"CHEMICAL-LOOPING COMBUSTION (CLC)
Status of development

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Content

- what is chemical-looping combustion (CLC) ?
- operational experience
- what are oxygen carriers ?
- chemical-looping reforming
- chemical-looping for solid fuels
- chemical-looping with oxygen uncoupling (CLOU)
- additional concepts
- conclusions

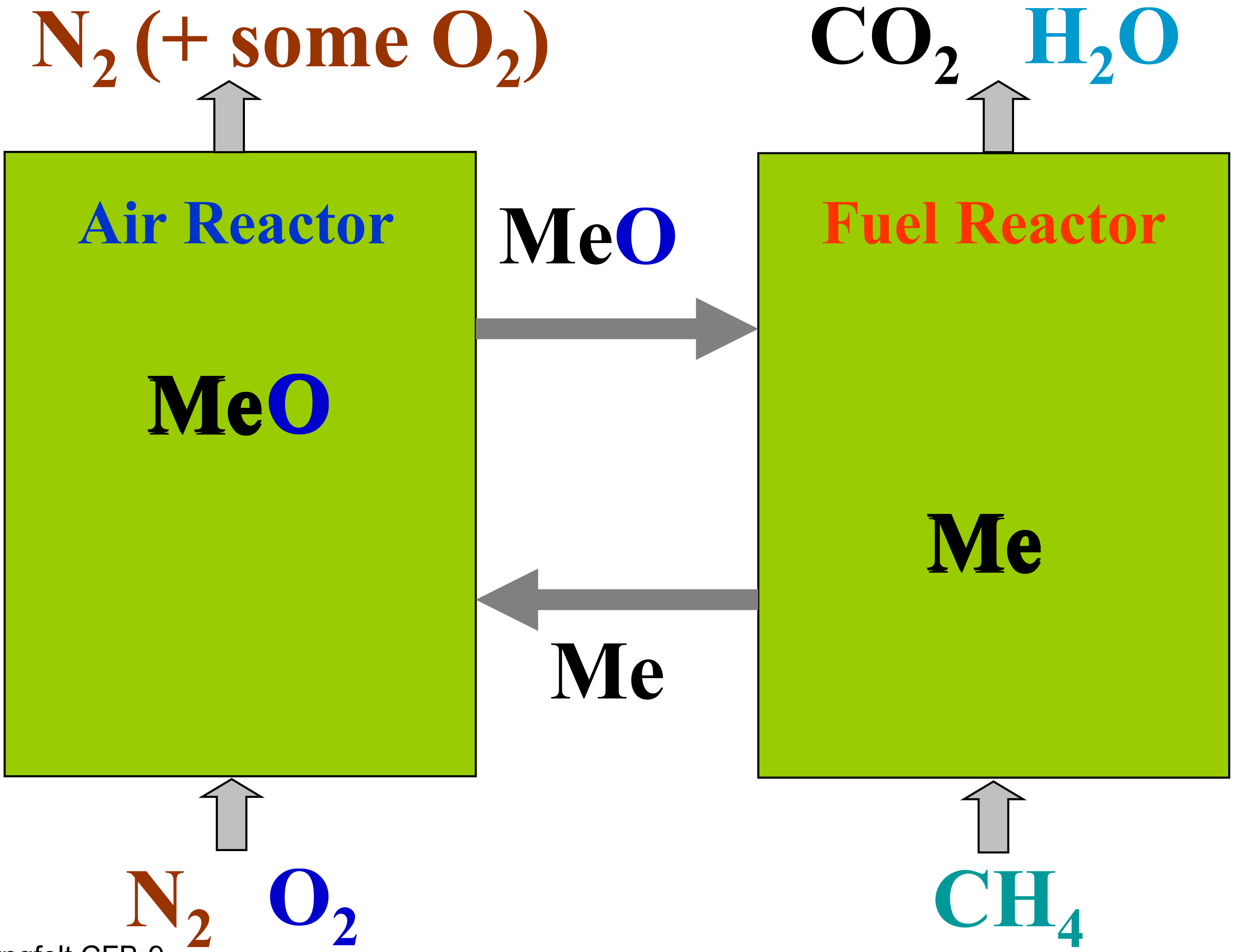
<u>WHY CLC ?</u>

CO_2 capture using post-, oxy- or pre-combustion:

- cost of gas separation
- energy loss power plant, 9-10% units

In Chemical-Looping Combustion (CLC) ***oxygen is transferred from air to fuel using an oxygen carrier*** (metal oxide particles)

CLC ("unmixed combustion") by-passes the gas-separation problem by <u>never mixing air and fuel</u>,
=> gas <u>separation is not needed</u> to capture CO_2



