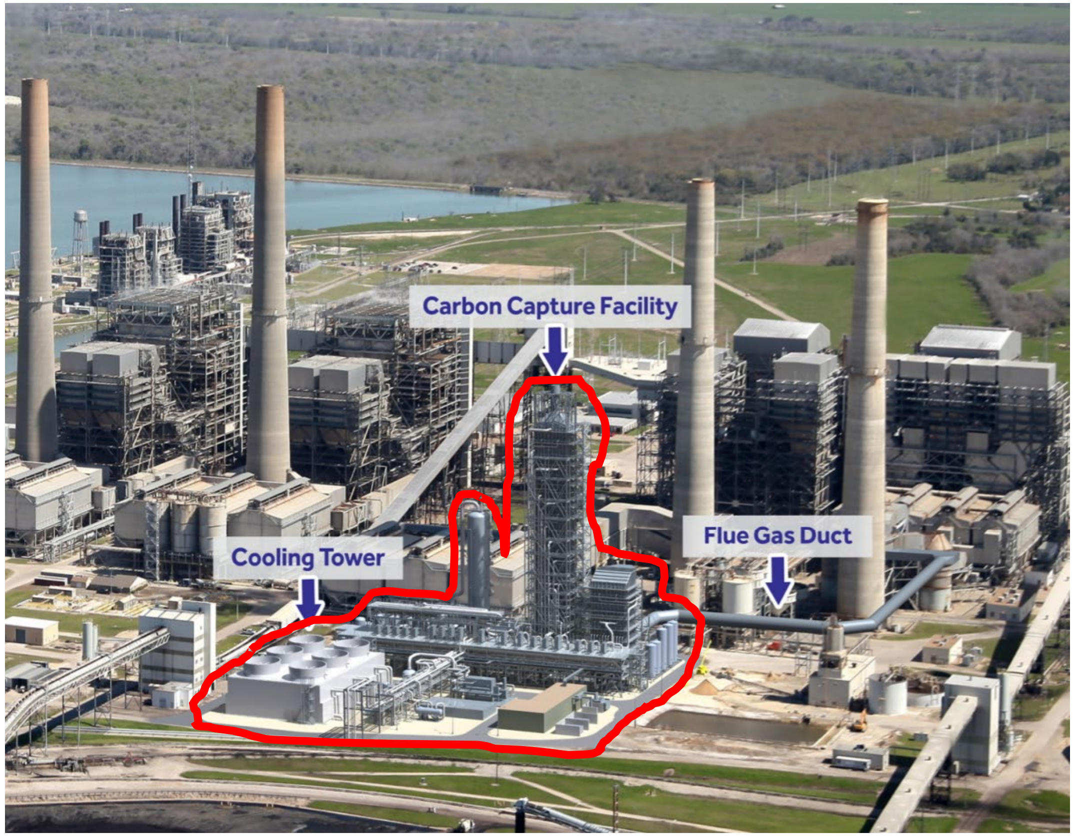
Status CCS

Boundary Dam, Unit 3, 110 MW, 1 MtCO_2/year, start 2014



Capture: 0.62 Mt/year first 6.5 years

Petra Nova, 1.4 Mt/year, start 2017



Shut down 2020

Large cost for equipment, operation and energy.

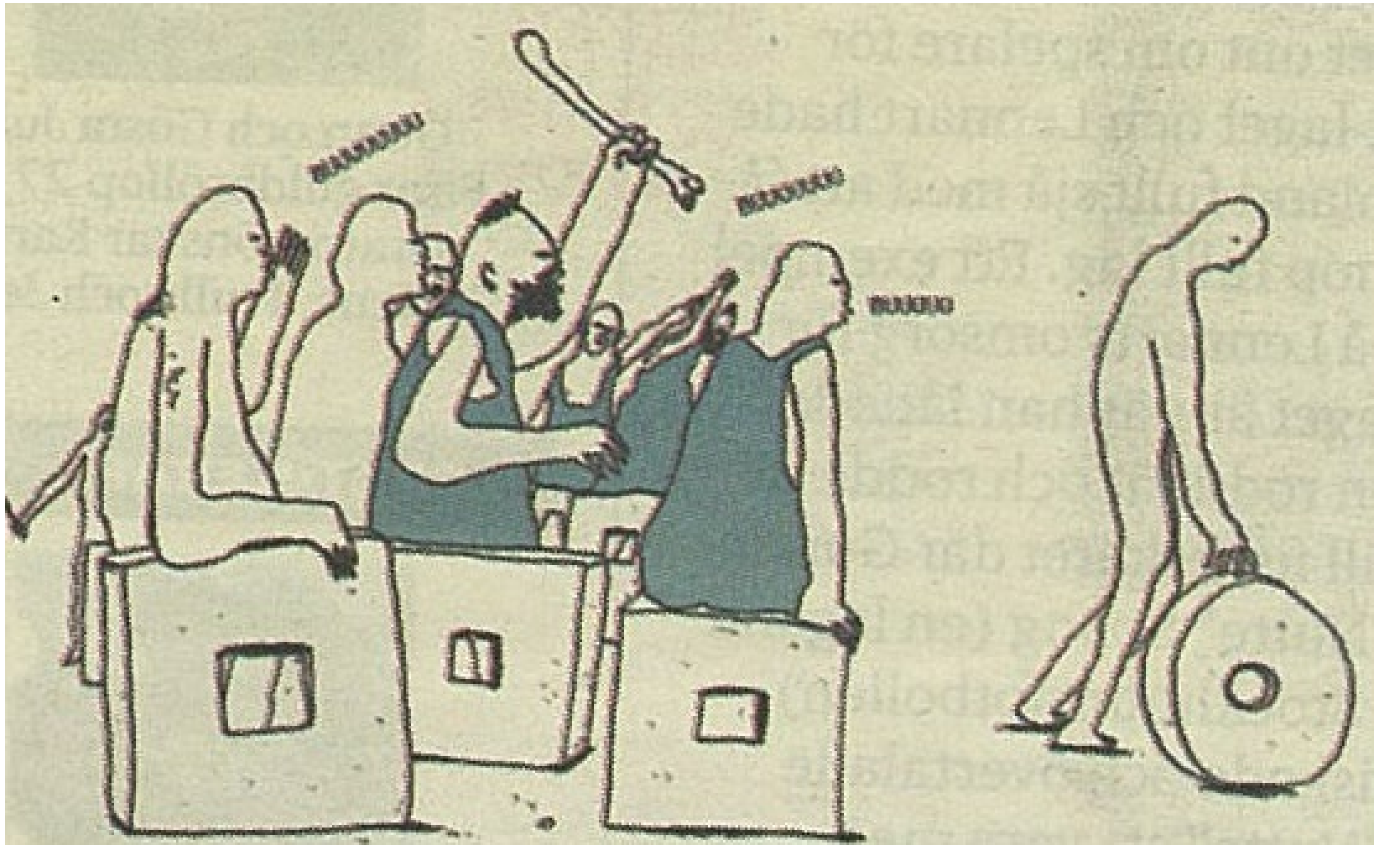
Problem:

Gas separation

Why:

fuel is mixed with combustion air

>> CO_2 diluted in nitrogen



Can it be avoided?

