CHEMICAL-LOOPING TECHNOLOGIES FOR HYDROGEN PRODUCTION WITH CO_2 CAPTURE

Three processes with oxygen transfer by metal oxide particles in H_2 production with CO_2 capture, thus reducing need for costly energy demanding for gas separation.

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Partners:

- Chalmers Univ. of Techn. (Sweden)
- CSIC (Spain)
- Vienna Univ. of Techn. (Austria)
- ENI (Italy)
- ALSTOM Power Boilers SA (France)
- SINTEF (Norway)
- BP (UK)
- PDC (Netherlands)
- IFP (France)
- NTUA (Greece)

The chemical-looping concept can be used for generation of hydrogen from natural gas, with capture of carbon dioxide :

Three processes :

Chemical-Looping autothermal Reforming, CLR (a)

Chemical-Looping steam Reforming, CLR(s):

One-Step Decarbonization, OSD

One-step Decarbonization (OSD)

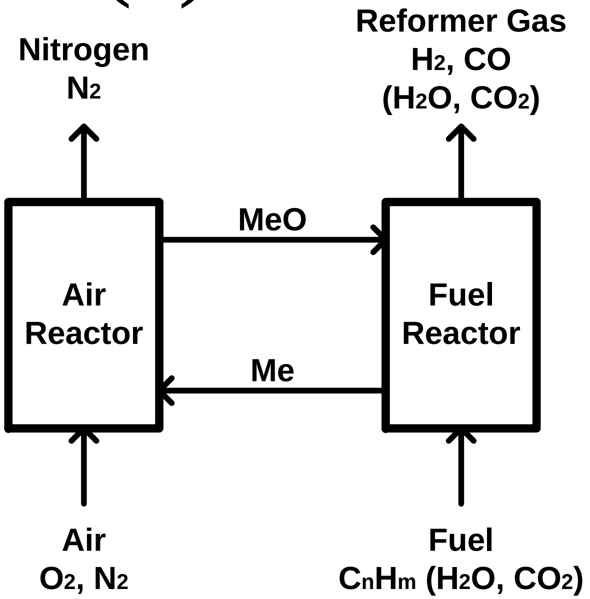
OSD oxidizes oxygen carrier in two steps, the first being used for producing hydrogen from water, producing H_2 / H_2O mixture.

Produces essentially pure CO_2 and H_2, *without any actual gas separation*

CLR (a)	CLR (s)
• Produces a syngas suitable for H_2 production and CO_2 capture, without the energy penalty of an air separation unit.	• Provides CO_2-free heat for conventional steam reforming • Facilitates the separation of H_2 and CO_2, by using a “dirty” off-gas from separation as fuel

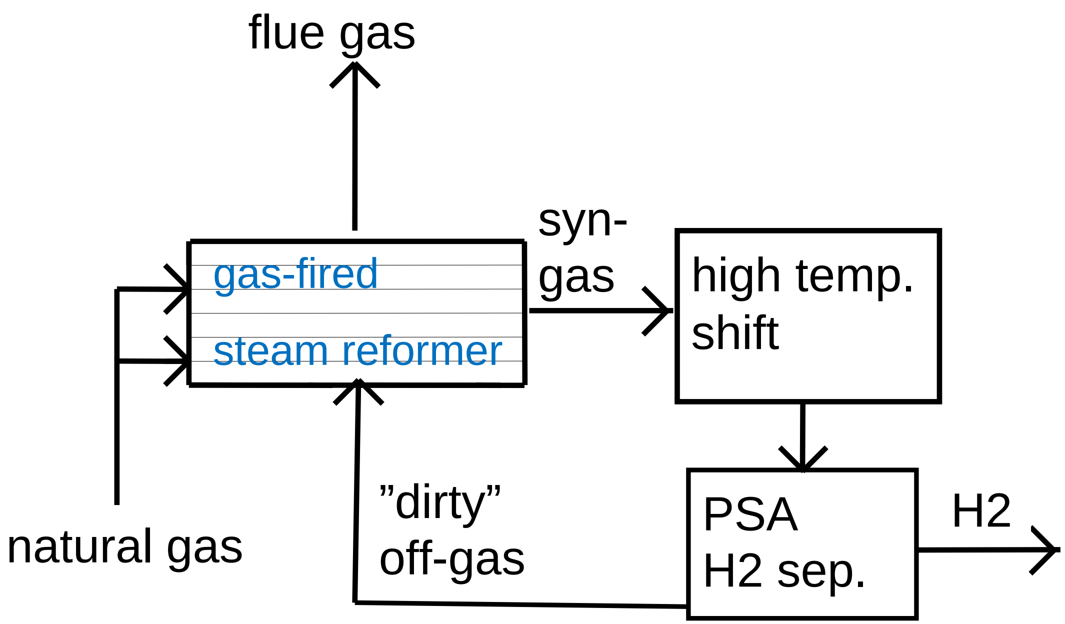
Chemical-Looping autothermal Reforming, CLR(a)

