

# HYDROGEN PRODUCTION VIA CHEMICAL-LOOPING

## IN A FIXED BED REACTOR

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### Summary

Chemical-looping steam reforming (CLSR) is a chemical-looping combustion (CLC) derived technology in which air is replaced by steam as oxidant. CLSR combines the inherent CO<sub>2</sub> capture of CLC with the production of PEMFC-ready hydrogen without further purification steps. CLSR thus results in strong process intensification in hydrogen production. We present results from a study of CLSR which combines thermodynamic screening for carrier selection with synthesis and characterization of highly active and high-temperature stable nanostructured oxygen carriers, and a reactor modeling study to demonstrate the feasibility of CLSR in a periodically operated fixed-bed reactor.

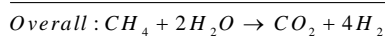
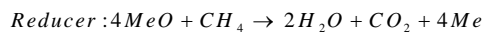
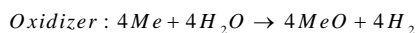
### Keywords

Chemical-looping, hydrogen production, nanomaterials, fixed bed reactors, periodic reactor operation

## Introduction

Chemical-looping combustion is an emerging combustion technology for ultra-clean fossil fuel combustion<sup>1-4</sup>. In CLC an oxygen carrier, typically a metal, is oxidized with air in one reactor (oxidizer) and then reduced in contact with a fuel in a second reactor (reducer). After condensation of steam from the effluent of the reducer, a sequestration-ready CO<sub>2</sub> stream is produced. CLC is hence a flameless combustion technology, which does not require air separation and produces sequestration-ready CO<sub>2</sub> streams without significant penalty on power plant efficiency. CLC thus allows for significant process intensification in clean combustion technology.

In principle chemical-looping can be used with any fuel and any oxidizing gas assuming that the oxygen carrier shows sufficient reactivity for both. When air is replaced by steam as oxidizing gas, ultra-pure hydrogen is produced as effluent of the reducer after condensation of unreacted steam. As a net reaction, this results in chemical-looping steam reforming (CLSR), which is illustrated with methane as fuel:



In contrast to conventional methane steam reforming, however, CLSR of methane results in full combustion of the fuel carbon to CO<sub>2</sub>, which is captured as a sequestration-ready high-pressure stream at the fuel reactor exit. Since the steam/hydrogen stream is never contacted with the fuel, the typical problems with CO contamination of the hydrogen stream are avoided, making the additional clean-up of the hydrogen stream via WGS, PrOX and/or other reactor stages unnecessary. CLSR can hence be regarded as a highly intensified process for the

production of PEM fuel cell-ready hydrogen streams. Major challenges for SCLR include the slower oxidation kinetics, since steam is a weaker oxidizer than oxygen, high temperature stability of the carrier material, and particle attrition.

In the present contribution, we present results from a study of CLSR which directly address the above issues: CLSR was investigated in a combination of thermodynamic calculations for carrier selection, synthesis and characterization of highly active and high-temperature stable nanostructured oxygen carriers, and a reactor modeling study to evaluate the feasibility of CLSR in a periodically operated fixed-bed reactor in order to avoid carrier attrition.

## Thermodynamic screening of carriers

A detailed thermodynamic screening study of a broad range of metals was conducted, evaluating their redox potential. This screening was based on thermodynamic calculations using a commercial software package (FACTSAGE 5.0).

Figure 1 shows results in terms of steam conversion vs temperature for select carriers. While a range of metals show very high steam conversion over the entire temperature range, most were discarded either due to low melting points, toxicity of the metal, or the irreversibility of the oxidation process. Among all screened metals, Fe (purple line) and its lowest-valent oxide FeO (green line) showed most promise as carrier for CLSR, combining good reactivity with low cost and low toxicity.