YES!

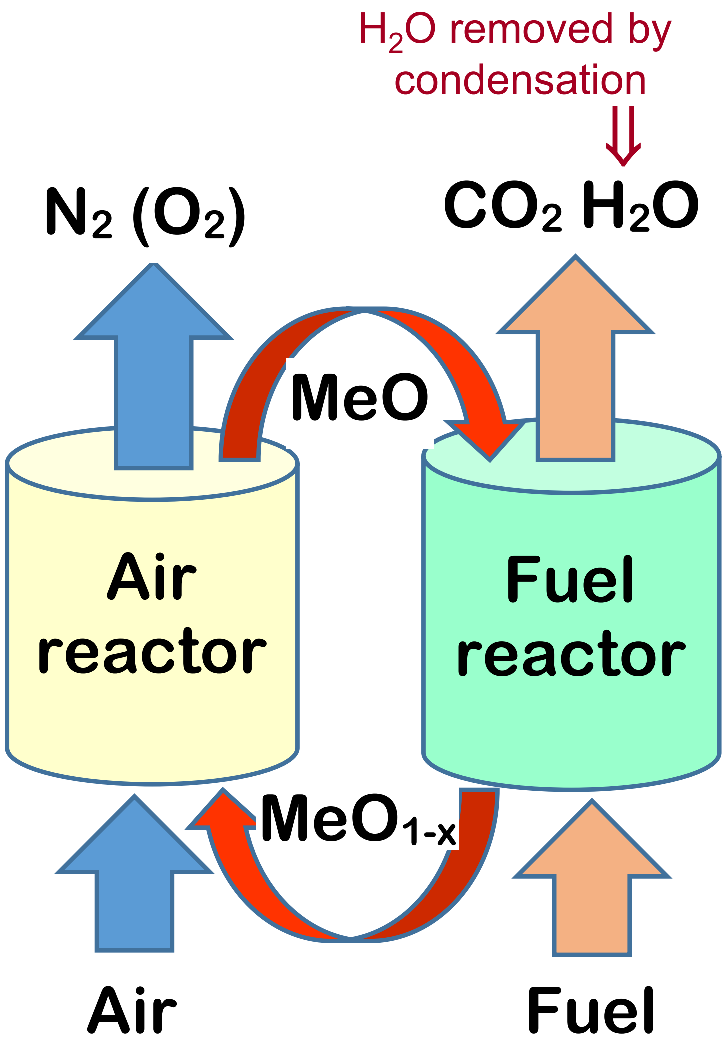
Chemical-Looping Combustion (CLC)

Oxygen is transferred from air to fuel by metal oxide particles

Inherent CO_2 capture:

- fuel and combustion air *never mixed*
- *no active gas separation needed*

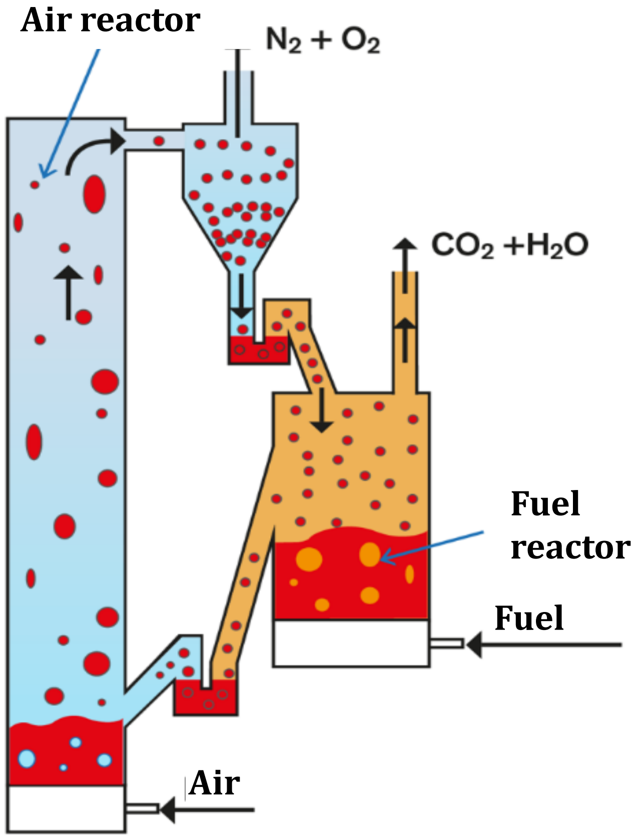
<u>Unique</u> potential for reducing costs of CO_2 capture!



High similarity between Chemical Looping Combustion and Circulating Fluidized-Bed (CFB) boilers

Circulating fluidized-bed boiler
(commonly used for solid fuels)

Chemical Looping Combustion
(typical pilot design)



But, does it work in practice ?