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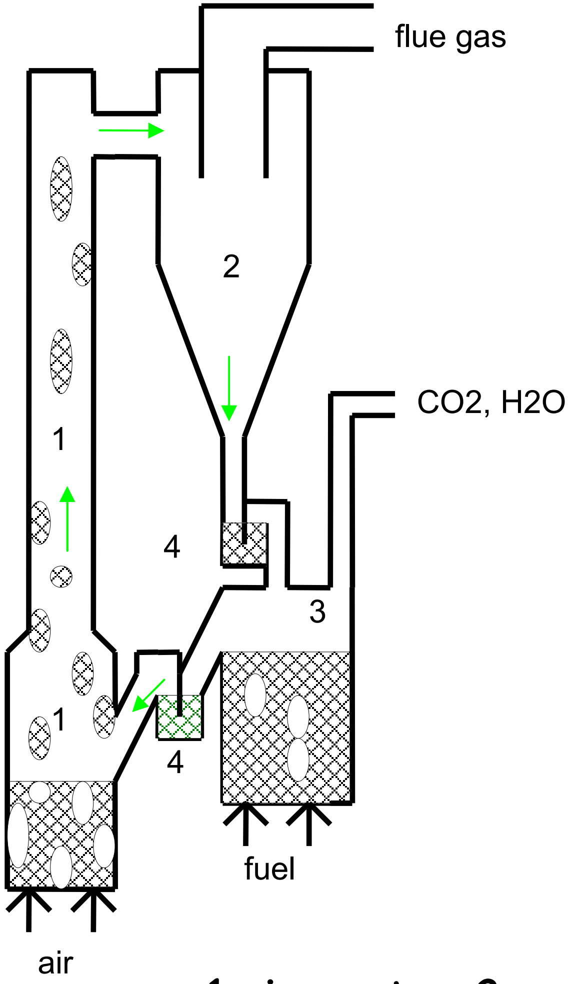
CLC reactor system



1 air reactor, 2 cyclone

3 fuel reactor, 4 particle locks

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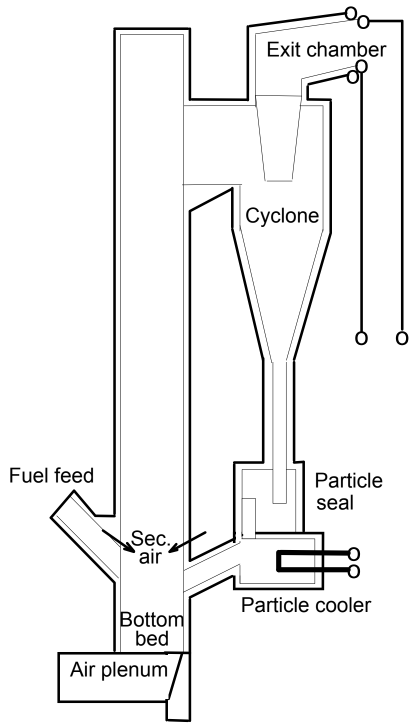
Circulating fluidized bed boiler for solid fuels



Ex. Chalmers-boiler 10 MW,
(12 m high, 35 ton coal/day)
Commercial:
250 MWe
600 MWe (designed)