- Instead of <u>full</u> conversion of fuel, as in chemical-looping combustion, the same cycle is used for <u>partial</u> oxidation of the fuel, to produce a <u>syngas,</u> suitable for production of hydrogen and separation of CO_2.



Q: What is the normal commercial (cheapest) way to produce hydrogen ?

A: Steam reforming of natural gas



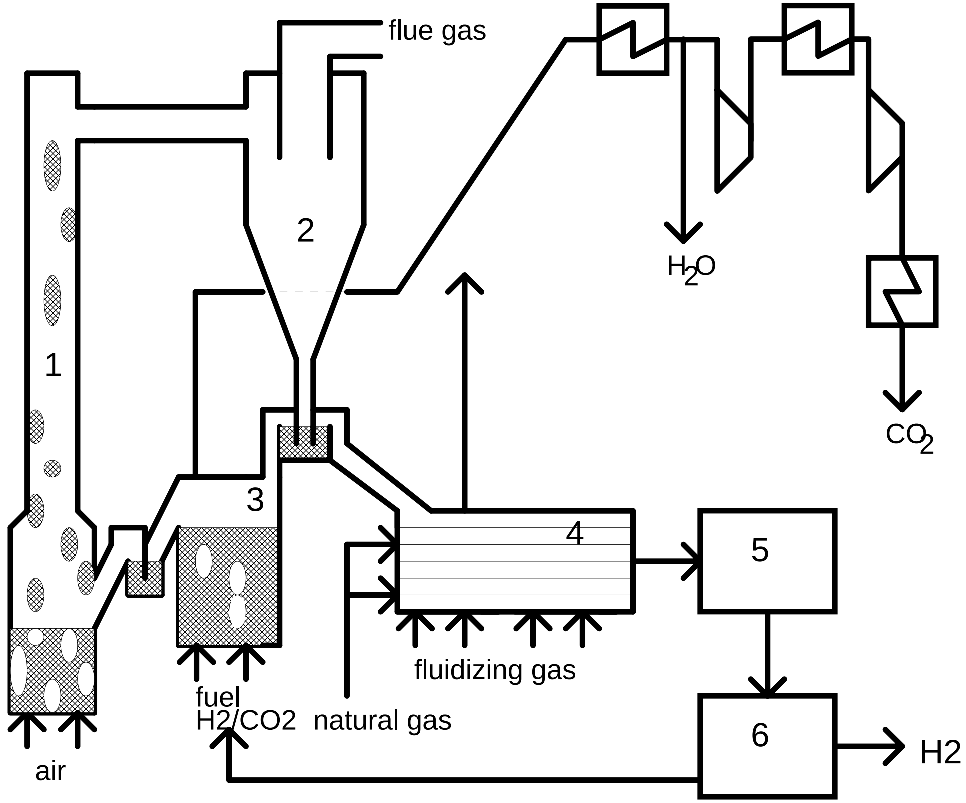
Q: What is chemical-looping steam reforming ?

A: Substitute gas-fired steam reformer, with chemical-looping combustor:

- **All carbon comes out as CO_2 when "dirty off-gas" is oxidized in fuel reactor, e.g. 100% capture.**
- **Excellent heat transfer in fluidized-bed steam-reformer, lowers heat losses and increases reforming efficiency.**
- **Only known CO_2 capture process that gives increased efficiency (excluding of course CO_2 compression).**

CLR (s) chemical-looping steam reforming

A chemical-looping combustion cycle using a "waste" H2/CO2 stream as fuel, for producing heat to a conventional reformer in the form of an "external fluidized bed heat exchanger".



