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Experimental demonstration of CLC and the pressure effect in packed bed reactors using $NiO/CaAl_2O_4$ as oxygen carrier

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HIGHLIGHTS

- CLC is demonstrated in a lab scale pressurized packed bed reactor.
- $NiO/CaAl_2O_4$ has been successfully used as oxygen carrier material.
- The pressure effect is small for both the oxidation and the reduction cycles with H_2 or syngas.
- The Ni-based material is suitable OC for packed bed CLC operating at high temperatures and pressures.

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ABSTRACT

Chemical-looping combustion is an emerging technology for power production with integrated CO_2 capture. With this combination, the energy penalty is expected to be relatively low, provided that the reactors are operated at elevated pressures (20 bar). Packed bed reactors can better accommodate high pressures compared with interconnected fluidized bed systems, while the challenging gas/solid separation is circumvented. In this work, CLC is demonstrated in a lab scale pressurized packed bed reactor using $NiO/CaAl_2O_4$ as oxygen carrier material. H_2 and syngas with a typical composition obtained from coal gasification are used as fuel in the reduction step. The pressure has been varied between 2 and 7.5 bar, while it is demonstrated that the pressure has quite a small effect on the overall performance of the CLC reactor. The experiments are well described by a one-dimensional pseudo-homogeneous reactor model, with which it is shown that the required high temperatures for power production can be reached in case the reactor is scaled-up (decreasing the heat losses). A drawback of the oxygen carrier used is that the reduction kinetics depend on the temperature during the previous oxidation, which has been fixed during all the experiments. The reduction kinetics decrease with the oxidation temperature, which is probably caused by interaction with the support material and therefore some further modifications on the support material are required for high temperature applications. In case the process is carried out with syngas and steam, the heat management strategy has to be adapted because of the heat produced by the water gas shift reaction.

1. Introduction

It is well accepted that the observed climate change is related with increasing anthropogenic CO_2 emissions and therefore ways to reduce these emissions are under investigation. CO_2 capture and storage is one of these solutions with the highest impact on the emissions in the mid-long term [1]. Power plants contribute to 25% of the CO_2 emissions and thus most of the research on CCS is carried out on coupling the power production with CO_2 capture [2]. CCS is, however, an energy intensive process, while the CO_2 separation step contributes the most to the total energy penalty of CCS. The research on CCS is thus focusing on decreasing the energy penalty of the capture step. In this respect, if the power plant is integrated with chemical-looping combustion (CLC), the energy penalty is lower compared with other capture technologies, especially because the CO_2 capture is integrated in the combustion process as a mechanical separation step instead of a physical separation. With CLC, in fact the fuel is not combusted with air, but with a solid oxygen carrier (MeO), producing CO_2 and H_2O (unmixed with nitrogen). Afterward, the oxygen carrier (Me) is oxidized to the original species (MeO) by reacting it with air (thus the

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Nomenclature

Abbreviations

CLC	chemical-looping combustion
OC	oxygen carrier

Symbols

b	stoichiometric factor in the reduction reaction of metal oxide, –
C	concentration, mol m^{-3}
C_p	heat capacity, J mol^{-1} K^{-1}
D_{ax}	axial dispersion coefficient, m^2 s^{-1}
d	diameter, m
E_A	activation energy, J mol^{-1}
ΔH_R	enthalpy of reaction, J mol^{-1}
k_0	pre-exponential factor, mol^{1-n} m^{3n-3} s^{-1}
M	molar mass, kg/mol
n	reaction order in gas, –
p	pressure, Pa
R	gas constant, J mol^{-1} K^{-1}
r	reaction rate, mol m^{-3} s^{-1}
T	temperature, K
t	time, s
v	superficial velocity, m s^{-1}
x	axial position, m
X	particle conversion, –
y	mole fraction in gas feed, –