CLC is a *new* principle of fuel conversion

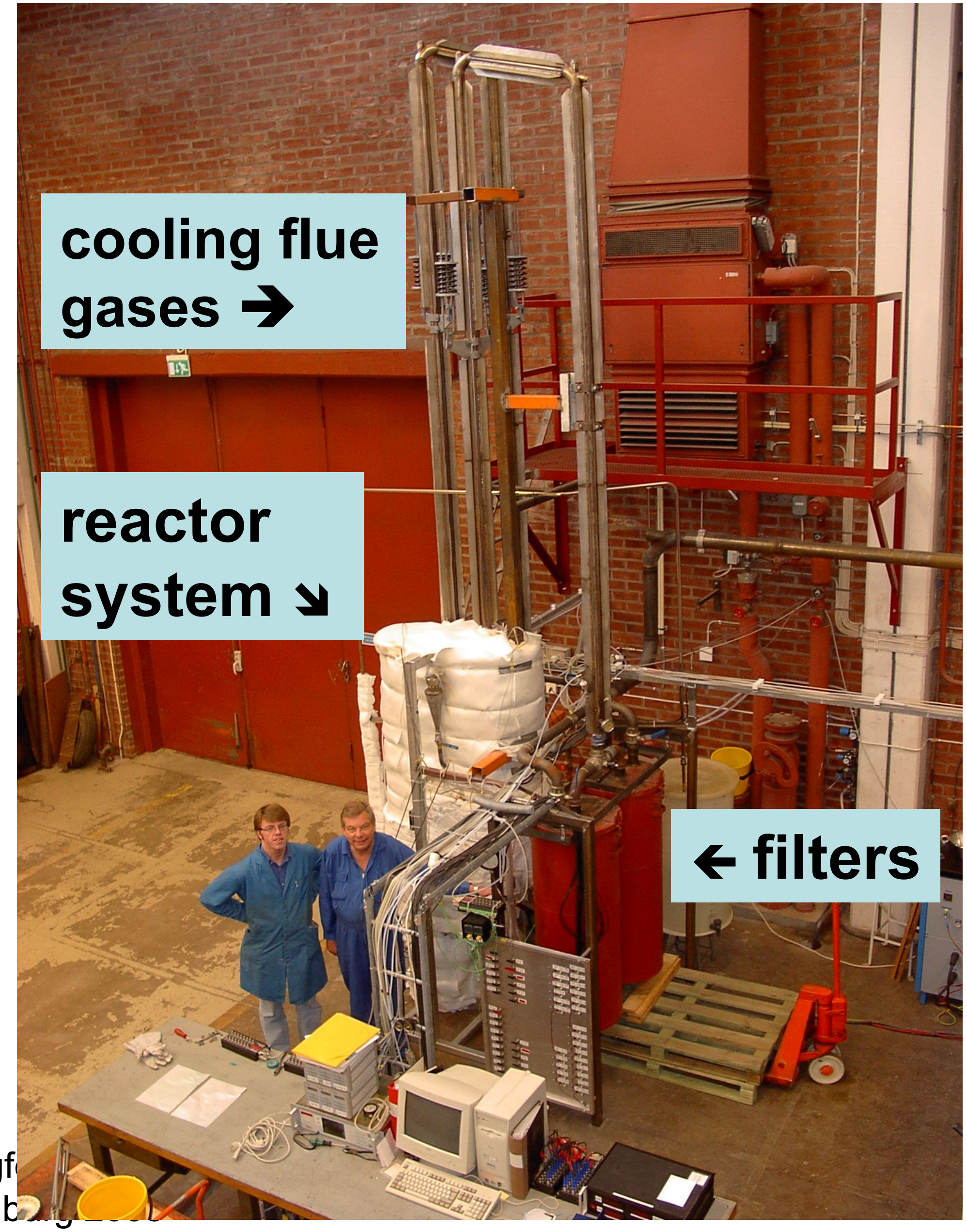
Energy production from fuels

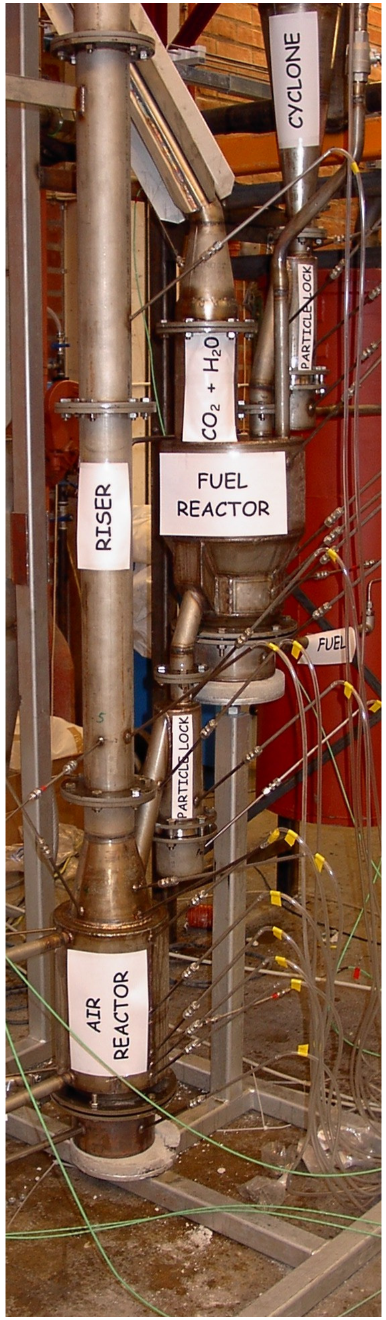
respiration	~2 000 000 000 BC
fire	~500 000 BC
fuel cell	1839
chemical-looping combustion	2003

CLC, status 2002:

- only a limited number of laboratory tests with particles tested in few cycles
- "paper concept"; the process never tested in real operation

Chalmers' 10 kW chemical-looping combustor 2003





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2003

>100 h operational experience in 10 kW CLC combustor showing

- *<99.5% fuel conversion*
- *100% CO_2 separated*
- *minimal physical degradation, i.e. very small loss of fines (0.002%/h)*
- *no loss in particle reactivity*
- *stable operation*

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>2800 h of operational experience in chemical looping combustors

- >9 CLC units, 300 W – 100 kW
- >24 different materials tested
- tested oxides include: NiO, CuO, Fe_2O_3, Mn_3O_4, CoO, $CaSO_4$, ilmenite (natural mineral, $FeTiO_3$)
- fuels: natural gas, CH_4, CO/H_2, bit. coal, petcoke
- one material tested for >1000 h

