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Chemical Looping Combustion of gaseous and solid fuels with manganese-iron mixed oxide as oxygen carrier

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ABSTRACT

Synthetic manganese-iron mixed oxides are considered promising materials to be used as oxygen carriers for Chemical Looping Combustion of coal with carbon dioxide capture at low cost. The aim of this work was to evaluate a manganese-iron mixed oxide material with a manganese to iron molar ratio of 0.77:0.23 as oxygen carrier for coal combustion by means of chemical looping processes, including both *ex-situ* and *in-situ* gasification of coal. The preparation method -spray drying followed by calcination- was optimized in order to produce particles with high reactivity and mechanical strength. The material was studied in two continuously operated facilities designed to burn either gaseous or solid fuels. While full combustion was achieved burning syngas, showing the feasibility of the use of this material considering the *ex-situ* gasification process. Coal combustion efficiency by *in-situ* gasification process was improved in comparison with other previously tested low-cost materials such as ilmenite and iron ore. Moreover, the oxygen carrier particles showed an interesting magnetic behavior that was able to facilitate oxygen carrier recovery from the purge ash stream. In view of these results, the manganese-iron mixed oxide as oxygen carrier is proposed as a promising candidate for use coal combustion by the chemical looping process.

1. Introduction

Nearly 70% of global carbon dioxide (CO_2) emissions are the result of the use of fossil fuels in power generation, of which coal is the most carbon-intensive fossil fuel [1]. This figure highlights the need for clean coal combustion technologies, such as those allowing CO_2 capture, in order to minimize CO_2 emissions. Several emerging CO_2 capture technologies including chemical looping processes, adsorption systems based on solid sorbents [2], and membrane separation systems [3] have been tagged as the most promising CO_2 capture modes. A review of all these technologies and their advantages and disadvantages can be consulted elsewhere [4]. Of these, Chemical Looping Combustion (CLC) has as main advantage of CO_2 capture being inherent to the process, which considerably reduces the cost per the tonne of CO_2 captured [5].

1.1. Chemical looping concepts for coal combustion

The CLC concept is based on the transfer of oxygen from the air to the fuel through an oxygen carrier in order to prevent contact between the air and fuel. Metal oxides are generally used as oxygen carriers because they are easily able to provide the required oxygen transfer because of their redox properties. Oxygen transfer is achieved by continuously circulating the oxygen carrier between two interconnected fluidized bed reactors: the fuel and air reactors. In the fuel reactor, the fuel is mainly oxidized to carbon dioxide (CO_2) and steam (H_2O) by the reduction of the metal oxide. The reduced oxygen carrier is subsequently transported to the air reactor where it is reoxidized with the oxygen from air. Combustion of coal and other solid fuels (e.g. petcoke or biomass) using CLC technology can be achieved by means of three processes: via *ex-situ* Gasification Chemical Looping Combustion (*e*G-CLC), *in-situ* Gasification Chemical Combustion (*i*G-CLC) and Chemical Looping Oxygen Uncoupling (CLOU) [5].

1.1.1. Chemical looping combustion of coal via ex-situ gasification

The *e*G-CLC process involves coal gasification with oxygen in a gasifier to produce syngas, which is subsequently fed into the fuel reactor in the CLC system [6]. High-efficiency power generation is expected by combining CLC with an Integrated Gasification Combined Cycle (IGCC) [7], which requires the use of a pressurized CLC unit, or of Combining Cooling, Heating and Power production (CCHP) [8]. An additional advantage of the *e*G-CLC process is that oxygen carrier particles do not come into contact with the ash from coal, eliminating any

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Nomenclature

d_p	particle diameter
$(F_i)_{out\ j}$	total molar flow gas of each compound i (i = CO_2, CO, H_2 or CH_4) in the exit stream of each reactor (j = fuel or air reactors) (mol/s)
$F_{O,\ fuel}$	stoichiometric molar flow of atomic oxygen needed to oxidize fully the fuel fed to CO_2 and H_2O (mol/s)
K_m	*relative permeavility* (–)
m	instantaneous mass of the oxygen carrier (kg)
m_{bix}	mass of the sample assuming full oxidized to bixbyite (kg)
m_o^i	mass of oxidized sample between bixbyite and spinel (i = ou) or between spinel and mangano-wüstite (i = g) (kg)
m_r^i	mass of reduced sample between bixbyite and spinel (i = ou) or between spinel and mangano-wüstite (i = g) (kg)
$\dot{m}_{OC}$	solids circulation flow rate (kg/h)
m^*_{OC}	specific solids inventory in the fuel reactor (kg/MW_{th})
P_{ref}	reference partial pressure of reacting gas (atm)
P_{TGA}	partial pressure of the gaseous fuel used in the TGA (atm)
R_{OC}^{ou}	oxygen transport capacity by the oxygen uncoupling reaction between bixbyite and spinel (kg oxygen per kg oxygen carrier)
R_{OC}^{g}	oxygen transport capacity by the solid-fuel gas reaction between spinel and mangano-wüstite (kg oxygen per kg oxygen carrier)
R_{OC}^{t}	total oxygen transport capacity of the oxygen carrier between bixbyite and mangano-wüstite (kg oxygen per kg oxygen carrier)
T_{FR}	fuel reactor temperature (°C)