Total chemical-looping operation at Chalmers: 4 200 h in four pilots

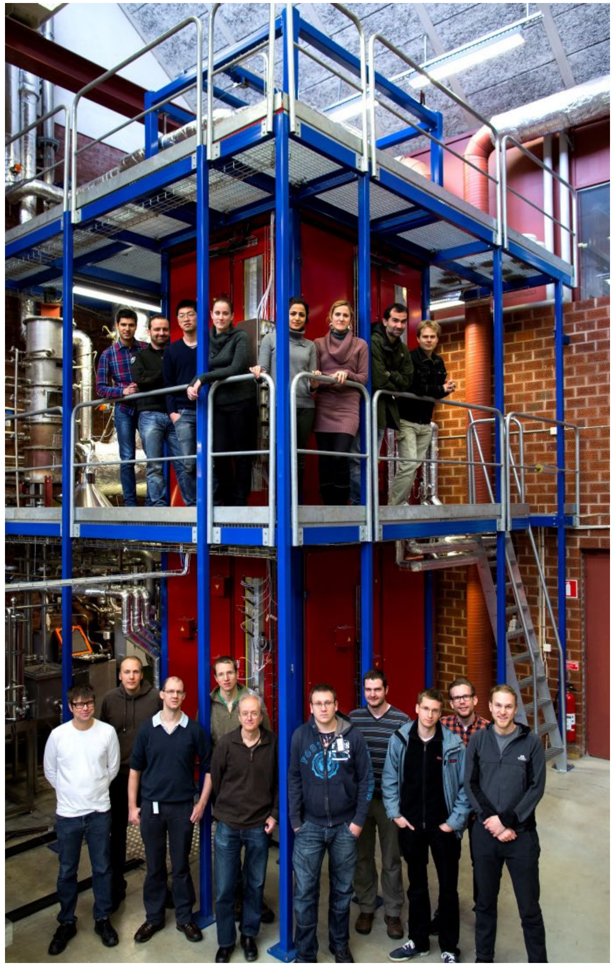
Yes, it works!!

Worldwide: >12 000 h in >50 pilots

10 kW gas, 2003

300 W gas, 2004

10 kW solid fuel, 2006



100 kW solid fuel, 2011

The oxygen carrier is the cornerstone of CLC
(analogous to the blood transferring oxygen in the body)

The oxygen carrier is made up of metal oxide particles of size 0.1-0.3 mm.

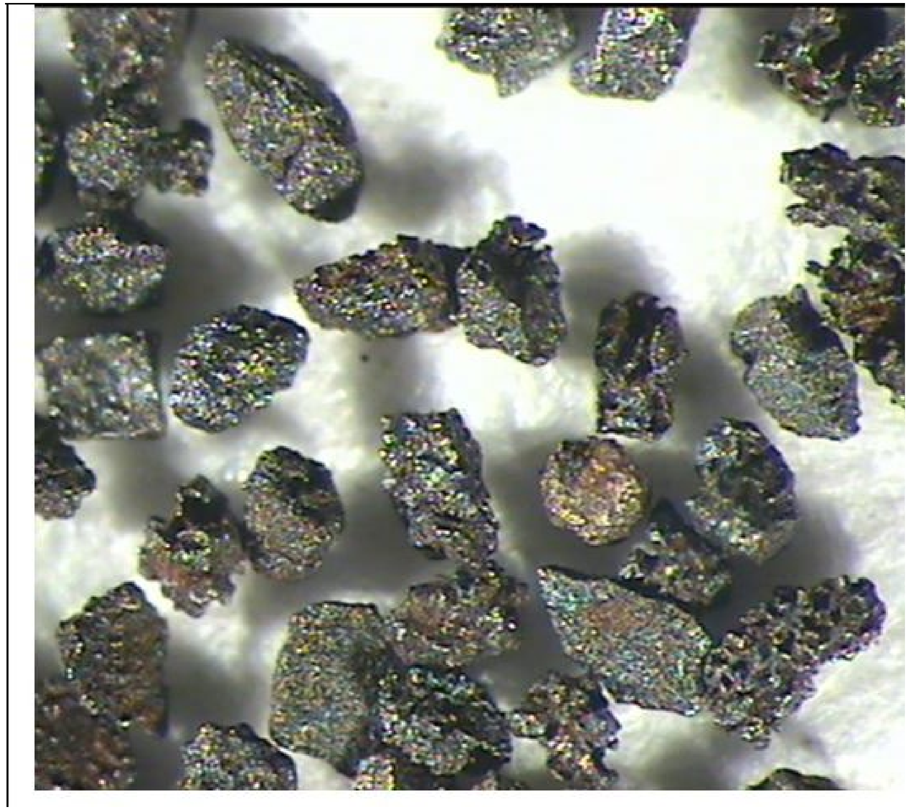
Operational temperature in CLC is typically 900 – 1100°C

Manganese, iron, copper, nickel and ***combined* oxides*** have been successfully used in chemical-looping pilot operation.

Low-cost natural ores, e.g. manganese, iron or ilmenite, are well suited for solid fuels.

Highly performing manufactured materials are better for ash-free gaseous fuels,

e.g. calcium manganate ($CaMnO_3$)
- Full gas conversion
- Long lifetime
- From low cost raw materials



Manganese ore particles used in CLC.
Size fraction 0.18-0.21 mm

* e.g. Mn + Ca/Fe/Mg/Si and Fe + Ti (=ilmenite)