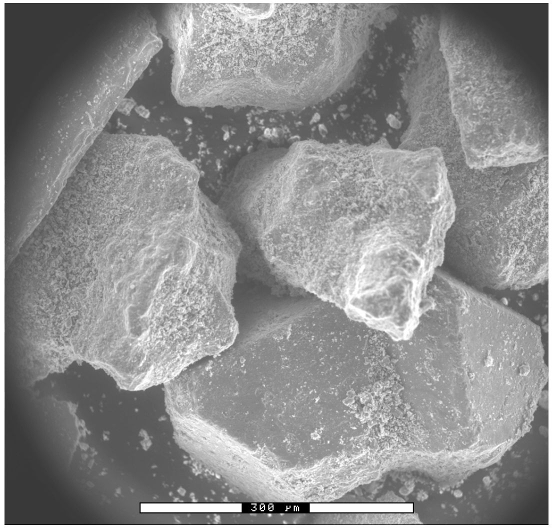
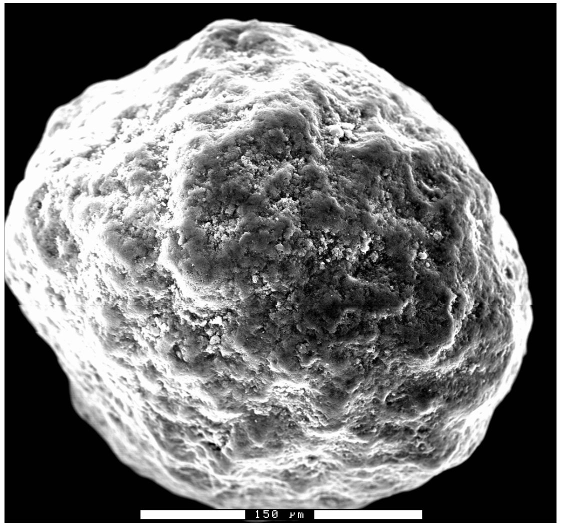
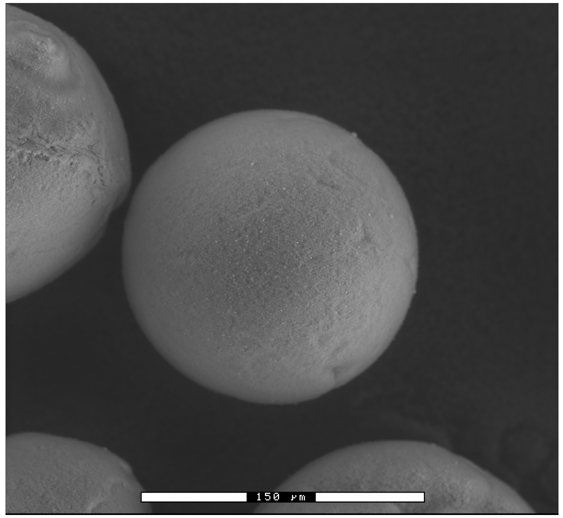
Chemical-looping combustors

Location	Unit	Oxides tested	Operation hours	Fuel
Chalmers	10 kW	NiO, Fe_2O_3	1355	nat. gas
KIER, S Korea	50 kW	NiO, CoO	28	nat. gas
CSIC, Spain	10 kW	CuO, NiO	140	nat. gas
Chalmers	300 W	NiO, Mn_3O_4, Fe_2O_3, ilmenite	559	nat. gas, syngas
CSIC, Spain	500 W	CuO, NiO	660	nat. gas
Chalmers	10 kW – solid fuel	ilmenite	50	coal, petcoke
Daejong, S Korea,	1 kW	NiO + Fe_2O_3	?	CH_4
Vienna, Techn. Univ.	100 kW	ilmenite, NiO	50	nat. gas, CO, H_2
Alstom				

>600 materials tested in laboratory under cycling conditions

- most testing with thermogravimetric analysis
- >200 materials also tested in laboratory batch fludized tests
- particle manufacture includes: impregnation, extrusion, freeze-granulation, spray-drying, spin-flash drying, precipitation ...
- Regeneration, i.e. reaction with O_2 normally very fast, and complete consumption of all O_2 not needed. Therefore focus on reaction with fuel.