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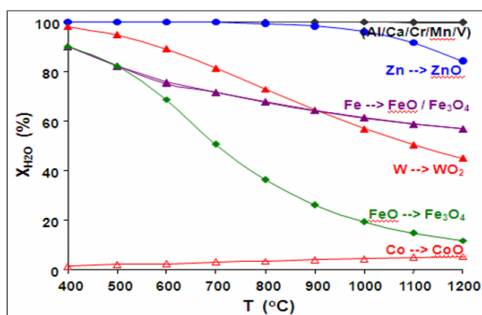


Figure 1. Equilibrium steam conversion for metals and metal oxides versus temperature.

## Synthesis and evaluation of carriers

Since steam is a weaker oxidant than oxygen, oxidation kinetics is expected to be slower in CLSR than in CLC. We have previously shown that nanostructuring of the oxygen carrier via a nanocomposite synthesis yields highly robust materials with significantly accelerated oxidation kinetics<sup>5-7</sup>. Here, nanostructured Fe-BHA (barium hexa aluminate) and Fe-SiO<sub>2</sub> were synthesized, characterized (via XRD, BET, TEM, and TPO/TPR), and tested in a fixed bed reactor with a controlled steam feed.

First results from the reactor tests are shown in figure 2 for a 40wt% Fe-BHA sample in a pure steam stream at 500°C. One can see the appearance of hydrogen right at the onset of the steam feed. After less than 2 min. the sample has been fully oxidized, as apparent from the break-through of steam. While more quantitative studies are obviously needed (and currently under way), these results confirm that nanostructured iron-based carriers do indeed allow for surprisingly fast oxidation with steam.

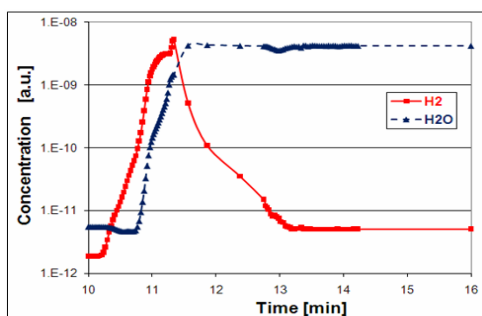


Figure 2. Oxidation of Fe-BHA with steam at 500°C

## Fixed bed reactor simulations

Finally, a fixed-bed reactor model was developed and analyzed in order to evaluate the feasibility of SCLR in a periodically operated fixed-bed reactor. The analysis is built on a previously published model by Kuipers and coworkers who analyzed a similar periodic fixed-bed process for conventional chemical looping combustion<sup>8</sup>. The computations are based on a dynamic analysis of the pseudo-homogeneous energy and mass balance equations for a fixed-bed process. Since robust oxidation/reduction kinetics for the selected carriers are not available at this point yet, the simulation are conducted under the

assumption of instantaneous chemical reaction (i.e. infinitely fast kinetics).

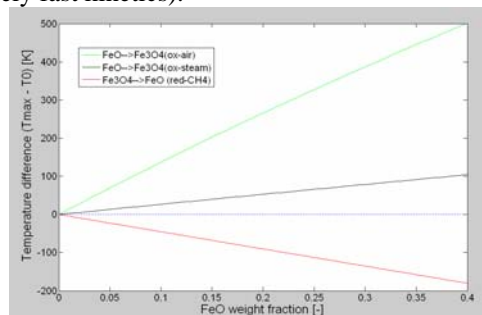


Figure 3. Fixed bed analysis of CLC and SCLR using Fe-based carrier.

Figure 3 shows the maximum temperature change in CLC and CLSR during the reduction and oxidation as a function of the FeO weight fraction in the oxygen carrier. Replacing air with steam as oxidizer results in strongly reduced temperature maxima during carrier oxidation. For FeO loadings below ~40%, maximum temperature excursions remain below 100K, i.e. well below the >400K temperature rise observed in the air-blown process, indicating that a fixed-bed reactor configuration is feasible without problems of heat accumulation or excessive hot spots during the oxidation phase.

Ongoing work is focused on the effect of co-feeding air with steam in the oxidation phase in order to increase the exothermicity of the process, and on a more detailed kinetic analysis of the fixed bed operation.

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