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Testing of Innovative Fe- and Ca-Mn-based Oxygen Carriers with Natural Gas in Continuous Operation

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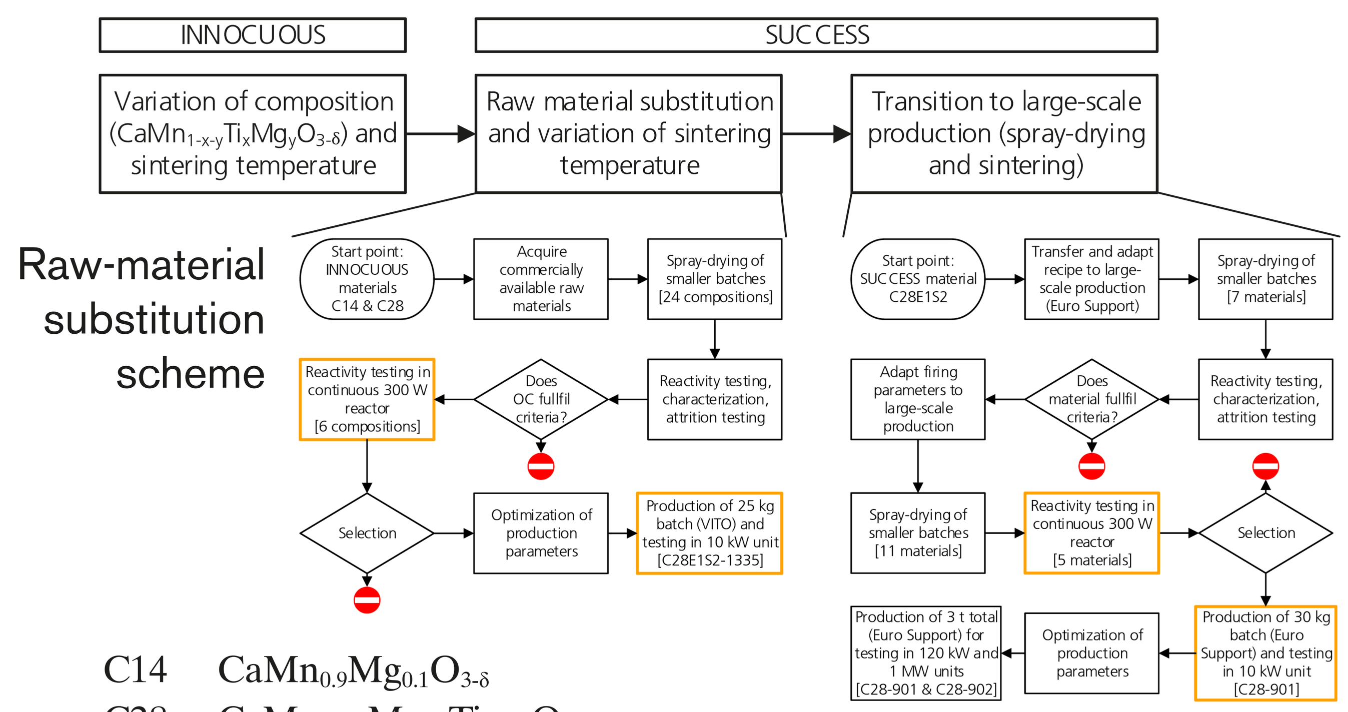
Summary

Chemical-looping combustion (CLC) of gaseous fuels, such as natural or refinery gas, could be a viable option in a variety of industries for production of heat and electricity with CCS. Further, CLC can be combined with conventional steam–methane reforming for efficient carbon-neutral hydrogen production. A series of collaborate European projects have been carried out since 2002, which focused on oxygen-carrier development and upscaling of both the CLC process and oxygen-carrier production with sulfur-free natural- and refinery gases as fuel. In the latest project, SUCCESS (2013-2017), a series of oxygen carriers based on Fe and Ca-Mn materials were developed using commercial and low-cost raw materials. Two commercial methods for particle production were used: impregnation of Fe_2O_3 on Al_2O_3 and spray-drying of $CaMnO_3$. These two oxygen carriers were tested using a continuously operating laboratory-scale unit, which has a nominal fuel input of 10 kW_{th}. In this unit, the gas velocities in the riser and in the grid-jet zone of the gas distributor come close to gas velocities of industrial-scale units and the material is exposed to a large number of redox cycles. Both materials functioned well during operation with natural gas, with low agglomeration. Although the degree of particle elutriation was high for both materials, the actual fines production (< 45 µm) was high only initially, but decreased as a function of time.