Three different types of oxygen carriers based on Fe_2O_3

Iron ore	Impregnated	Freeze granulated
		
BET=3,7 m^2/g	BET=80,8 m^2/g	BET=8,3 m^2/g (high)
Pore volume=0,012 cm^3/g	Pore volume=0,35 cm^3/g	Pore volume=0,33 cm^3/g

Tested materials (in laboratory)

Manufactured particles:

- active oxides primarily NiO/Ni, CuO/Cu, Mn_3O_4/MnO, Fe_2O_3/Fe_3O_4
- support materials, e.g. Al_2O_3, TiO_2, SiO_2, ZrO_2, sepiolite, bentonite, Al_2MgO_4 ...
- various mixing ratios active oxide/support
- heat treatment: typically 900-1300 C

Natural ores (iron ore, manganese ore, ilmenite)

Industrial waste materials

Pros and cons for the active oxides

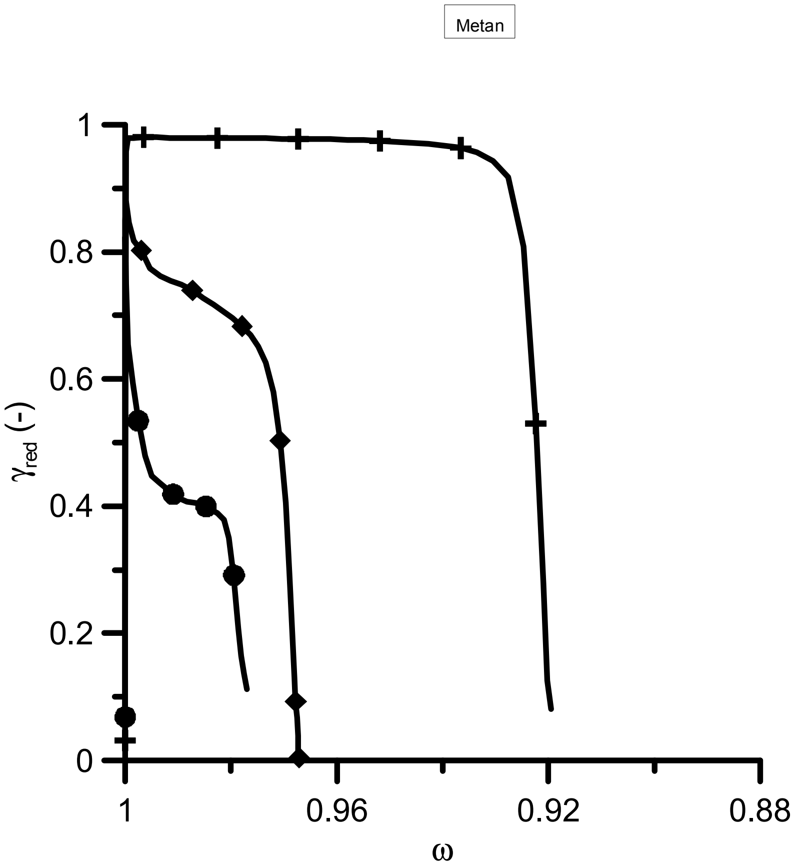
	Fe	Mn	Cu	Ni
Oxygen ratio, %	3	7	20	21
Reactivity (to CH_4)	- -	-	+	++
Cost	++	+	-	- -
Health				-
Thermodynamics				-[1]
Reaction with CH_4			+[2]	
Melting point			-[3]	

