

SMR ♥ CLC = the perfect match for blue hydrogen?

By combining Steam Methane Reforming with Chemical-Looping Combustion, SMR-CLC, it should be possible to produce hydrogen from natural gas and capture CO₂ with higher energy efficiency than conventional SMR. By Professor Anders Lyngfelt, Chalmers University of Technology

The need for zero-emission fuels in combination with large resources of natural gas has raised the interest in blue hydrogen. However, blue hydrogen comes with the well-known issues of CO₂ capture, i.e. the cost and energy penalty of CO₂ separation.

Moreover, CO₂ separation becomes significantly more costly if all the CO₂ needs to be captured, which is why conventional capture typically stops at around 90%. But will this be enough, when the rapidly dwindling carbon budgets indicate we need to reach zero emissions?

Today, the most common way to produce hydrogen is steam-methane reforming, SMR, of natural gas. The major constituent of natural gas is methane, CH₄, and the name of the process refers to the key reaction, the heat-demanding reaction between steam and methane to produce a syngas, consisting of CO, H₂, CO₂, H₂O and some unreacted CH₄, Figure 1.

In a subsequent process step called water-gas shift, WGS, the hydrogen content is increased by the reaction of H₂O with CO, giving H₂ and CO₂. The hydrogen can be extracted from the gas using pressure swing adsorption, PSA, providing high purity hydrogen. The remaining off-gas is burnt together with additional natural gas to provide the heat needed for the steam-methane reforming process.

The flue gas from burning off-gas needs to be stripped of CO₂ in order to achieve a CO₂-free hydrogen. It should be said that a part of the CO₂ can be captured upstream of the combustion, i.e. from the flows going into and out of the PSA step.

The steam-methane reforming takes place in long tubes filled with catalyst where the inside gas temperature may vary from around 600 to 900°C, with the heat provided by radiation from high-temperature flames outside the

tubes. To achieve sufficient heat transfer the temperature of the gases leaving the furnace is high, typically around 1200°C, which means that the major part of the heat produced by the combustion leaves the furnace instead of being utilized for the steam-methane reforming.

The locally high temperatures of flames in combination with a varying gas temperature and heat consumption inside the tubes means that the tubes are exposed to harsh conditions, and local hot spots may cause damage to the expensive tubes and catalyst.

Chemical-Looping Combustion, CLC, is a process where the oxygen is transferred from the air to the fuel using an oxygen carrier, circulating between the air reactor and the fuel reactor, Figure 2. Ideally, the exhaust from the fuel reactor only contains CO₂ and H₂O, the latter easily removed by condensation.

Thus, pure CO₂ can be obtained without any costly and energy demanding gas separation. This is because the combustion is accomplished without the air meeting with the fuel. The exhaust from the air reactor is just air which has lost most of its oxygen content.

Similar to circulating fluidized-bed combustion, FBC, and fluidized catalytic cracking, FCC, the chemical-looping process uses fluidized-bed technology, albeit with the oxygen carrier as bed material. The air reactor, having the major gas flow, can be used as a riser to

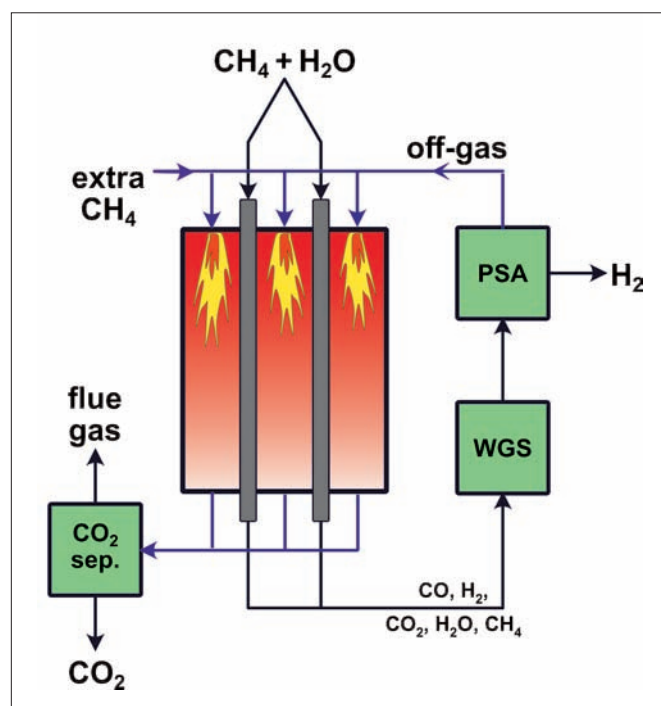


Figure 1. SMR, Steam-Methane Reforming with CO₂ capture

drive the circulation between the two reactors, and loop-seals fluidized by steam can be used to prevent any mixing of gas between the air and fuel reactor.

If the high temperature furnace used for burning off-gas and methane for heating the steam reforming tubes is replaced by chemical-looping combustion, CO₂ can be captured without a costly and energy demanding gas separation process, Figure 3.