Testing of oxygen carriers:

- lab fluid-bed batch under cyclic conditions
- 300 W CLC unit (Chalmers)
- 500 W CLC unit (CSIC)
- semicontinuous under pressure (CSIC)
- 120 kW CLC in Vienna
- 2 semicontinuous fluidized beds (ENI)
- batch fluidized bed reactor, pressure (ENI)

Chalmers' 300 W chemical-looping combustor

Example: Cachet 300 W testing

180 h of testing in chemical-looping combustor/gasifier with four Ni-based oxygen carriers (2 from Chalmers / 2 from CSIC)

•all excellent for CLR(a), syngas with **no** methane

•no problem to run at low stoichiometric ratios, suitable for CLR(a)

•no degradation or deactivation of particles

•one particle also excellent for CLR(s), ***cf. also CLC GP***

Non-nickel particles have been tested with good results for CLR(s),

•mixed oxides, e.g. ilmenite (cheap natural mineral with high reactivity towards CO/H_2) in combination with small amounts of NiO (as reforming catalyst, converting CH_4 to CO/H_2),

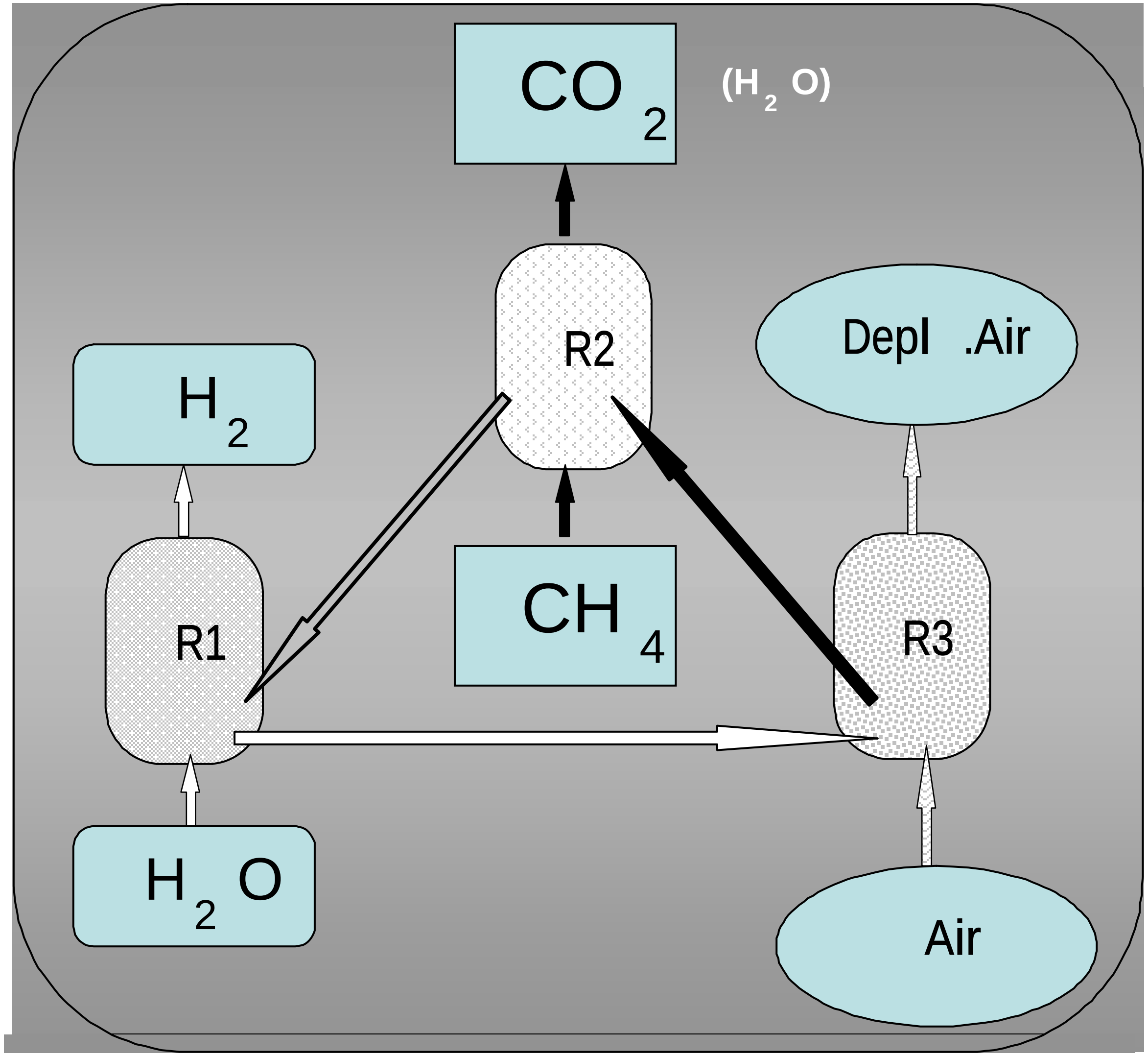
Vienna‘s 120 kW dual CFB hot unit

Operation in CLR(a) mode (syngas generation) successful:

Complete conversion of methane.