[1]maximum conversion 99-99.5%

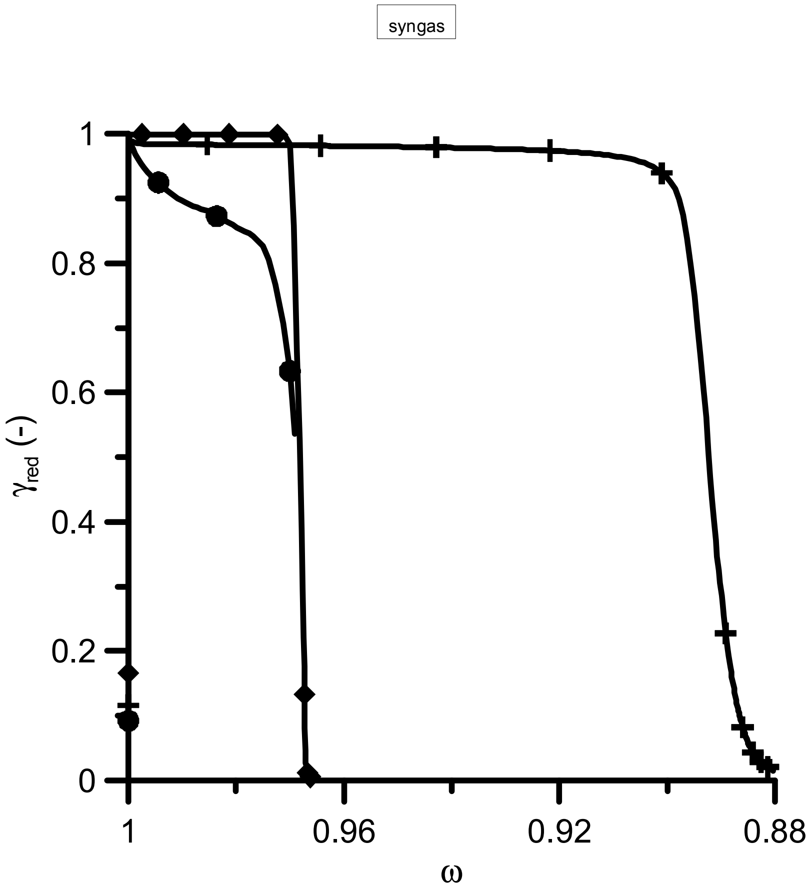
[2]exothermic reaction in fuel reactor

[3]melting point Cu: 1085 C

Strong difference in reactivity with respect to methane, but not CO/H_2 Ni(+), Mn(♦), Fe(•)



Ni > Mn > Fe, + CH4



Ni > Mn > Fe, + CO/H2

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MIXED OXIDES

Ni	Mn, Fe & related mtrls
high reactivity vs CH_4	high reactivity vs CO, H_2
reforming catalyst :	moderate/low vs CH_4
$CH_4+H_2O \Rightarrow CO+3H_2$	low cost / low toxicity
high cost / toxic	(>0.01×cost of Ni-mtrl)

Ni-materials with high reforming capacity

+

low cost materials

$\Downarrow$

high reactivity vs CH_4

in combination with small amount of Ni

Additional oxides being studied

- **Ilmenite ($FeTiO_3$/Fe_2TiO_5+TiO_2): cheap mineral, major drawback is moderate reactivity towards methane**
- **Cobalt oxide (CoO/Co): more expensive and less healthy than NiO, maximum conversion 95-97%**
- **Calcium sulphate ($CaSO_4$/CaS): maximum conversion of fuel 98-99%, SO_2 release ??, cheap**
- **Perovskites, (e.g. $La_xSr_{1-x}Fe_yCo_{1-y}O_{3-\delta}$) normally small transfer capacity, thermodynamics not clear**

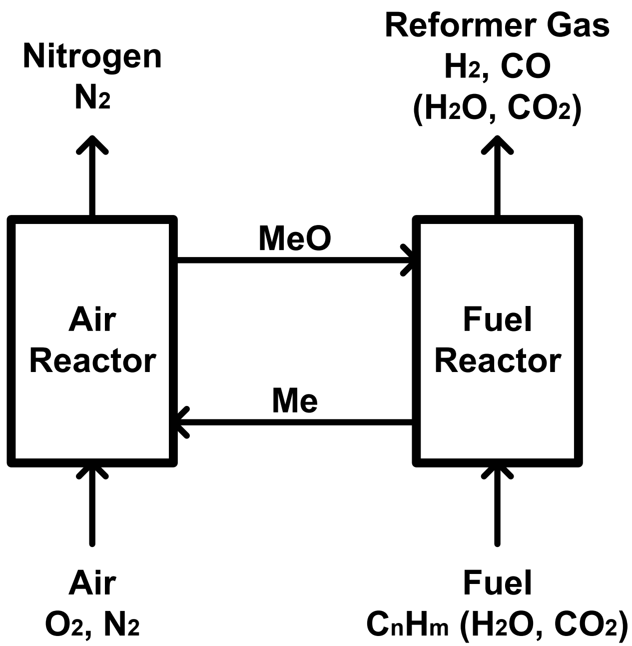
Chemical-Looping Reforming (CLR):

- autothermal reforming, CLR(a)
- steam reforming, CLR(s)

two processes to convert natural gas to hydrogen, with simultaneous capture of CO_2

Chemical-Looping autothermal Reforming, CLR(a)