Greek letters

ε	porosity, m^3 m^{-3}
Δt	time difference between two measurements, s
ζ	stoichiometric factor, mol gas/mol solid
λ_{eff}	effective heat dispersion coefficient, W m^{-1} K^{-1}
η_g	dynamic gas viscosity, kg m^{-1} s^{-1}
ω	mass fraction, kg kg^{-1}
τ	Time delay in the thermocouple, s

subscripts

act	active
i	gas component
j	solid component
p	particle
red	reduction
eff	effective
g	gas
r	reactor
s	solid
TC	thermocouple
w	reactor wall

superscripts

in	inlet

oxygen carrier is used to separate the oxygen from air). The oxidation of the metal is a very exothermic reaction and the heat released during this reaction is used for power generation in a gas turbine and in a steam cycle.

The general reactions taking place during CLC are:
Oxidation

$$Me + \frac{1}{2}O_2 \rightarrow MeO \tag{1}$$

Reduction

$$MeO + H_2 \rightarrow Me + H_2O \tag{2}$$

$$MeO + CO \rightarrow Me + CO_2 \tag{3}$$

Most of the studies on chemical looping combustion focused on the use of circulating fluidized bed reactors, where the solid material is circulated between the air reactor (where it is oxidized) and the fuel reactor (where it is reduced). Cyclones are required to achieve the separation of gases and solids at the exit of both reactors. However, it has been demonstrated that high temperatures and pressures (~20 bar and 1200 °C) are required for operation with a high overall energy efficiency [3–5]. These operating conditions are very demanding for circulating fluidized bed reactors, especially for the gas–solids separation and loop seals; in practice, a CLC system based on fluidized bed reactors operating at elevated pressures has never been tested. On the other hand, high pressure and high temperature conditions can be easily accommodated in packed bed reactors. In packed bed reactors, the solids are stationary in the reactor and the gases are periodically switched. The complete CLC system with packed bed technology requires a gas switching system that needs to be operated at high temperatures. It should also be noted that if one assumes that also fluidized beds can be operated at high pressures and temperatures the system analysis shows similar efficiencies as for packed beds around 41–42% for for an IGCC with chemical looping. A complete analysis can be found in Hamers et al. [5].

A packed bed configuration for CLC consists of several dynamically operated reactors placed in parallel. A process cycle consists of the following consecutive operating steps: oxidation, heat removal, reduction and purge. Starting with a reduced oxygen carrier (OC) and the reactor mainly at 450–600 °C, the oxygen carrier is oxidized with air and heat is produced inside the reactor (step 1). When the complete bed has been oxidized, a hot air steam is produced at 1200 °C (step 2) while feeding air at 450 °C (gas temperature after adiabatic compression from ambient conditions to 20 bar). After the heat is blown out of the reactor, the reactor is purged with N_2 to avoid direct contact between O_2 and the fuel. Subsequently, the fuel (syngas produced in the coal/biomass gasifier) is fed to the reactor, the OC is reduced again and a CO_2/H_2O stream is produced, which is cooled down, the steam condensed and separated and the CO_2 is compressed and ready for storage or further utilization. After the reduction, the bed needs to be purged again. To have a continuous process, at least one reactor has to be operated in each operating step.

Several oxygen carriers (OCs) could be selected for this process [6], in general Ni-based OCs, ilmenite and a combination of Cu/Mn-OCs seem to be good candidates. Ilmenite has the advantage that it is a natural material and thus that the costs of the raw material are low and it is environmentally friendly. With ilmenite the temperature rise in the reactor should be sufficient to reach 1200 °C [7] while also the selectivity to H_2O and CO_2 is not an issue. The main drawbacks of the material are that the reaction rates are relatively low at low temperatures and it needs to be activated at high temperatures to get a reasonable reaction rate [8]. To work with ilmenite, the operation strategy needs to be adapted so that the reduction can be carried out at high temperature [9]. On the other hand, nickel and copper OCs have a better reactivity at low temperatures. While the melting point of copper does not