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

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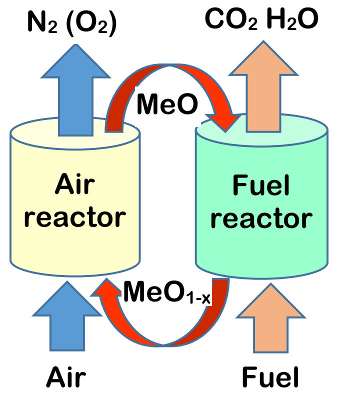
Blue Hydrogen at negative cost and energy penalty compared to conventional Steam Methane Reforming



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Idea for Joint Industrial Project

Bring novel technology for blue hydrogen production to commercialization.

The process features:

- lower energy penalty than conventional SMR[1]
- lower cost than conventional SMR[2]
- 100% CO_2 capture
- no NO_x emissions

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[1]For clarity, this means lower energy penalty for a process with CO_2 capture, than for conventional SMR without capture

[2]Again, the aim is to reach lower cost for a process with CO_2 capture, than for conventional SMR without capture

Chemical-Looping Combustion (CLC)

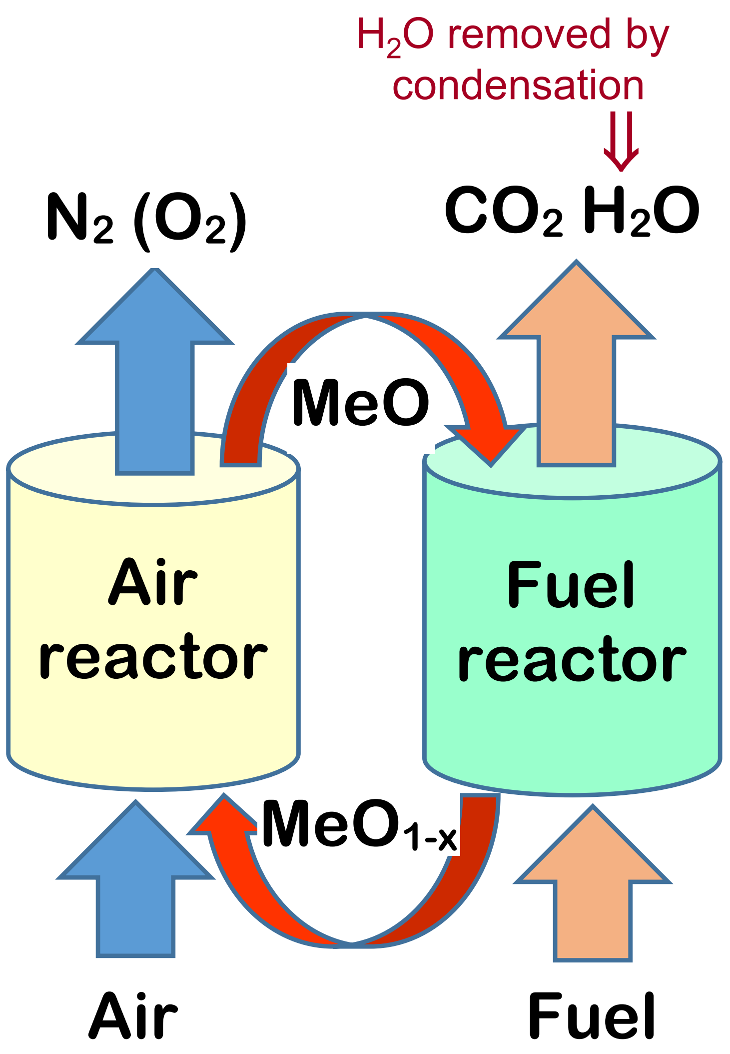
Oxygen is transferred from air to fuel by metal oxide particles

Inherent CO_2 capture:

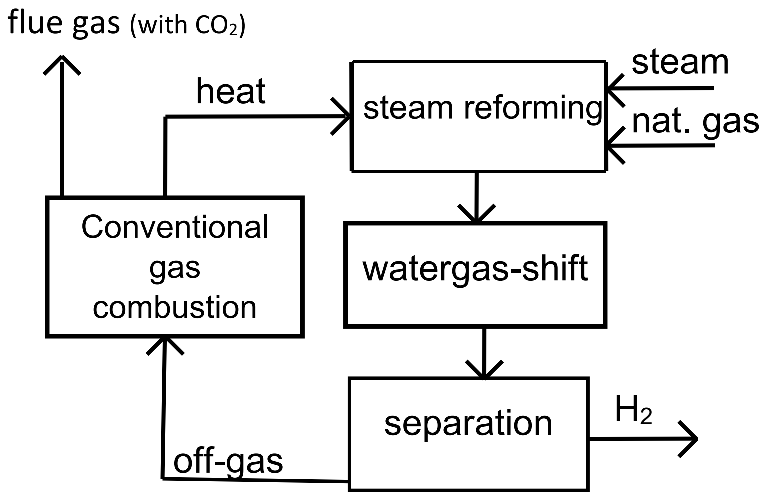
- fuel and combustion air *never mixed*
- *no active gas separation needed*

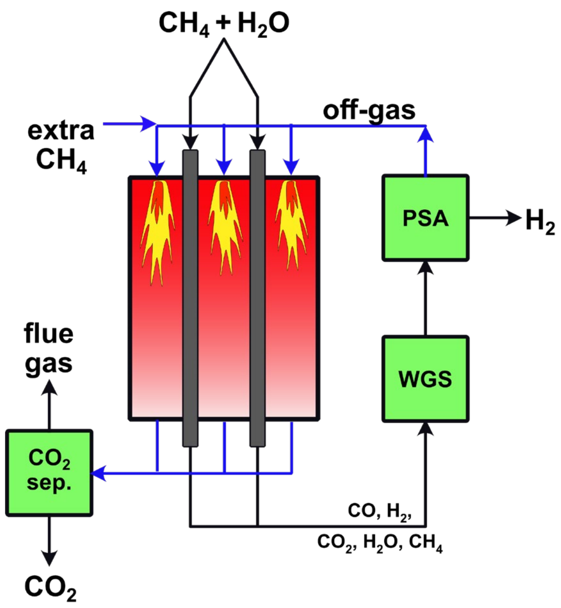
Unique potential for avoiding the large costs and energy penalty of gas separation in CO_2 capture.

Combination of CLC with steam-methane reforming can give 100% CO_2 free hydrogen at low cost and negative energy penalty