Chalmers' research in CLC

26 years development

>450 scientific publications

>260 peer-reviewed articles

23 doctoral theses

>20,000 citations

>500 oxygen carriers tested in the lab

>70 oxygen carriers in pilot operation

4 CLC pilots with ⅓ of global operating experience

Close collaboration with leading partners in Europe in >10 EU projects

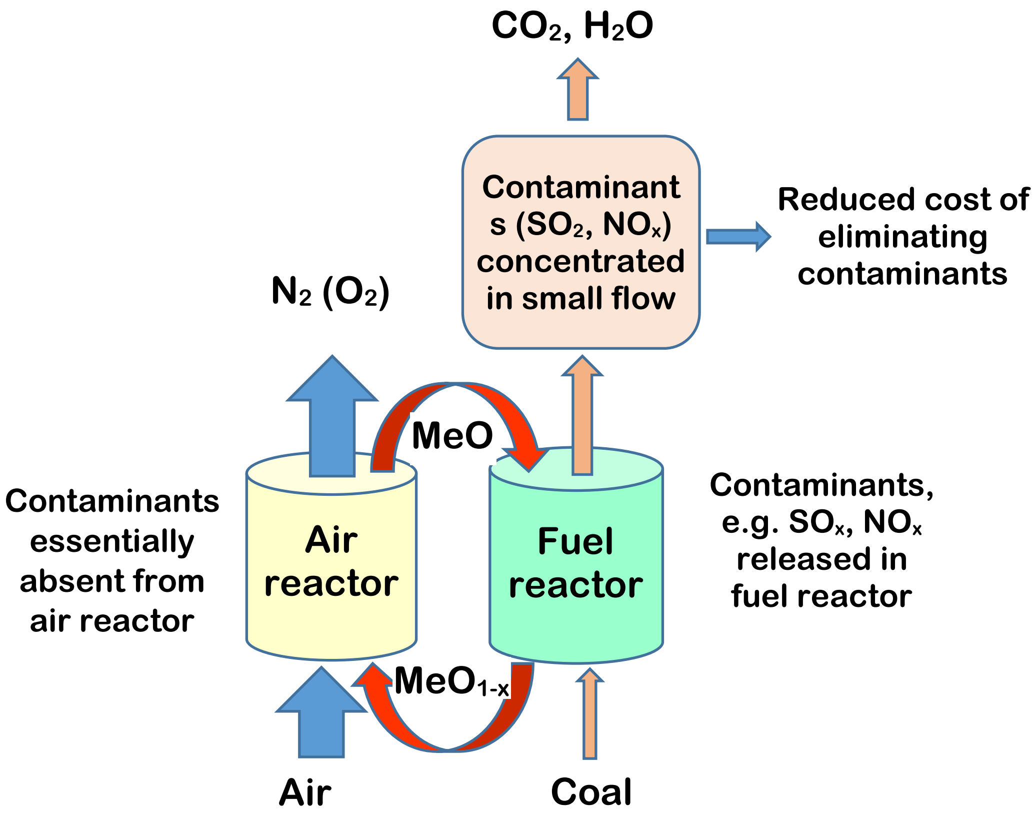
> 20 M€ (our share), >50 M€ (including partners)

Potential applications of CLC technology

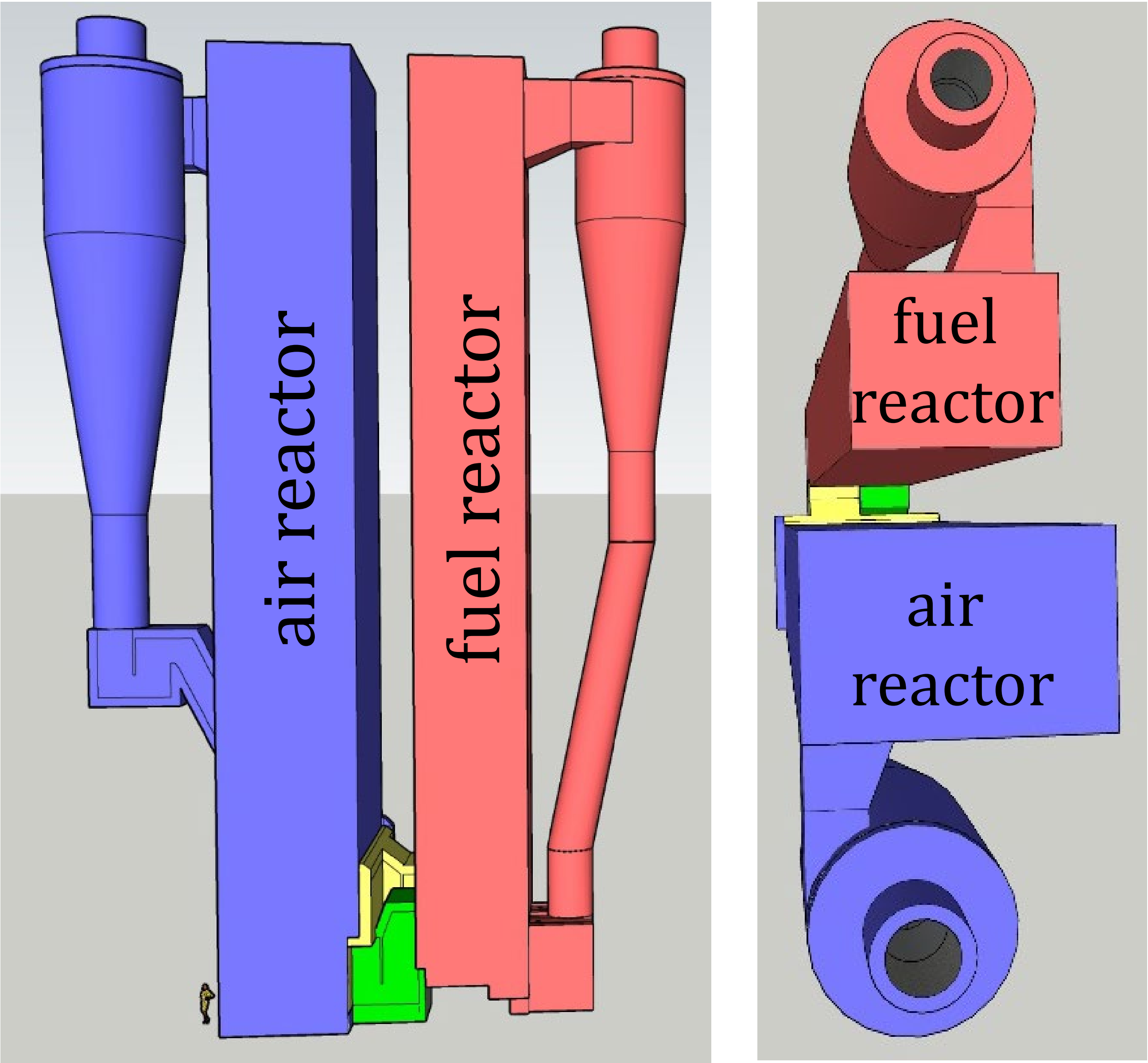
- Coal combustion
- Biomass/waste combustion (negative emissions)
- Steam-Methane Reforming with Chemical-Looping Combustion (SMR-CLC)

Chemical-looping combustion of biomass/waste

- high similarity to normal circulating fluidized bed combustion
- small added cost, low energy penalty
- pollutants concentrated in CO_2 could reduce costs of SO_x/NO_x reduction
- large potential market
- important advantage with respect to alkalis
- negative emissions, future need for meeting exceeded carbon budgets
- ***unique potential for dramatic reduction in CO_2 capture cost***