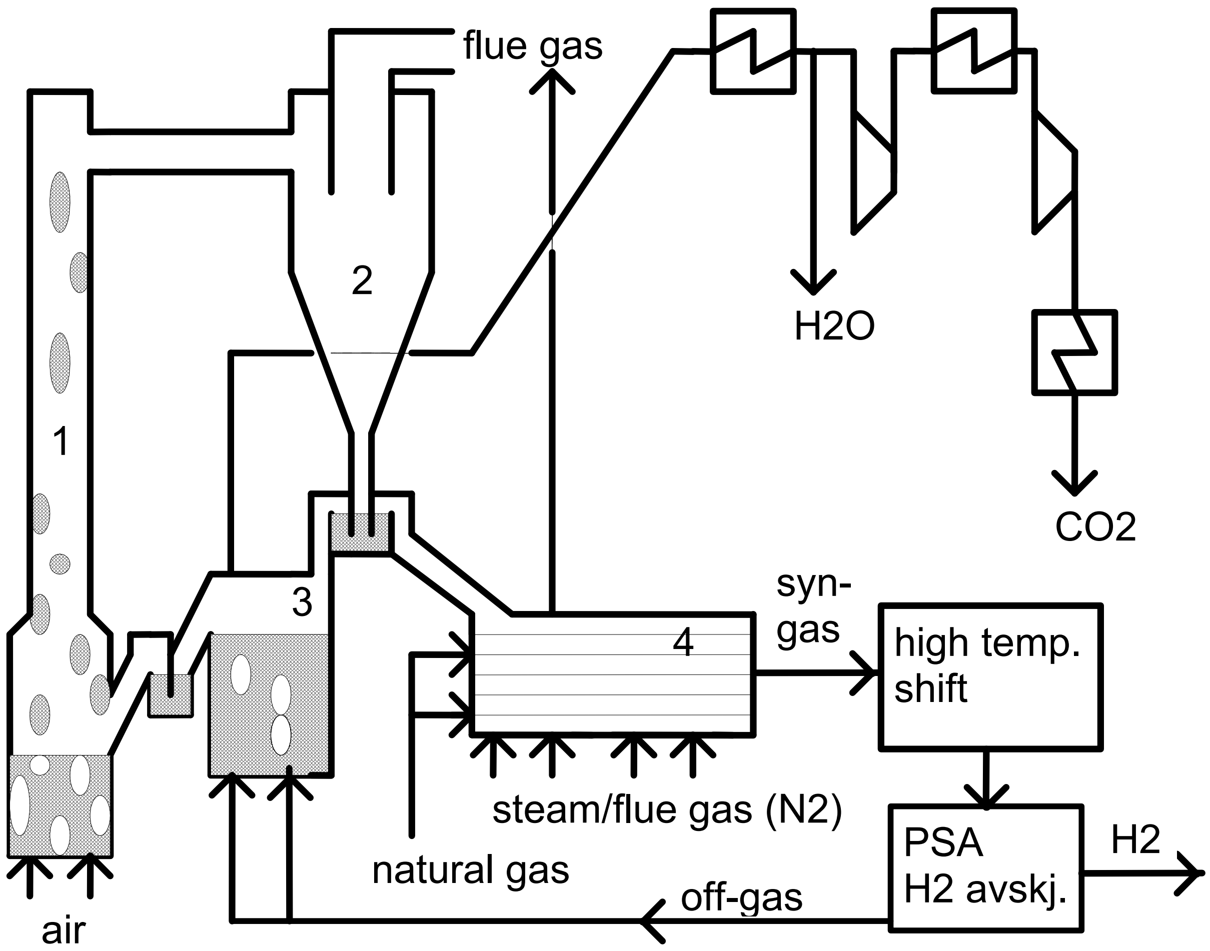
- Partial oxidation (instead of full conversion of fuel, as in CLC).
- => syngas suitable for H_2 production and CO_2 capture.
- Works: >250 h with 4 different materials



Chemical-Looping steam Reforming

Conventional steam reforming, but heated by CLC in fluidized bed heat exchanger. Fuel is "off-gas" from the H_2 separation.

Higher reforming efficiency than conventional reforming (exlud. CO_2 compression)



1) air reactor/riser, 2) cyclone, 3) fuel reactor,
4) fluidized bed heat exchanger / reformer
(Return flow from 4 to 1 not shown)

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CLC for solid fuels

- Solid fuels react indirectly with ox.carrier, via gasification step
- Char may follow particles to air reactor => incomplete capture
- Gasification slow => long residence time => large solids inventory in fuel reactor
- Less effective contact between fuel gas and oxygen carrier
- Ash may reduce oxygen carrier life-time

Fundamental principles

Gasification

Char is gasified in environment of highly <u>reducing gas</u>, in order to achieve gas with high heating value.
=> low concentration of reacting gas (H_2O, CO_2), high concentration of inhibitor (H_2, CO)

Chemical-looping combustion

Char is gasified in environment of <u>oxidizing gas</u> (H_2O + CO_2), with rapid removal of gasification products (CO, H_2) already inside the particle phase
=> high concentration of reacting gas (H_2O, CO_2), low concentration of inhibitor (H_2, CO)