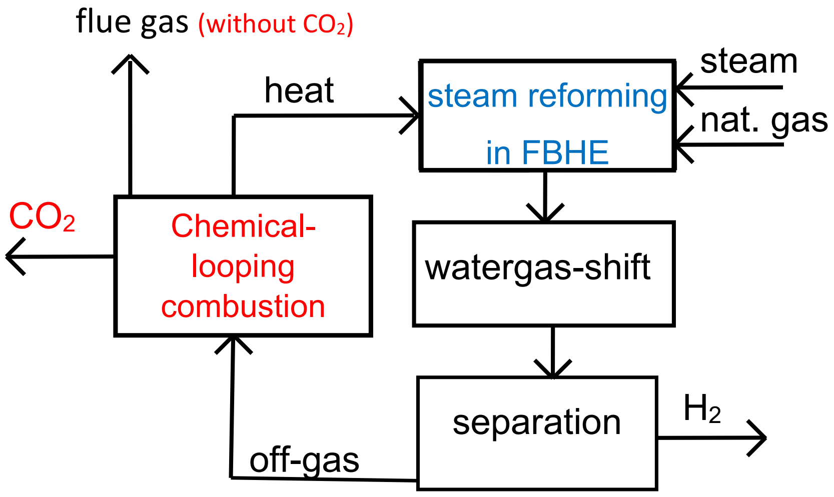


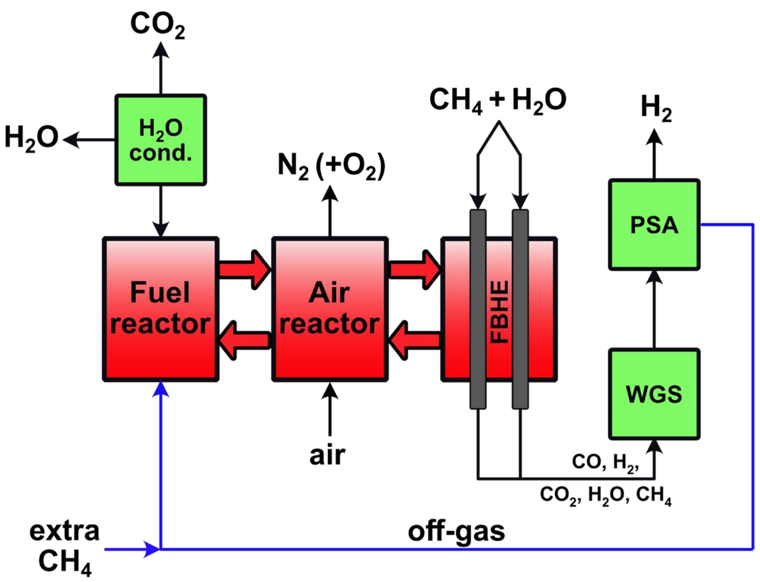
Conventional steam reforming





Steam reforming with CLC





Advantages with CLC-SMR

Energy efficiency 1

All gas separation technologies require energy.
Typical energy demand, e.g. regeneration of MEA absorbent, is around 38% of fuel heating value in combustion

In CLC the capture is inherent.
No gas separation is needed because fuel and combustion air are not mixed.
Thus, CO_2 comes in separate flow (with H_2O) without any gas separation.

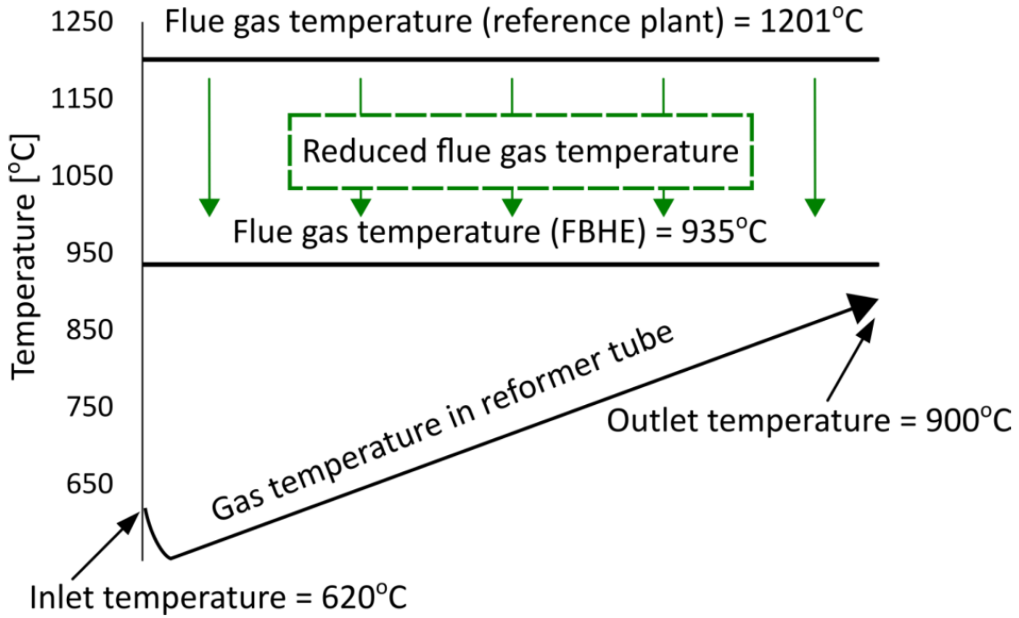
Advantages with CLC-SMR

Energy efficiency 2

Outlet temperature from combustion chamber lowered from *e.g.*

1200°C to 935°C

more heat to the endothermic reaction
=>
more H_2 per heat supplied



CLC-SMR only CO_2 capture process with ***<u>negative</u>*** energy penalty

Advantages with CLC-SMR

Efficient heat transfer 1

SMR (technology reference, and main technology for H_2 production):

Number of flame burners restricted.

High temperature gradients from radiating flames to tubes with varying cooling due to endothermic reaction.

Risk for local hot spots.

Thus large and thick reformer tubes to withstand extreme conditions and high pressure.

Large heat-transfer resistance in tube walls, and more important, inside the thick tubes.

Much catalyst and long tubes needed.

Advantages with CLC-SMR

Efficient heat transfer 2

CLC-SMR (fluidized-bed heat exchanger used for heat transfer):

Highly efficient heat transfer from bed to tubes.

High temperatures / intense radiation not needed.

Low outside temperature means no risk for hotspots even if cooling by reaction fails locally.

More benign conditions for tubes.

Tubes can have smaller diameters.

Smaller diameters means thinner walls possible (to take the pressure difference)

Smaller diameters mean much more efficient heat transfer inside tubes.