200 MW combined CLC-CFB boiler, 40 m high

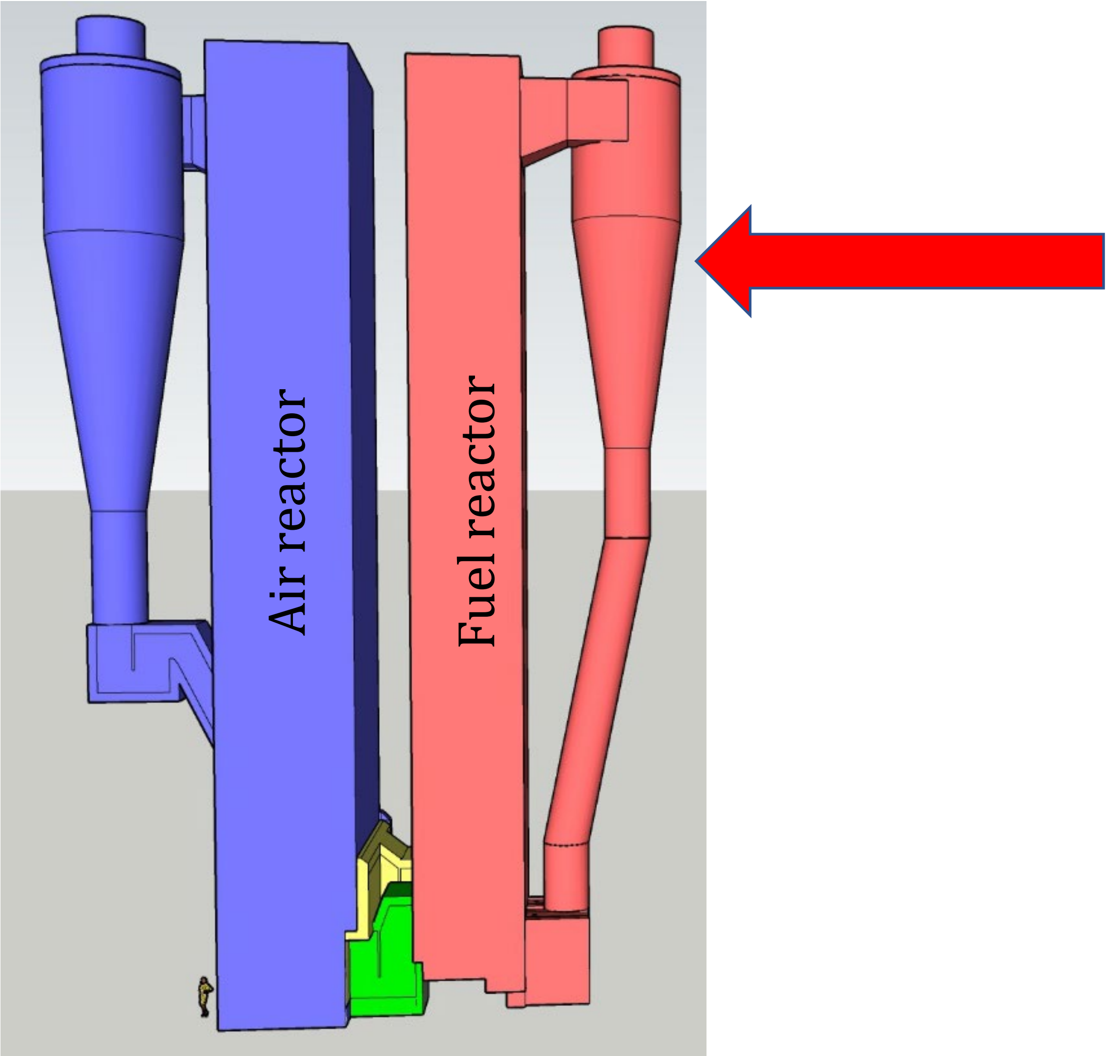


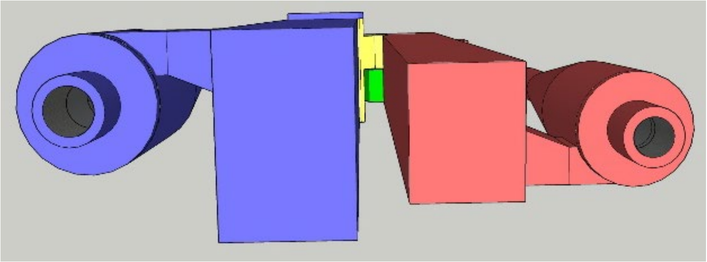
Air reactor can also be used as CFB boiler

- Seamless switching between CLC and CFB operation

Circulation based on collecting downfall along riser walls of air reactor

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





200 MW CLC-CFB, added cost of Fuel Reactor:

1500 m^2 insulated wall
at
2000 €/m^2

>>> 3 M€

or

0.3 M€/year

capture: 0.4 Mt CO_2/year

cost of fuel reactor : **0.75 €/t CO_2**

Cost of post-combustion CO_2 capture:
around 100 €/t CO_2 ?

Costs, CLC of solid fuels, estimated at 16-26 €/tCO_2

big cost

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
Total	20	15.9-25.8	3.9

small cost

[1]Lyngfelt, A., and Leckner, B., A 1000 MW_{th} Boiler for Chemical-Looping Combustion of Solid Fuels - Discussion of Design and Costs, *Applied Energy* 157 (2015) 475-487

Blue hydrogen (=”CO_2-free” hydrogen)

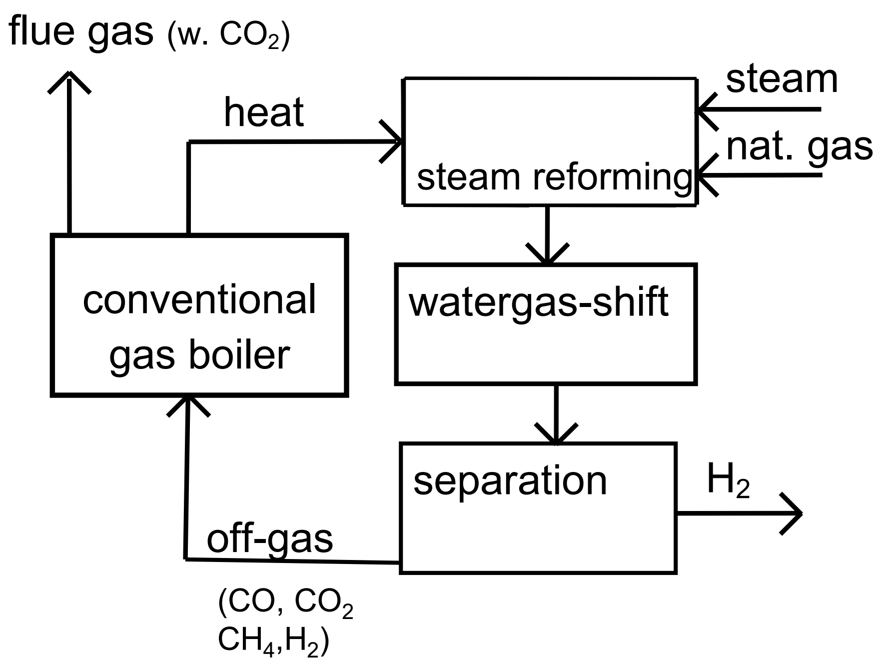
can be produced at low cost by combining