Conclusions

- A series of oxygen-carrier particles based on $CaMnO_{3-\delta}$ (C14, C28) were produced up to multi-ton scale using spray-drying. It was found that the perovskite structure is simple to produce, also with highly heterogeneous and low-grade raw powders.
- The important CLOU property was seen for all Ca-Mn-based oxygen-carrier materials produced.
- Several of the Ca-Mn-based oxygen-carrier materials produced with substitute raw-materials could match the performance of the reference materials produced with high-purity raw materials, and several oxygen carriers showed a combination of high reactivity and and low attrition.
- For the impregnated Fe-based material, the gas yield was less than 85%, even at specific solid inventories of more than 1000 kg/MW_{th}.
- For the $CaMnO_3$-based materials, the expected lifetime is 700-12 000 h, and for the Fe-based oxygen carrier, the expected lifetime was around 700 h.

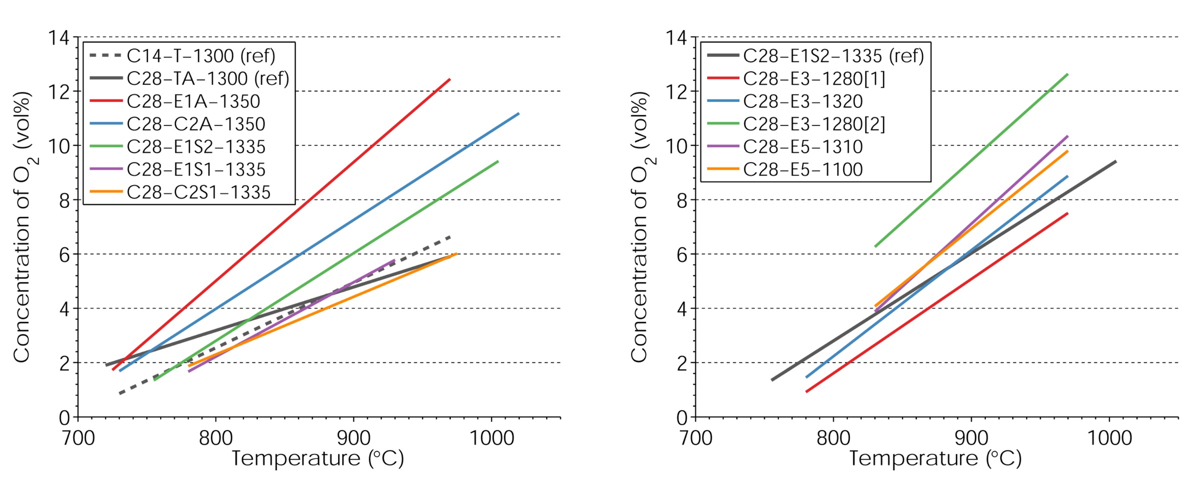
Development route (Ca-Mn-based OCs)



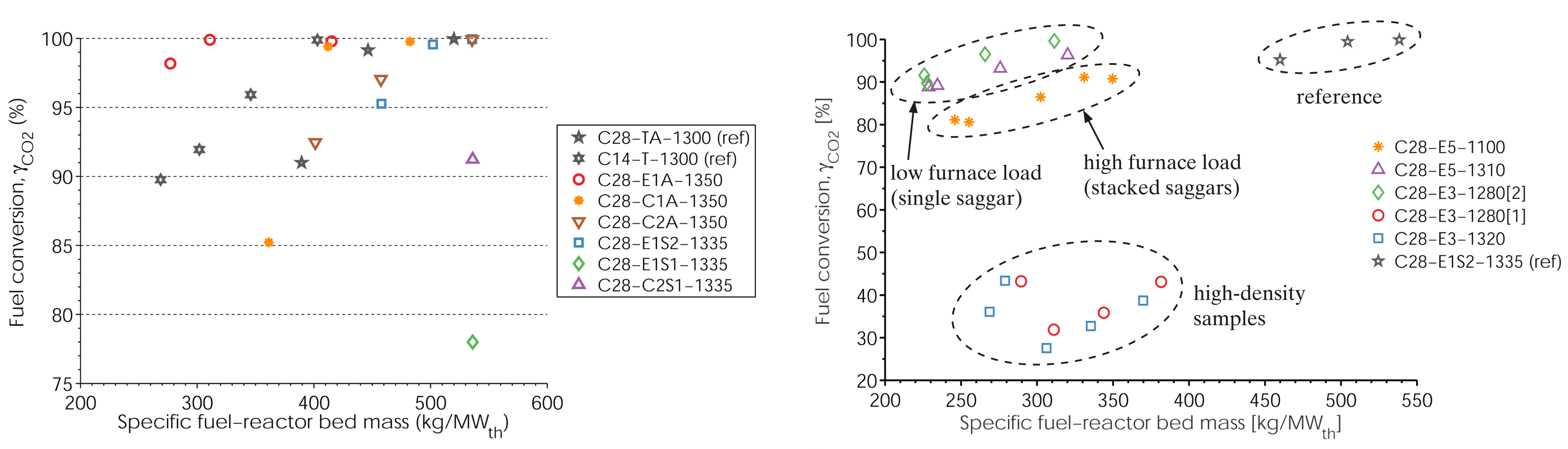
C14 $CaMn_{0.9}Mg_{0.1}O_{3-\delta}$
C28 $CaMn_{0.775}Mg_{0.1}Ti_{0.125}O_{3-\delta}$