Less catalyst needed and shorter tubes possible. Reduction by ***two thirds*** estimated.[15]

Advantages with CLC-SMR

100% CO_2 capture

No pollutants in gas stream from air reactor.

All CO_2 is found exit stream from fuel reactor.

All of the CO_2 is captured, in contrast to gas separation technologies.

Thus, truly fully CO_2-free hydrogen possible.

This could be very important for future acceptance of blue hydrogen, as CO_2 emissions will need to go to zero.

This will also give CLC-SMR lower CO_2 emissions than green hydrogen in most countries, where fossil fuels are still used for power production.

Advantages with CLC-SMR

No pollutants

No pollutants are generated in air reactor.

Thus, the exhaust stream is very clean.

If fuel is free from nitrogen compounds other than N_2, NO_x cannot form in the fuel reactor.

If the fuel contains nitrogen compounds other than N_2, NO_x will form in the fuel reactor, but can be removed from the concentrated CO_2 stream. Thus, no NO_x emissions.

Similarly, any sulphur will be found in the CO_2 stream and possible to remove from this concentrated flow. (Some oxygen carriers are not compatible with too much sulphur. Thus, removal of sulphur from fuel could be motivated depending on the oxygen carrier.)

Advantages with CLC-SMR

Costs 1

The heat from burning the off-gas and anly supplementary fuel will be removed from boiler system via external fluidized-bed heat exchangers (FBHEs). Thus, the fluidized air and fuel reactors will be adiabatic and the reactors will come with an added cost as compared to normal SMR.

What is the essential cost of the fluidized-bed reactor system?
Example: a plant producing 300 MW of H_2, could capture 0.6 Mt CO_2/year
Assuming 50 m high air and fuel reactors, the total wall area of risers, cyclones and ducts is around 3000 m^2. The estimated cost of 0.4 m thick adiabatic wall is 1500-2000 €/m^2, corresponding to a cost of <6 M€, or <0.6 M€ yearly.

This gives a cost around 1 €/ton CO_2 for the fluidized-bed reactor system.

Advantages with CLC-SMR

Costs 2

Furthermore, the cost of the external fluidized-bed heat exchangers (FBHEs) is expected to be much lower than the conventional steam reformer tubes. As noted above the more benign conditions and effective heat transfer allow for reduced tube diameter. Thus, it is estimated that tube length and amount of catalyst could be decreased by a factor of three,* which means a significant cost reduction compared to conventional SMR.

In combination with higher thermal efficiency this should give negative cost of CO_2 capture.

*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 https://pubs.acs.org/doi/pdf/10.1021/acs.energyfuels.2c01086

STATE-OF-THE-ART, Chemical-looping combustion

Operation of 49 CLC pilots in sizes of 300 W to 3 MW with gaseous, solid and liquid fuels has been presented in 222 publications.[1,2] The work comprises more than 70 different oxygen-carrier materials and 12 000 h of operational experience.

A techno-economic study of a solid-fuel CLC boiler of 1000 MW_{th},[3] found a cost of 16-26 €/tonne CO_2, with the majority of the cost related CO_2 compression and oxygen production for the oxypolishing step, i.e. the oxidation of unconverted combustibles from the fuel reactor. The latter step would be avoided with gaseous fuels, where manufactured oxygen carriers with CLOU properties make more sense.

A design with focus on securing adequate circulation for CLC has been proposed for a 200 MW_{th} CLC boiler.[4] The study recommends "that the scaling-up of the CLC technology goes directly to industrial-scale demonstration; firstly, with the great experience already available, it can be questioned whether an intermediate step would really provide any conclusive answers to the key questions that remain to be answered with respect to the industrial scale operation. Secondly, an intermediate demonstration would not necessarily be less costly than adding the necessary parts for making an industrial-scale CFB into a CLC-CFB boiler. Moreover, an intermediate size demonstration step would cause unwanted delay of the industrial implementation of CLC."

STATE-OF-THE-ART
Oxygen carrier

Oxygen-carrier materials used in pilot operation include manufactured monometallic oxide systems, *e.g.* oxides of Ni, Fe, Mn, Cu and Co, as well as a number of combined oxide systems, primarily combined Mn oxides. Further, more than 3400 h of operation has been reported for low-cost natural ores, *i.e.* ilmenite ($FeTiO_3$), manganese and iron ore.[1,2] Thermodynamics and oxygen carrier capacity are well established for these systems.[5,6]

Low-cost natural ores is the most relevant option for solid fuels with ash, whereas more costly manufactured oxygen carriers could be motivated for gaseous fuels. Of greatest interest here are so called CLOU (Chemical-Looping with Oxygen Uncoupling) materials, which spontaneously release gaseous oxygen under the reducing conditions in the fuel reactor. In contrast to "normal" CLC oxygen carriers CLOU materials can reach full conversion and even produce a slight excess of O_2. Materials with CLOU properties include combined manganese oxides, i.e. manganese combined with calcium, iron, magnesium, silicon, and copper oxide.