50 h operational experience

- **gas: incomplete oxidation**

>>>> oxypolishing

- **CO_2 from air reactor**

>>>> carbon stripper,
>>>> increased residence time in fuel reactor

- **char loss**

>>>> better cyclone

- **cheap oxygen carrier, ilmenite, 100 €/ton**

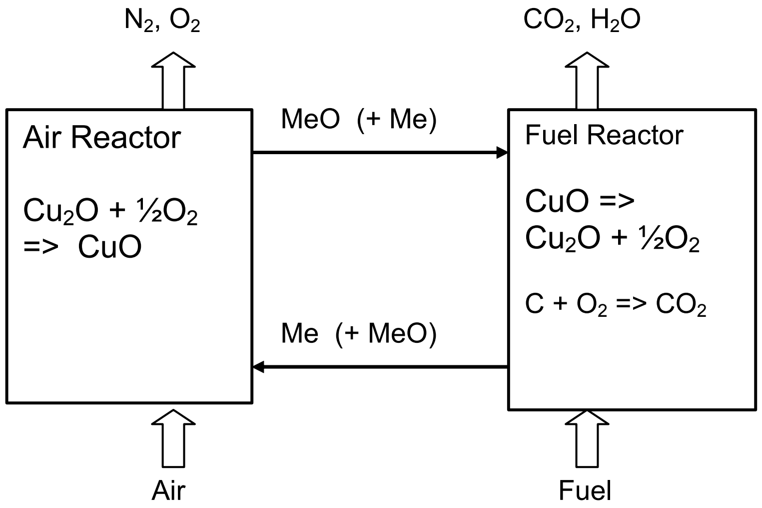
Loss efficiency power plant:

>2-3% units

Cost :

>10 €/tonne CO_2

Chemical-Looping with Oxygen Uncoupling – CLOU



Uses the equilibrium of the reaction

$$CuO \Leftrightarrow Cu_2O + \tfrac{1}{2}O_2$$

p_{eq} = 0,02 bar vid 913°C

In the air reactor O_2 conc. can be lowered to appr. 2%

In the fuel reactor the temperature increases due to exothermic reaction => partial pressure of O_2 increases.

O_2 released is consumed by the fuel, leading to new release of O_2.

E.g. petroleum coke can be completely converted in 20-30 s

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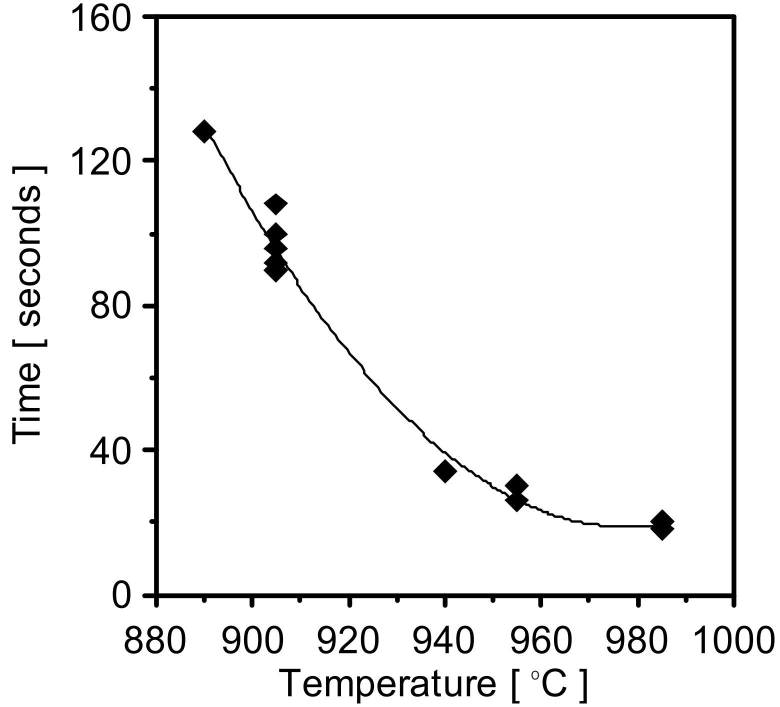
Chemical-Looping with Oxygen Uncoupling with petroleum coke



Time needed to convert fuel vs. temperature

Additional concepts being studied

- One-step hydrogen, direct conversion of CH_4 to H_2 using three reactors, i.e. air reactor + fuel reactor + water splitting reactor (ENI).
- Chemical-looping reforming of solid fuels to produce hydrogen (Alstom, Ohio State University)
- Rotating reactors with coated monoliths (IFP)
- Membrane assisted reactors - fixed beds (TNO).

Reactor system (circulating fluidized beds):

- well established
- commercially available
- simple
- moderate costs
- up-scaling needed
- development needed for special applications like solid fuels and reforming

Oxygen-carrier particles:

- durability and reactivity confirmed
- scale-up of particle manufacture established
- commercially available raw materials established
- long-term testing performed
- needed: portfolio of materials to:
  - cover different looping technologies
  - reduce commercial risks, 1) access of different suppliers, 2) backup for unexpected difficulties
  - produce confidence in new technology
  - cover uncertainties regarding what is optimal between with respect to reactivity, cost, health

Conclusions

- Proof of concept. High conversion, successful operation, particles not damaged by operation.
- A number of possible applications available, involving direct "combustion" and hydrogen production for gaseous, liquid and solid fuels .
- Unique features for CO_2 capture.
- A number of oxide materials available from expensive high reactivity Ni-oxides, to cheap natural ores like ilmenite.