Steam Methane Reforming (SMR)
with
Chemical-Looping Combustion (CLC)

Natural gas is typically 90-95% methane

Steam Methane Reforming (SMR)
of natural gas
is the most common way of producing hydrogen,
but involves large emissions of CO_2

Normal steam methane reforming (SMR)



Reforming:

CH_4 (methane) + H_2O + **heat** ⇒ CO_2 + CO + H_2O + H_2

Water gas shift:

CO + H_2O ⇒ CO_2 + H_2

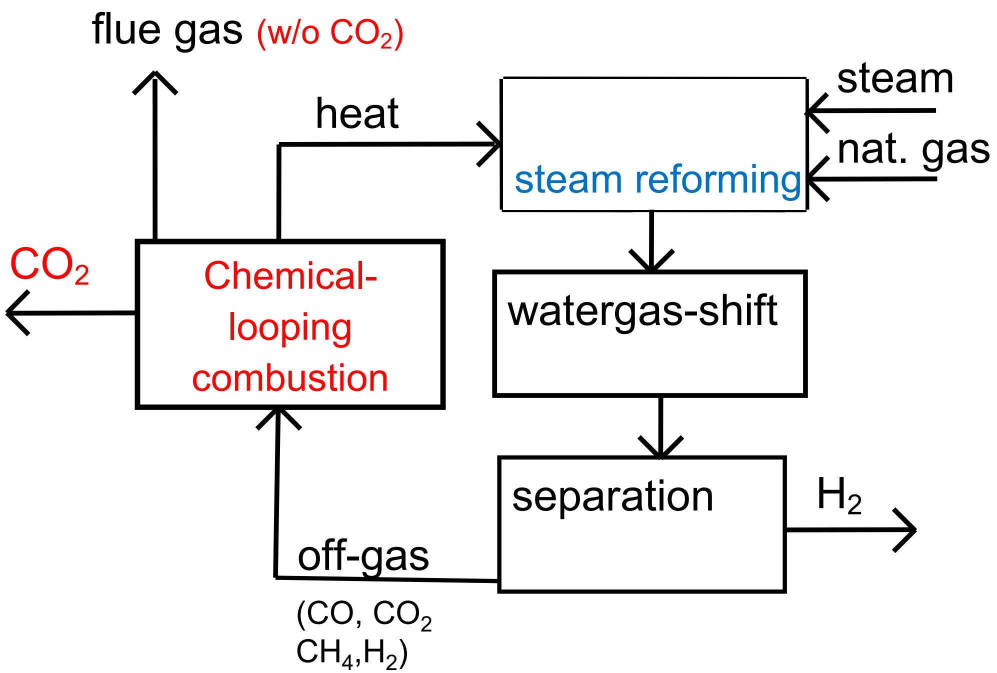
Separation:

H_2(hydrogen) is removed from the gas mixture

Combustion:

Remaining gas + extra methane => **heat**

Steam reforming with CLC

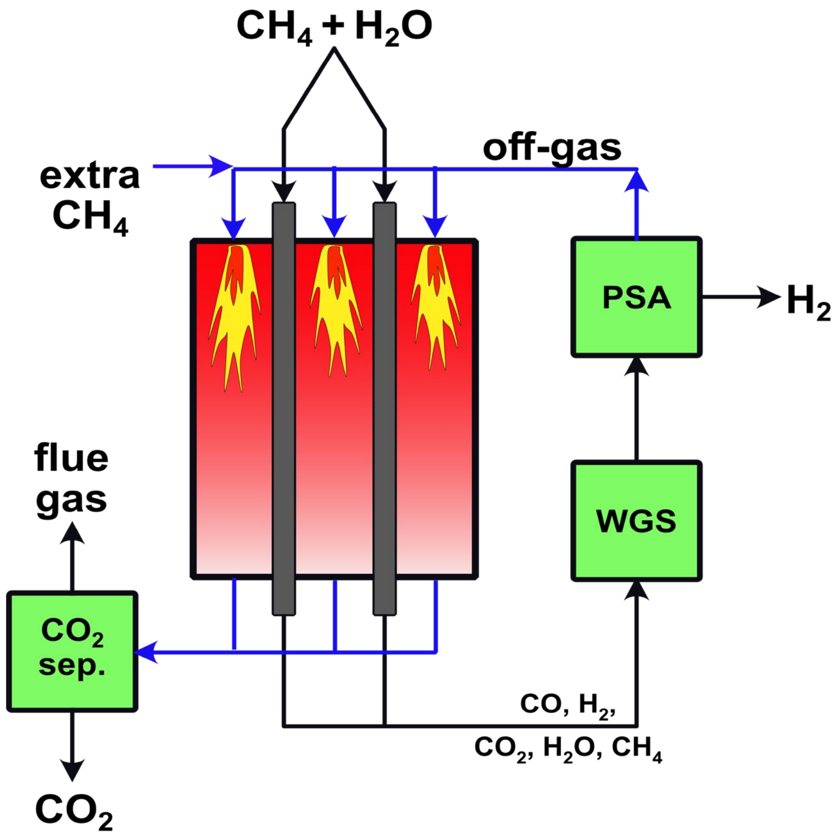


Carbon dioxide in a separate flow w/o separation

⇒ Natural gas converted to carbon-free fuel: i.e. hydrogen

Heat is transferred in a fluidized-bed heat exchanger (FBHE)

Steam Methane Reforming (SMR)