An additional advantage with SMR-CLC is that the heat can be transferred to the steam reforming tubes using fluidized-bed heat exchangers, FBHE, with high heat transfer and low excess temperature. Thus, the temperature of the outgoing flue gases can be reduced from 1200 to 935°C, which means that a significantly higher proportion of the combus-

tion heat is used for heating of the steam-methane reforming reaction [1]. Thus, not only is the energy penalty of CO₂ capture avoided, furthermore the energy efficiency can be increased at the same time as CO₂ is captured. This is likely the only CO₂ capture process with raised energy efficiency. To be fair, this is true for the capture of CO₂, but transport and storage also requires pressurized CO₂.

A further advantage is that CLC-SMR can eliminate NO_x emissions. Firstly no thermal NO_x is formed in the air reactor because of the low temperature and the absence of flames. Secondly, the absence of any nitrogen compounds other than N₂ in the natural gas will also prevent the formation of fuel-NO_x in the fuel reactor.

But does it work? Although no full-scale applications have been built, there is significant experience from around 50 smaller CLC pilots of 0.3 kW to 3 MW, with a total operational experience nearing 12,000h, using around a hundred different oxygen carrier materials for burning gaseous, solid and liquid fuels [2].

Methane is the most difficult molecule to oxidize in chemical-looping combustion of off-gas. Early work on chemical-looping focused on oxygen carriers based on nickel oxide, which has high reactivity towards methane. Unfortunately, nickel oxide is quite expensive, comes with health and safety issues, and is not able to give full gas conversion because of thermodynamic constraints. Since then, however, novel combined manganese oxides with the ability to release gas phase oxygen have been developed. Thus, pilot operation has verified that full conversion of natural gas with a slight excess of oxygen can be reached

with calcium manganite, [3].

The material can be manufactured from low cost manganese ore and limestone and pilot operation verifies that materials with high mechanical and chemical integrity can be produced. Moreover, these materials are environmentally benign and any fines formed by attrition can be recovered and used for production of new oxygen carrier, provided that the natural gas is free of ash.

Both pilot operation and modelling indicate that the solids inventory needed to achieve full conversion is viable [4, 5].

Thus, by combining Steam Methane Reforming with Chemical-Looping Combustion, SMR-CLC, it should be possible to:

- produce hydrogen from natural gas and capture CO₂, with higher energy efficiency (not counting the CO₂ compression) than conventional SMR
- avoid costs of CO₂ separation
- avoid difficulties with high temperatures in SMR
- capture 100% of the carbon
- eliminate NO_x emissions

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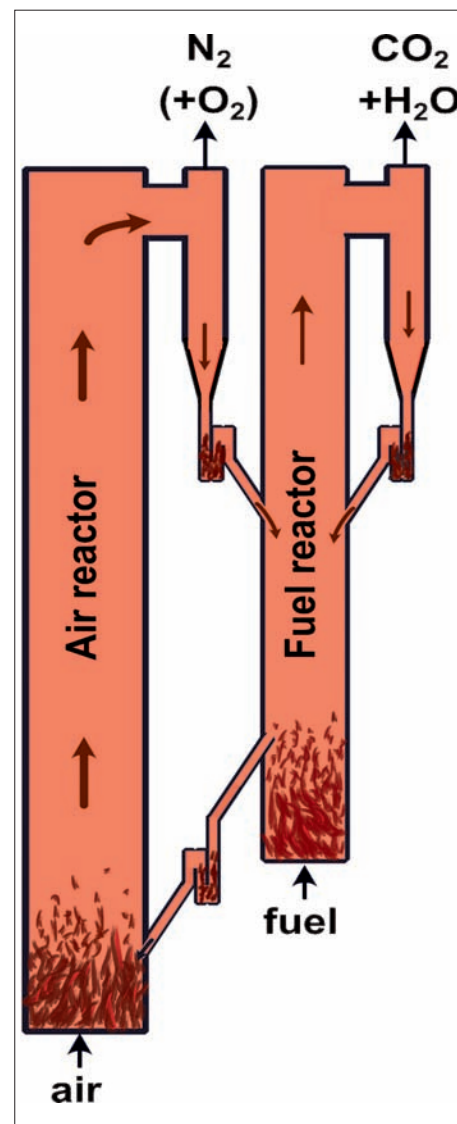


Figure 2. Example of a CLC reactor system

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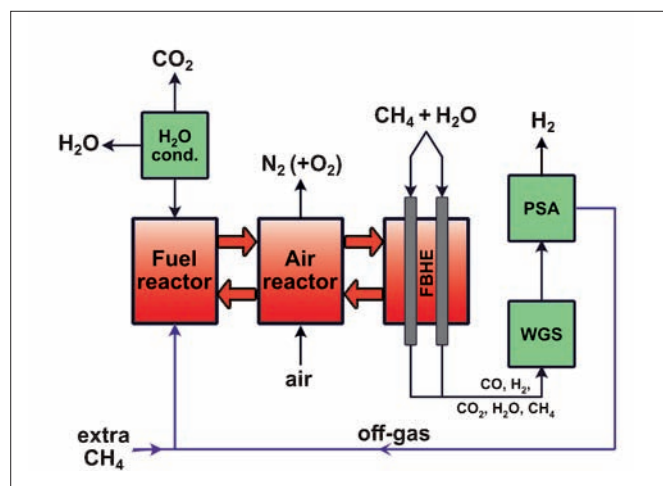


Figure 3. SMR-CLC, Steam-Methane Reforming and Chemical-Looping Combustion

More information

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