Applied Energy 196 (2017) 1–17

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

The Oxy-CaL process: A novel CO_2 capture system by integrating partial oxy-combustion with the Calcium-Looping process

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HIGHLIGHTS

- A novel CO_2 capture process (Oxy-CaL) is proposed.
- Carbonation in the diffusion stage is analyzed by varying the CO_2 concentration.
- Simulation results show that energy consumption in the Oxy-CaL is below of 4 MJ/kg.
- Smaller amounts of solids inventory are needed in the Oxy-CaL system.

ARTICLE INFO

Article history:
Received 12 December 2016
Received in revised form 3 March 2017
Accepted 24 March 2017

Keywords:
Calcium-Looping
Oxy-combustion
CCS
SPECCA

ABSTRACT

This paper proposes a novel CO_2 capture technology from the integration of partial oxy-combustion and the Calcium-Looping capture process based on the multicycle carbonation/calcination of limestone derived CaO. The concentration of CO_2 in the carbonator reactor is increased by means of partial oxy-combustion, which enhances the multicycle CaO conversion according to thermogravimetric analysis results carried out in our work, thus improving the CO_2 capture efficiency. On the other hand, energy consumption for partial oxy-combustion is substantially reduced as compared to total oxy-combustion. All in all, process simulations indicate that the integration of both processes has potential advantages mainly regarding power plant flexibility whereas the overall energy penalty is not increased. Thus, the resulting energy consumption per kilogram of CO_2 avoided is kept smaller than 4 MJ/kg CO_2, which remains below the typical values reported for total oxy-combustion and amine based CO_2 capture systems whereas CO_2 capture efficiency is enhanced in comparison with the Calcium-Looping process.

1. Introduction

Carbon Capture and Storage (CCS) is considered as one key short to médium-term measure to mitigate global warming [1,2]. In order to achieve a commercial deployment of post-combustion CO_2 capture in fossil fuel power plants, several technologies are being analyzed aimed mainly at maximizing the capture efficiency while energy penalty and capital cost are minimized [3,4]. Among diverse possibilities, already commercial amine-based capture systems and the Calcium-Looping (CaL) process, currently under pilot-scale stage, have attracted a great deal of attention in the last years [5,6]. Although CO_2 capture by using MEA (monoethanolamine) is an industrial mature process, its commercial deployment as post-combustion CO_2 capture technology is hampered by the high energy penalty (8–12%) mainly due to sorbent regeneration [7–9], amine toxicity [10] and degradation [11].

The CaL process is based on the carbonation/calcination reaction of solid CaO particles, which is carried out in two interconnected circulating fluidized bed (CFB) reactors [12]. This second generation capture technology has several potential advantages when compared with amine-based process such as a lower energy penalty over the power plant (4–9%) [6], higher CO_2 capture efficiency (above 90%) and the use of low cost, widely available and non-toxic natural minerals as CaO precursors such as limestone or dolomite [13]. Even though several pilot scale plants (~1–2 MW_{th}) are already showing promising results [14,15] the CaL technology has not reached a demonstration stage yet. The

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http://dx.doi.org/10.1016/j.apenergy.2017.03.120
0306-2619/