Results

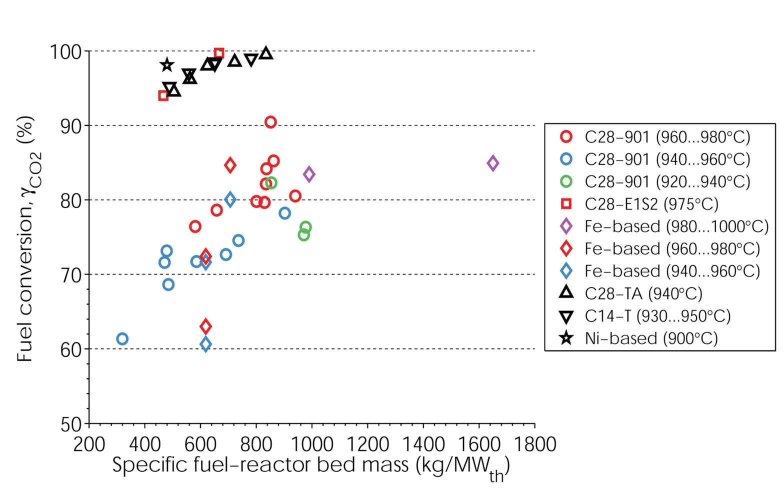
Raw-material substitution — Up-scaling



CLOU properties



CH_4 conversion at 900°C in 300 W reactor



CH_4 conversion in 10 kW reactor

Experimental details

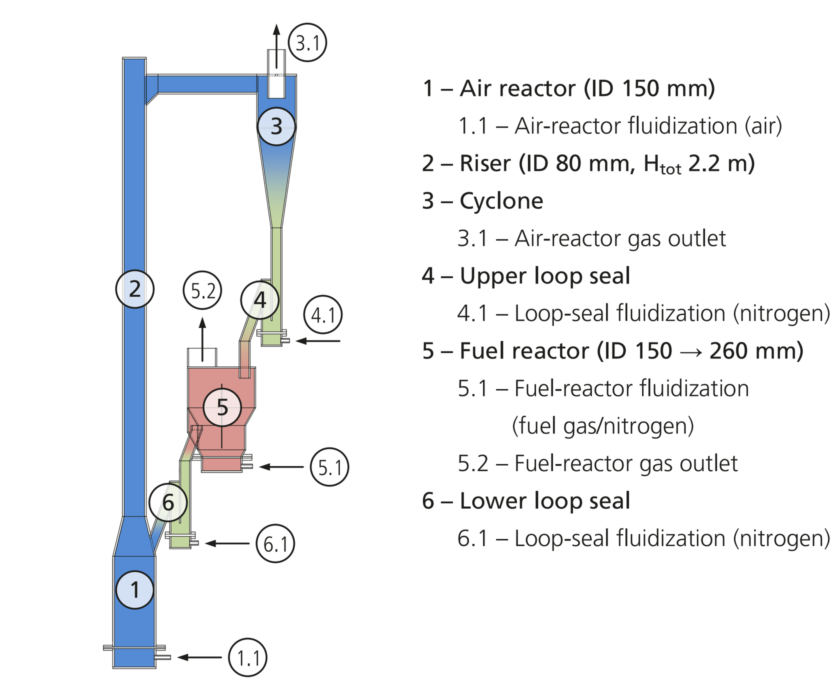
Fe-based, impregnated OC

Fuel input	3.2-5.8 kW_{th}
Fuel-reactor temp.	900-970°C
Gas vel. in Riser	1.4-1.7 m/s
Solids inventory	9-12 kg
Spec. FR bed mass	620-1650 kg/MW_{th}

Ca-Mn-based, spray-dried OC (2 OCs)

Fuel input	1.2-8.9 kW_{th}
Fuel-reactor temp.	850-980°C
Gas vel. in Riser	1.9-2.9 m/s
Solids inventory	8-16 kg
Spec. FR bed mass	320-2300 kg/MW_{th}