Greek symbols

ϕ	oxygen carrier-to-fuel ratio
η_{CC}	CO_2 capture efficiency
η_{comb}	combustion efficiency in the fuel reactor
τ_{oc}	mean residence time of solids in the fuel reactor (s)
Ω_{SF}	oxygen demand of the coal (kg oxygen per kg solid fuel)
Ω_T	total oxygen demand

Acronyms

AJI	Air Jet Index
ANT	Anthracite
BIT	Bituminous
CCHP	Combining Cooling, Heating and Power Production
CLC	Chemical Looping Combustion
CLOU	Chemical Looping with Oxygen Uncoupling
IGCC	Integrated Gasification Combined Cycle
*i*G-CLC	*in-situ* Gasification Chemical Looping Combustion
*e*G-CLC	*ex-situ* Gasification Chemical Looping Combustion
JCPDS	Join Committee on powder Diffraction Standards
NDIR	Non-Dispersive Infrared
LIG	Lignite
SUB	Subbituminous
TGA	Thermogravimetric Analyzer
LHV	Lower Heating Value (kJ/kg coal)
VITO	Flemish Institute for Technological Research
XRD	X-ray Diffraction

possible ash-oxygen carrier interaction or oxygen carrier losses in the ash purge stream. However, the requirement of an external gasifier and oxygen for the coal gasification is an added cost of the process.

Different oxygen carriers have been evaluated by burning syngas with different results. High syngas conversions to CO_2 and H_2O have always been achieved with synthetic materials formed using nickel (Ni), manganese (Mn), iron (Fe) or copper (Cu) oxides as active phases and supported on inert materials. Johansson et al. [9] achieved combustion efficiencies higher than 99% through the use of an oxygen carrier with a 40 wt.% nickel oxide (NiO) active phase supported on magnesium aluminate ($MgAl_2O_4$). Similar results were obtained by Dueso et al. [10] with another Ni-based material obtained by impregnation of an 18 wt.% NiO on alumina. Complete combustion of syngas was obtained by Abad et al. [11] in a 0.3 kW_{th} CLC rig by using a Mn-based oxygen carrier supported on magnesia-stabilized zirconia. Likewise, these authors [12] reached high syngas conversion (99%) in the same facility with another material by supporting a 60 wt.% hematite (Fe_2O_3) on alumina. Forero et al. [13] obtained complete syngas combustion with an oxygen carrier prepared by impregnation of a 14 wt.% copper oxide (CuO) on alumina. However, lower combustion efficiencies were achieved by using natural ores as oxygen carriers. Kolbitsch et al. [14] conduced syngas combustion tests with ilmenite ($FeTiO_3$) in a 120 kW_{th} facility. They observed high H_2 oxidation (around 90–95%) and low carbon monoxide (CO) conversion (around 65–70%) at fuel input capacities of between 60 and 80 kW_{th}. Syngas conversions of around 85% were found by Zheng et al. [15] when calcium sulfate ($CaSO_4$) was used as the oxygen carrier.

When selecting an oxygen carrier for CLC using coal gas as fuel the most important aspect to consider is the ability to convert the gaseous fuel to CO_2 and H_2O. In this sense, after a theoretical thermodynamic analysis, Jerndal et al. [16] proposed Cu-, Fe-, and Mn-based materials as the more suitable oxygen carriers. However, other factors, such as cost, sulfur, and environmental aspects should be always taken into account. From an economic perspective, the comprehensive study by Abad et al. [17] on CLC rig operating conditions indicated that the use of an Fe-based oxygen carrier was more advantageous than of Cu- or Ni-based materials for burning syngas. With regard to sulfur deposition on the oxygen carrier, García-Labiano et al. [18] advised against using Ni-based materials. In this sense, de Diego et al. [19] showed that Fe-based oxygen carriers were sulfur resistant, while the Cu-based materials were sulfur sensitive. Finally, Mendiara et al. [20] analyzed the toxicity of Fe-based materials after their use in a CLC facility, confirming the environmental suitability of the use of these types of materials.

1.1.2. *Chemical looping combustion of coal via in-situ gasification*

In *i*G-CLC, solid fuels are gasified in the fuel reactor using steam and/or recycled CO_2 as gasifying agents. Oxidation of the gasification products to CO_2 and H_2O subsequently takes place by means of a gas-solid reaction with the oxygen carrier. Oxygen carrier losses are expected during ash purging, so the use of low-cost materials is encouraged in order to reduce the cost associated with compensating for those losses. Thus, minerals and wastes materials based on iron and manganese oxides have mostly been evaluated as oxygen carriers for *i*G-CLC where coal or biomass are considered for use as fuels [21]. Gasification is the limiting step for coal conversion, and some unburned char particles may reach the air reactor together the oxygen carrier, which would mean a decrease in CO_2 capture efficiency. A strategy to prevent char particles from reaching the air reactor could consist of raising the residence time of these type of particles inside the fuel reactor. Su et al. [22] observed that this could be achieved through a reduction in the gas velocity at the bottom part of the fuel reactor. However, this action would entail a decrease in the solids circulation rate between the air and fuel reactors [23], which would affect the amount of oxygen available in the fuel reactor. Another alternative for preventing char particles from reaching the air reactor is to include a carbon stripper between the fuel and air reactors. Pérez-Vega et al. [24]