The most developed CLOU materials are copper oxides and calcium manganate. The former with very rapid oxygen release but higher raw material cost and the latter with slower oxygen release but possible to manufacture from low-cost manganese ore and limestone. Both materials have reached full gas conversion in pilot operation. Further, operation with calcium manganate indicated a lifetime of thousands of hours, based on the loss of fines during 100 h of operation.[7]

Scale-up of calcium manganate production to around 3 tonnes was demonstrated in EU project SUCCESS using commercially available raw materials. This was done by Euro Support (the Netherlands), who is willing to scale up production further.

Furthermore, long-term operation with ilmenite for Oxygen Carrier Aided Combustion (OCAC) has been done in industrial-scale boilers, including 20 000 h burning municipal solid waste in a 75 MW CFB boiler[8-10] where 1000 tonnes of ilmenite was procured, and 500 h with a mix of recycled waste wood and wood chips in a 115 MW CFB boiler.[11] In addition, there is 830 h of OCAC operation with ilmenite and wood chips in a 12 MW CFB.[12,13] In the same boiler a manganese ore has been used in operation during 580 h, with an estimated oxygen-carrier lifetime of more than 1000 h.[14]

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Chalmers' CLC development

Chalmers University of Technology has been a key contributor to the development of chemical-looping combustion, having worked with development of oxygen-carrier material for the process since 1998 and being first to successfully demonstrate this fundamentally new fuel conversion process in sustained operation in a 10 kW prototype unit for gaseous fuel in 2003. Moreover, Chalmers was first to operate a 10 kW CLC unit designed for solid fuel (2006) and was also first to operate CLC with liquid fuels (2011). Chalmers now has more than 4 000 h of operational experience of chemical-looping combustion in four units, the largest being a 100 kW dual CLC for solid fuels. This is a third of global operational experience and involves first successful demonstration of chemical-looping combustion with oxygen carriers based on nickel, iron and manganese oxides, combined oxides like $CaMnO_3$ and $FeTiO_3$, as well as natural minerals, such as ilmenite and manganese ore, using natural gas, syn-gas, heavy oil, coal, pet coke and biomass as fuels. Chalmers has investigated more than 500 different oxygen carrier materials in laboratory fluidized-bed batch reactors and more than 70 in actual operation.

In addition to first demonstration of CLC with gaseous, solid and liquid fuels, as well as the first demonstration of the use of a number of monometallic or combined oxygen carriers, the work involves a number of breakthroughs in different aspects of chemical-looping technology, e.g. i) Proposal of: chemical-looping steam reforming for hydrogen production with simultaneous CO_2 capture[1], ii) Proposal of Chemical-Looping with Oxygen Uncoupling (CLOU),[2,3] iii) Finding the potential for CLOU using oxygen releasing capabilities of a number of combined manganese oxides, i.e. Mn combined with Fe, Ni, Si, Mg and Cu.[4-6]

Chalmers has >450 publications on CLC, including >250 reviewed articles and 20 PhD theses: http://www.entek.chalmers.se/lyngfelt/co2/co2publ.htm

Chalmers has been in close collaboration with more than 25 companies, universities and research institutes on CLC development and has been deeply involved in the conception of ten EU/ EU-RFCS projects on CLC and coordinated several.

Moreover, Chalmers coordinated the Nordic CO_2 Sequestration Programme ($NoCO_2$), 2003-2006, funded by Nordic Energy Research as well as the Nordic Project "Negative CO_2", one of three flagship projects selected for funding out of appr. 100 applications. Chalmers has also received a prestigious "Forskningsmiljö" from Swedish Research Council, i.e. appr. 2.5 M€ during 6 years.

Total funding for CLC-related research obtained by Chalmers is more than 20 M€.

The CLC research at Chalmers has been honoured with a Special Issue in Energy & Fuels: "2022 Pioneers in Energy Research: Anders Lyngfelt"[7]

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