Experimental parameters

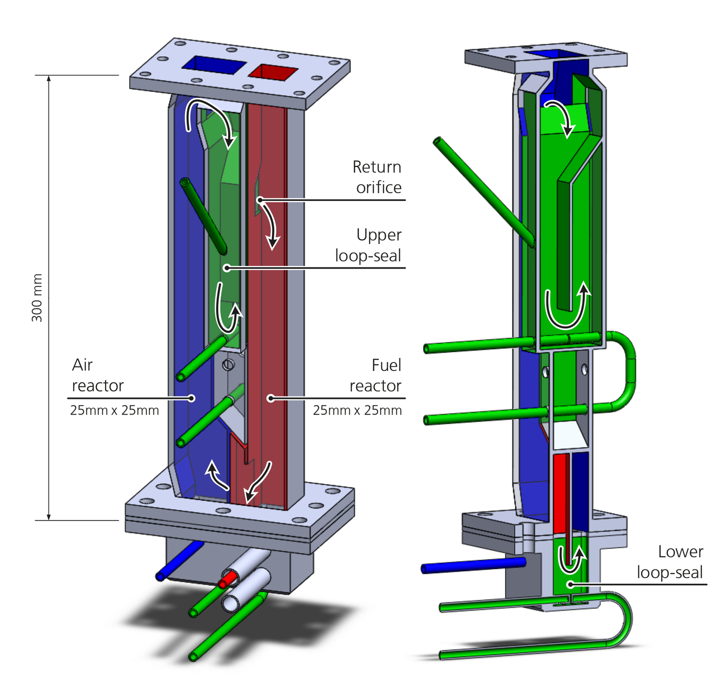


10 kW chemical-looping reactor

Ca-Mn-based, spray-dried OC (11 OCs)

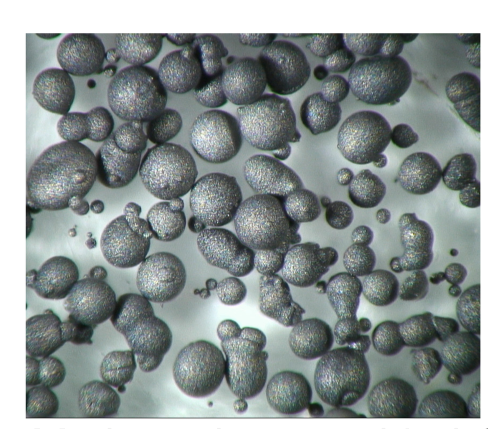
Fuel input	180-300 W_{th}
Fuel-reactor temp.	850-975°C
Gas vel. in Riser	0.7-1.0 m/s
Solids inventory	310-400 g
Spec. FR bed mass	225-540 kg/MW_{th}

Experimental parameters



300 W chemical-looping reactor

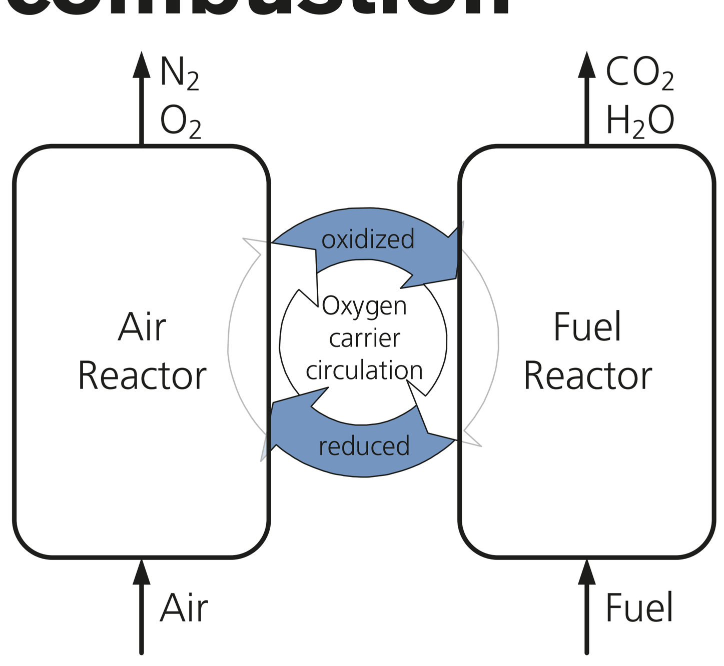
Fe-based, impregnated OC (≈ 100-200 µm)



Ca-Mn-based, spray-dried OC (≈ 100-200 µm)

Chemical-looping combustion

- Two interconnected fluidized-bed reactors
- No exchange of gas between reactors, i.e., air and fuel are not mixed.
- Oxygen is transported to the fuel by a solid oxygen carrier, which is cyclically oxidized and reduced.
- Net heat of reaction is the same as for regular air combustion, i.e., there is no energy penalty for separation of CO_2.



Contact information

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