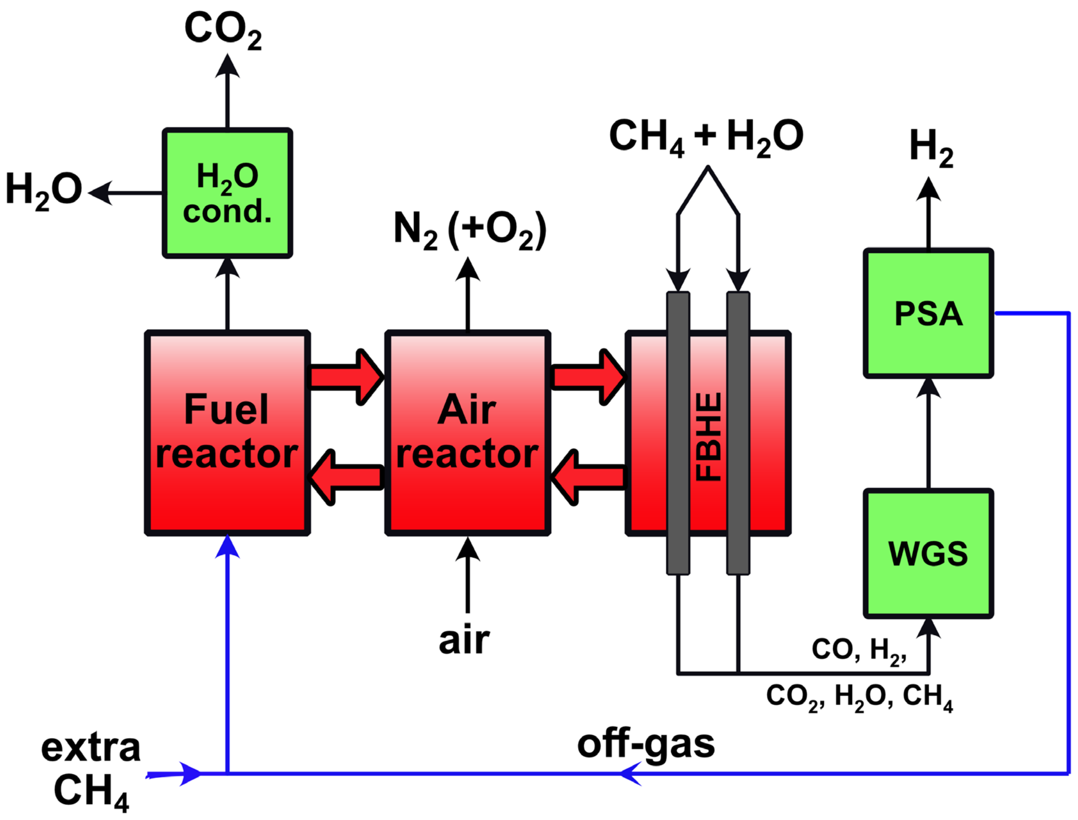


Flame radiation, high furnace temp., ***gas out 1200 ℃***

Temp. inside tubes: 600 – 900°C

Tubes, 13 m long, 13 cm diameter, 2 cm thick walls, filled with expensive catalyst

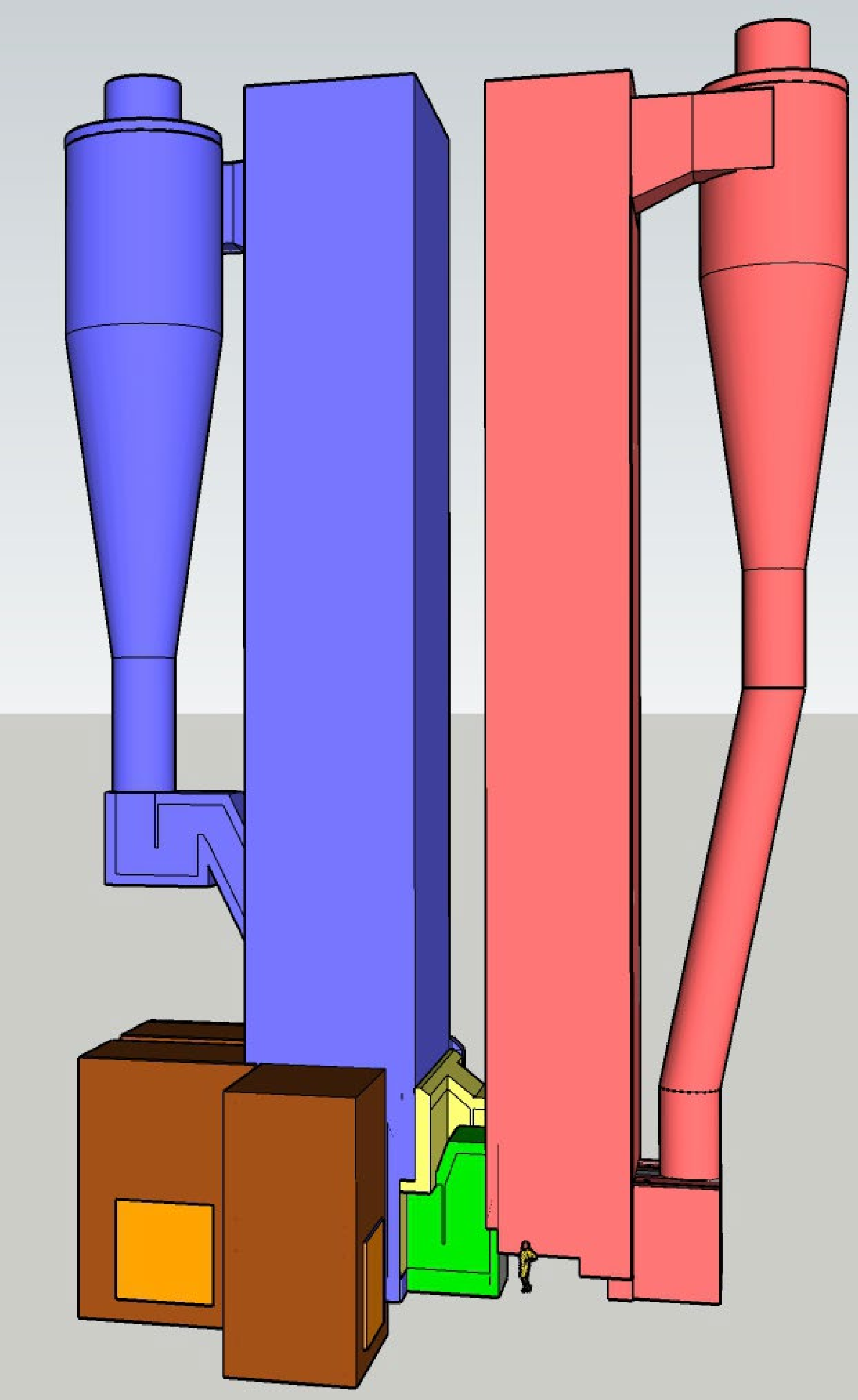
SMR with CLC



Low furnace temperature, ***gas out 950 ℃***

Effective heat transfer in fluidized-bed

Shorter tubes, smaller diameter, less catalyst
⇒ Lower cost



190 MW CLC-CFB boiler

with Fluidized-Bed Heat Exchangers (= steam reformers)

for production of :

410 MW hydrogen

and capture of

740 000 tCO_2/year

Summary: Why CLC-SMR?