Operation at low (relevant) air ratios with no formation of carbon.

(Combustion mode also successful as reported yesterday)

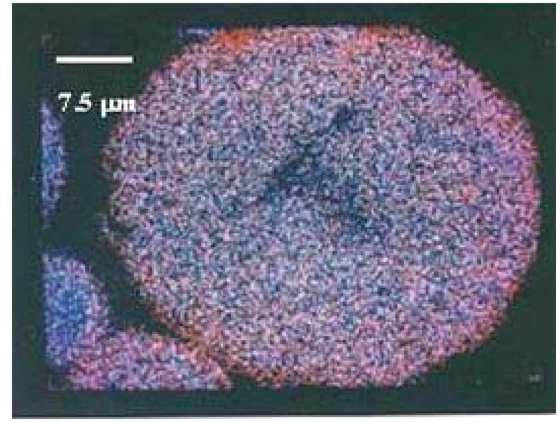


One-step produces essentially pure CO2 and H2, *without any actual gas separation*

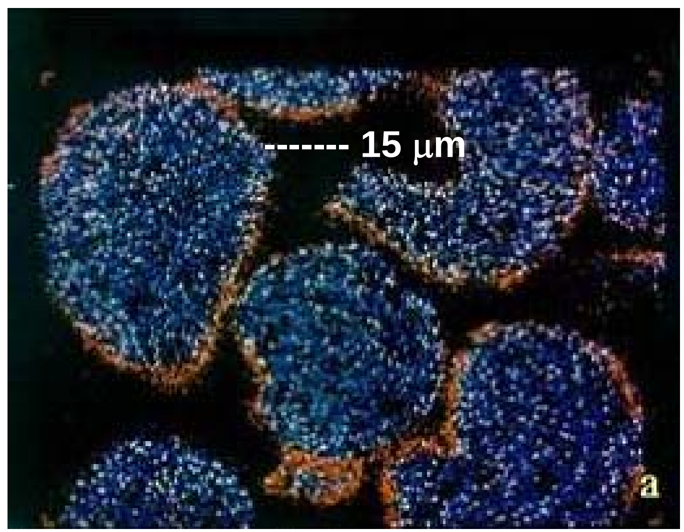
One-step, oxidizes oxygen carrier in two steps, the first being used for producing hydrogen from water, producing H_2 / H_2O mixture.

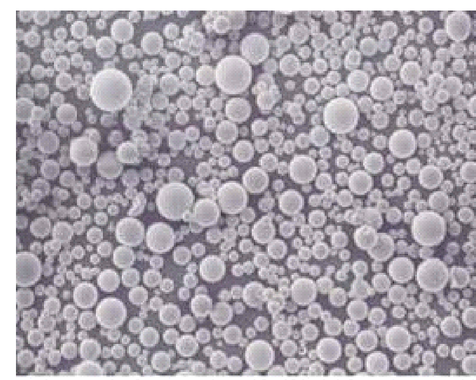
One-step Decarbonization (OSD)

Successful development of the OTM



- The variable production costs (raw materials and utilities) are in the range of 21 Euro/kg
- New dual oxide material underway with higher oxygen transfer capacity





66 µm

One-step Decarbonization (OSD)

FUEL REACTOR – R2 - (one-step)

- With reactor internals, combustion of 30 nL/h of natural gas/kg of oxygen-carrier was accomplished
  - Conversion of the fuel 99.7%
  - CO_2 purity > 95%
- The effect of pressure up to 10 barg is:
  - Negligible on coke depostion
  - Negligible on OTM stability
  - The reforming of NG is promoted vs the combustion

One-step Decarbonization (OSD)

STEAM REACTOR – R1 - (one-step)

- The steam/wuestite molar ratio is an effective parameter With 30% excess of steam is achieved 82 nL/h of H_2 per kg of oxygen-carrier
- Conversion of steam ranges between 55 – 60% (limited from thermodynamic constrain)
- Purity of H2 is 100%

Conclusions

- **CLR(s): higher reforming efficiency than conventional H_2 production (excl. CO_2 compression); technology (combustion) demonstrated in 120 kW scale**
- **CLR(a): produces syngas free from CH_4, and without oxygen separator unit, successfully demonstrated in 120 kW unit**
- **one-step: H_2 production with no active gas separation; significant progress in development of this more complex process**