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Chemical-looping combustion of synthetic biomass-volatiles with manganese-ore oxygen carriers

Patrick Moldenhauer[a,*], Sebastian Sundqvist[b], Tobias Mattisson[a], Carl Linderholm[a]

[a] Chalmers University of Technology, Department of Space, Earth and Environment, 412 96 Gothenburg, Sweden
[b] Chalmers University of Technology, Department of Chemistry and Chemical Engineering, 412 96 Gothenburg, Sweden

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ABSTRACT

Carbon capture and storage of CO_2 from combustion of biomass, i.e., bio-energy carbon capture and storage (BECCS), makes it possible to obtain so-called negative emissions – the atmosphere is cleansed from carbon dioxide. The purpose of the present study was to investigate the suitability of different manganese ores as oxygen carriers in chemical-looping combustion of biomass fuels. For this screening study, a laboratory-scale, circulating fluidized-bed CLC system with a nominal fuel input of 300 W_{th} was used. The primary focus was to investigate the reactivity of these oxygen carriers towards biomass fuels, and find a reactive oxygen carrier with sufficient mechanical stability that could be suitable for large-scale chemical-looping combustion of biomass. A synthetic "biomass volatiles" gas was used to study how the different gas components react with the oxygen-carrier particles. Additional experiments were conducted with methane and a syngas. Parameter studies concerning temperature and specific fuel-reactor bed mass (bed mass per fuel thermal power in kg/MW_{th}) were carried out. With the synthetic biomass volatiles, conversion of fuel carbon to CO_2 as high as 97.6% was achieved. For a majority of the investigated ores, essentially all C2 and C3 hydrocarbons were converted, as well as a very high fraction of the CO. Reactivity towards CH_4 was generally lower, but improved at higher temperatures. The resistance of the oxygen carriers towards mechanical degradation was measured in a jet-cup attrition test rig. The measured attrition was estimated as "intermediate" for four of the five tested materials, while one of the ores displayed high attrition.

1. Introduction

1.1. Chemical-looping combustion with biomass

Carbon capture and storage (CCS) has been recognized as a major option for climate change mitigation (IPCC, 2005; Azar et al., 2013). For CO_2 capture, first generation technologies include pre-combustion, post-combustion and oxyfuel, which all require an active gas separation. Gas separation involves substantial investment and operational costs as well as significant energy penalties, estimated to be in the order of about 10%-points of efficiency for a power plant (Ekström et al., 2009; Abanades et al.,2015).

Chemical-looping combustion (CLC) is a combustion principle that uses metal oxides for oxygen transfer from air to fuel. Thus, fuel can be oxidized without mixing fuel and combustion air and the combustion products, i.e., CO_2 and steam, are recovered in a separate flow without any active gas separation. After condensation of steam essentially pure CO_2 is obtained. Thus, CO_2 capture is inherent to the process and major costs and penalties for active gas separation are avoided. CLC is the only known CO_2 capture technology where a very significant breakthrough could be envisaged regarding the costs and energy penalty of gas separation.

Combustion of biomass is CO_2 neutral since biomass incorporates atmospheric CO_2 during its growth via photosynthesis. If the CCS strategy is applied to biofuel emissions, negative emissions are effectuated – the air is cleansed from carbon dioxide. The combination of CCS and biofuel is referred to as BECCS – Bio-Energy Carbon Capture and Storage. Large-scale implementation of BECCS is presented by the IPCC (Intergovernmental Panel on Climate Change) not as a possibility, but as a necessity, if the global average surface temperature is to be limited to 2 °C (IPCC, 2014). The climate efficiency of BECCS is superior to other options for utilizing biomass. This is due to the fact that each fossil-based carbon molecule that is replaced with a biomass-based carbon molecule and BECCS, results in a net decrease of two carbon molecules from the atmosphere, i.e., one due to the replacement and one due to the removal from the atmosphere. If, in contrast, biomass is used for the production of liquid fuels for transport at a conversion rate of 50%, the net decrease is only half a carbon molecule.

* Corresponding author.
E-mail address: patrick.moldenhauer@chalmers.se (P. Moldenhauer).

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Nomenclature

a	pre-exponential factor (–)
f_{Ci}	carbon fraction of i (CO, CH_4, C2 or C3), Eqs. (2)–(5) (mol/mol)
m	mass (kg)
$m_{bed,FR}$	bed mass in fuel reactor (kg)
$m_{OC,ox}$	mass of oxygen carrier in the most oxidized state (kg)
$\dot{m}_s$	mass flow of solids, Eqs. (9) and (11) (kg/s)
N	theoretic number of continuously stirred-tank reactors (CSTR) in series (–)
t	time (s)
T	temperature (°C)
u_0	superficial gas velocity (m/s)
u_{slip}	slip velocity, i.e., relative velocity between gas and particle (m/s)
u^*_{slip}	dimensionless slip velocity (–)
u_t	terminal velocity based on average values of particle size and density (m/s)
x_i	concentration of species i (mol/mol)
γ_{CO2}	CO_2 yield or carbon fraction of CO_2, Eq. (1) (mol/mol)
$\Delta\dot{m}_{O_2,AR}$	mass of oxygen consumed by the oxygen carrier in the air reactor during (continuous) fuel operation (kg/s)
τ	total residence time of an average particle in a series of N CSTRs (s)
ω	degree of mass-based conversion, Eq. (8) (kg/kg)
AR	air reactor
BECCS	bio-energy carbon capture and storage
CCS	carbon capture and storage
CLC	chemical-looping combustion
CLOU	chemical-looping combustion with oxygen uncoupling
CSTR	continuously stirred-tank reactor
FR	fuel reactor
ICP-SFMS	inductively coupled plasma-sector field mass spectrometry
LOI	loss on ignition, i.e., mass loss upon heating to 1000 °C
M_xO_y	oxidized metal oxide
M_xO_{y-1}	reduced metal oxide
TGA	thermo-gravimetric analyzer
XRD	X-ray (powder) diffraction