Capture of CO_2 with no/small energy penalty

Negative energy penalty for process[1] (T outlet reduced from 1200 to 950°C)

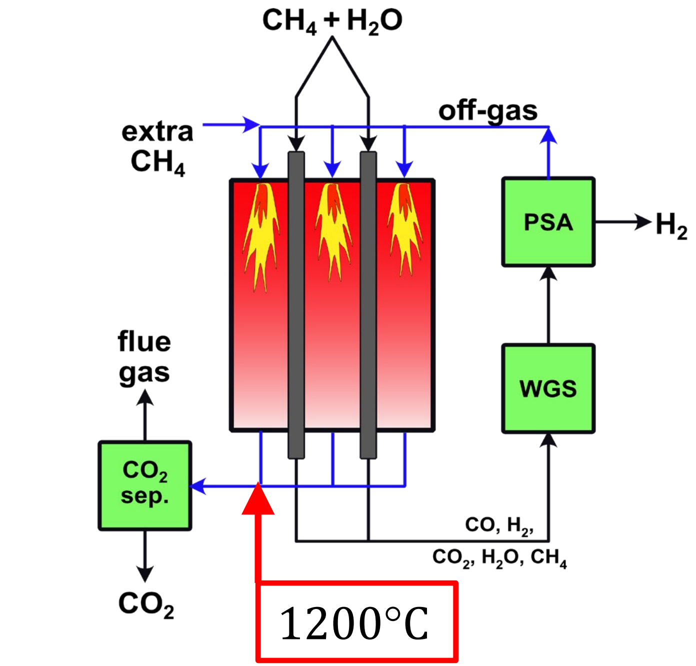
Capture of CO_2 with without high equipment/operational/energy cost for gas separation

More efficient heat transfer and more benign conditions

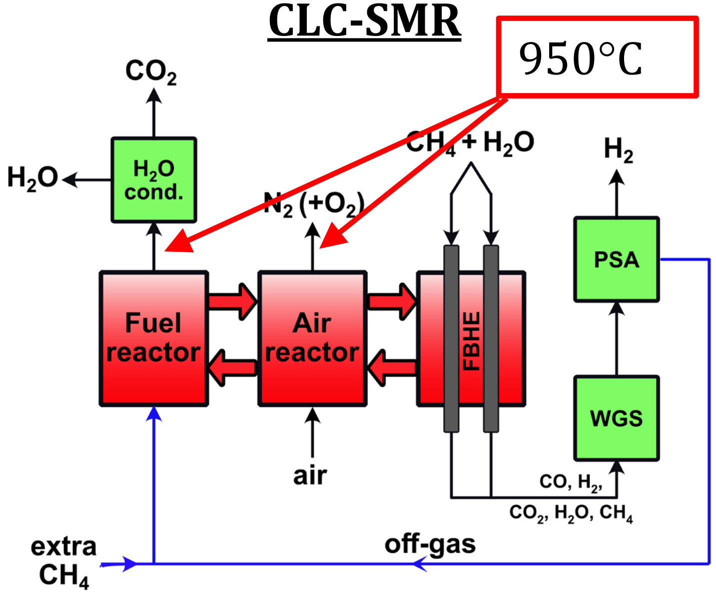
- smaller tube diameter possible in FBHEs (fluidized-bed heat exchangers)
- thus, shorter and thinner tubes (length decrease by factor 3 ?)[2]
- thus, less catalyst (amount decreased by factor of 3 ?)[2]
- thus, lower cost of reforming step

In total: Potential for transforming natural gas to CO_2-free H_2 with **<u>negative</u> energy penalty and <u>negative</u> cost penalty** for CO_2 capture. Gigantic potential future market.

<u>Steam Methane Reforming (SMR)</u>



<u>CLC-SMR</u>



1) Stenberg V, Spallina V, Mattisson T, Rydén M. Techno-economic analysis of H_2 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

Chemical Looping combustion (CLC)

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

Highly concentrated CO_2 stream can be obtained at small added cost

Cost: 25-50% of competing technologies for solid fuels, e.g. biomass

- Eliminate/reduce emissions of NO_x
- Eliminate/reduce problems with alkali ash components

Steam Methane Reforming with CLC

- Potential for lower cost than conventional SMR without CO_2 capture, i.e. ***negative*** capture cost

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Cheap oxygen carrier materials ?

	Ilmenite/Manganese ore	Manufactured ??	
World Market price	200		
Crushing/sizing/deposit	200		
ton CO_2/MWh_{th}	0.334	0.334	0.334
ton particles/MW_{th}	0.75	0.75	0.75
lifetime particles, h	200	200	1000
cost particles €/ton	**400**	**4000**	**4000**
€ /ton CO_2 captured	4.5	**45**	**9**

Conclusions:

Manufactured materials likely too expensive with solid fuels (ash)

Manufactured materials could make sense with gas fuels

- ”$CaMnO_3$”
  - low cost raw mtrls: limestone + Mn ore
  - long lift-time (10 000 h ?)

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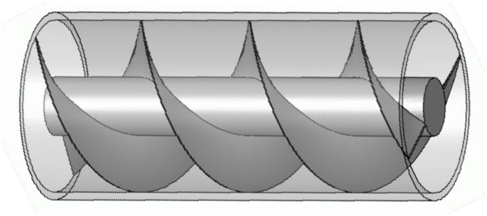
Steam reforming catalyst for SMR-CLC

- Change to smaller tube diameter
- Change from vertical to horizontal reformer tubes
  - Control of flow through catalyst
  - Structured catalyst



CATACEL SSR technology

Thank you!