Nomenclature

$[CO_2]$	average CO_2 concentration, mol/m^3
$[CO_2]_{eq}$	equilibrium concentration of CO_2, mol/m^3
D^*_{eff}	equivalent diffusion constant, m^3/(mol·s)
E	emissions ratio after CO2 capture, kg CO_2/kW he
E_{CO2}	carbon capture efficiency
E_{ref}	emissions ratio before CaL, kg CO_2/kW he
E_{max}	maximum capture efficiency
F_{CO2}	mole flow rate of CO_2 in flue gas entering the carbonator, kmol/h
F_O	mole flow rate of fresh makeup limestone, kmol/h
F_R	mole flow rate of CO_2 in flue gas entering the carbonator, kmol/h
F_{fg}	flue gas molar flow rate, kmol/s
FRP	fast reaction controlled phase
SDP	solid-state diffusion controlled phase
k_s	intrinsic kinetic constant m^4/(mol·s)
k	deactivation constant of a sorbent particle
$\dot{m}$	mass flow, kg/s
$\dot{m}_{CO2,calc}$	CO_2 mass flow exiting the calciner, kg/s
$\dot{m}_{gas,calc}$	total gas mass flow exiting the calciner, kg/s
N_{Ca}	mol of Ca in the carbonator, mol
P	pressure, bar
P_{vv}	live steam pressure, bar
$P_{HE,solids}$	solid-solid thermal power exchanged, MW
$SPECCA$	energy consumption for kg CO_2 avoided, MJ/kg CO_2
$r_{ave,SDP}$	average reaction rate in the diffusion regime, s^{-1}
$r_{ave,FRP}$	average reaction rate in the kinetic regime, s^{-1}
S_{ave}	average surface area available for reaction, m^{-1}
t	time, s
T_{calc}	calciner temperature, °C
T_{carb}	carbonator temperature, °C
T_{vv}	live steam temperature, °C
t_0	time lag of TGA multicycle test, s
t_{FRP}	time of the carbonation fast phase, s
t_{max}	total carbonation time, s
v_{CO2}	CO_2 v/v concentration at CFPP outlet
v_{O2}	O_2 v/v concentration at CFPP outlet
W_s	solid inventory in the carbonator per MW of a typical power plant, kg
$\dot{W}_{ASU}$	power consumption in the ASU, MW
$\dot{W}_{sec}$	net power production in secondary steam cycle, MW
$\dot{W}_{comp,CO2}$	power consumption in CO_2 compression, MW
$\dot{W}_{comp,fg}$	power consumption in flue gas compression, MW
$\dot{W}_{solid}$	power consumption in solids transport, MW
X	carbonation degree of CaO
X_{ave}	average conversion of the sorbent
$X_{ave,SDP}$	average conversion of the sorbent in the diffusion phase
$X_{ave,FRP}$	average conversion of the sorbent in the kinetic phase
W_s	solid inventory in the carbonator per MW of a typical power plant, kg
x_{CO2}	CO_2 molar fraction exiting the plant
x_{O2}	O_2 molar fraction exiting the plant
$y_{CO2,in}$	CO_2 molar fraction at carbonator inlet
$y_{CO2,eq}$	CO_2 molar fraction at carbonation equilibrium
η_{boiler}	boiler efficiency
η_{CFPP}	coal fire power plant efficiency
η_{ref}	reference plant efficiency
η_{int}	new global efficiency (CFPP-capture system)
τ	average residence time in the carbonator, s

main causes that hinder such step forward are linked to the excessively large size of the capture system (carbonator reactor height ~40 m; carbonator solids inventory ~400 ton; additional coal consumption for CO_2 capture ~45–55%), which increases significantly both capital and operating costs (CAPEX and OPEX) for power generation [16,17].

Another interesting possibility to mitigate CO_2 emissions from power plants is the oxy-combustion technology, which has been successfully demonstrated in large-scale pilot projects (30 MW$_e$) [18–20]. Essentially, oxy-combustion consists of replacing air by pure O_2 (mixed with CO_2-rich flue gas recycled) as combustion gas, which yields a highly-concentrated CO_2 flue gas stream. After purification, the CO_2 stream (~95% vol) is suitable for compression and storage or utilization [21]. The main drawback for the large-scale deployment of oxy-combustion is the high energy consumption for pure O_2 production in the cryogenic Air Separation Unit (ASU), which causes an energy penalty in the range of 7–13% [22,23] or, equivalently, over 20% additional fuel consumption for power production.

In this paper a novel system (Oxy-CaL) for CO_2 capture is investigated based on the combination of partial oxy-combustion and the CaL process with the goal of exploiting the synergies between such technologies. Basically, Oxy-CaL consists of carrying out a partial oxy-combustion process to produce a flue gas with a CO_2 concentration in the range 30–60% vol, which is then sent to the CaL capture process. In a similar way, other authors have analyzed the integration of partial oxy-combustion and MEA [24], which is expected to help mitigating MEA degradation and energy consumption.

The manuscript starts by showing experimental results from a thermo-gravimetric analysis (TGA) on the multicycle conversion of limestone derived CaO under realistic calcination conditions (high temperature and high CO_2 concentration). In these TGA tests, the CO_2 concentration in the carbonation environment was varied in the range 15–60% vol in order to address the effect of an excess of CO_2 in the carbonator over the typical vol% in the flue gas at typical combustion conditions (~15%). Moreover, the carbonation temperature was varied in the range 625–680 °C, which affects critically the carbonation kinetics in the solid-state diffusion-controlled stage as will be seen. These TGA results are used afterwards in the Oxy-CaL integration model to calculate the CO_2 capture efficiency from process simulations. The energy penalty arising from the diverse CO_2 capture technologies considered (total oxy-combustion, CaL and Oxy-CaL) is analyzed. Finally, the oxy-CaL performance is assessed and compared with those of other CO_2 capture systems.

Our results show that the Oxy-CaL system is a promising hybrid concept to be implemented in new power plants, allowing for a substantial reduction of energy penalty as compared to total oxy-fuel combustion. Moreover, the Oxy-CaL system leads to a high CO_2 capture efficiency in comparison with the CaL process, which would serve to reduce significantly the carbonator reactor size.

2. Thermogravimetric analysis

2.1. Materials and methods

The material employed in this work was natural limestone of high purity (99.6%wt $CaCO_3$), received from Segura S.L (Matagallar quarry, Pedrera, Spain). Carbonation/calcination multicycle tests were carried out using a thermogravimetric analyzer TGA Discovery (TA Instruments 2011) equipped with an infrared halogen lamp