The fundamental principle of CLC is that a fuel is oxidized using two separate reactors: an air reactor (AR) and a fuel reactor (FR), as shown in Fig. 1. A circulating flow of oxygen-carrier particles performs the task of transporting oxygen between these two reactors. Thus, direct contact between fuel and air is avoided, and, consequently, the combustion products CO_2 and H_2O are not diluted with N_2. The reactor system can consist of two interconnected fluidized beds, the air reactor and the fuel reactor, with the oxygen carrier circulating between the two.

Most research efforts within chemical looping have focused on gaseous fuels, but in the last years work has been dedicated to adapting CLC to solid fuels. Lyngfelt presented a review on chemical-looping combustion with solid fuels (Lyngfelt, 2014), where it is shown that solid-fuel studies concerning use of coal are numerous, whereas studies dealing with biomass fuels are few. Biomass consists mainly of volatile components and a minor share of fixed carbon. The volatiles can react with the oxygen carrier as a "normal" gaseous fuel, and the char remaining after devolatilization is more reactive as compared to chars from coal or petcoke, due to (1) a porosity, (2) a higher content of oxygen and hydrogen and (3) a higher content and dispersion of catalytic ash components (e.g., Ca, K, Na). Hence, higher solid fuel conversion as well as more effective CO_2 capture can be expected with biomass than with coal or petcoke.

1.2. Manganese-based oxygen carrier materials

Manganese-based oxygen carriers belong to a group of materials, which have the potential to release gas-phase oxygen in the fuel reactor. This oxygen release is triggered by differences in oxygen concentration and temperature between the air reactor and the fuel reactor. A chemical-looping process, where gas-phase oxygen is released in the fuel reactor is usually referred to as chemical-looping combustion with oxygen uncoupling (CLOU). In CLOU, the reactant, i.e., fuel, can react directly with gas-phase oxygen instead of the solid oxygen-carrier, as in regular CLC. For solid fuels, CLOU is potentially much faster than a solid–solid reaction as in CLC. But even for gaseous fuels, which includes volatiles, CLOU is expected to entail better conversion than CLC for three reasons (Moldenhauer et al., 2012);

1. Reactant gases that bypass the oxygen-carrier bed in bubbles can be oxidized by oxygen released on top of the bed. This applies especially in a bubbling fluidized-bed.
2. If the release of oxygen is fast, then normal combustion reaction occurs, which is likely to be faster than a gas–solid reaction in CLC.
3. In regular CLC and for a first order reaction, full conversion of gaseous reactant is approached asymptotically at increased bed mass. In consequence relatively large bed masses are needed to convert the last remains of fuel. In CLOU, the oxygen release occurs independently of the reactant concentration, and consequently a much lower bed mass is required the reach full conversion.

1.2.1. Existing studies with manganese ore-based oxygen carriers

There is a multitude of publications available that deal with the use of manganese ore-based oxygen-carrier materials in chemical-looping combustion.

Leion et al. (2009) published an experimental investigation of three untreated manganese ores, four beneficiated manganese ores, as well as 12 iron-based materials that were tested in a batch, fluidized-bed reactor. They found that several of the mineral-, Mn-based materials showed good reactivity with both syngas and methane, but only one of these materials was able to fulfil the criteria for crushing strength and fluidization properties (Leion et al., 2009).

Based on experiments conducted in a batch reactor as well as in a TGA, Fossdal et al. found that the addition of CaO to manganese ore resulted in the formation of a calcium-manganite perovskite, which has potential positive effects on reactivity and structural integrity (Fossdal et al., 2011).

Linderholm et al. tested a manganese ore in continuous CLC operation in a 10 kW unit with a bituminous coal and a petcoke. As compared to ilmenite, the manganese ore achieved a significantly higher rate of fuel gasification and higher gas conversion, while fines

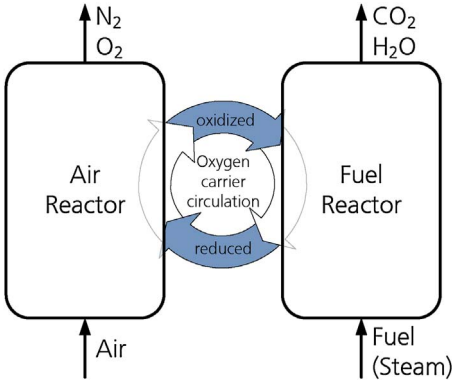

Fig. 1. Schematic description of chemical-looping combustion process.