Journal of CO_2 Utilization 25 (2018) 14–21

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

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

Integration of a calcium looping process (CaL) to molten carbonate fuel cells (MCFCs), as carbon concentration system: First findings

M. Della Pietra[a,b,*], M. Santarelli[a], S. Stendardo[b], S. McPhail[b], Juan Pedro Perez-Trujillo[c], Francisco Elizalde-Blancas[c]

[a] Department of Energy, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129, Torino, Italy
[b] ENEA R.C. Casaccia, Via Anguillarese 301, 00123, Rome, Italy
[c] Department of Mechanical Enginnering, DICIS, University of Guanajuato, 36885, Salamanca, Mexico

ARTICLE INFO

Keywords:
Calcium looping
CaL
Molten carbonate fuel cells
MCFC
CCS
CO_2
Syngas
Greenhouse gases
COP21
ZECOMIX
Lumped model
CaO
Integration
EIS
I–V curves
Clean coal

ABSTRACT

The utilisation of coal as fuel for the production of energy will grow parallel with the increase of the cost of oil in the next years. This paper aims to investigate the integration between two clean coal technologies: Calcium Looping (CaL) process and Molten Carbonate Fuel Cell (MCFC) in order to produce a high CO_2 concentrated stream.

The main goal of this work is to find out the optimum working point of a system using CaL and MCFC technologies, coupled together, to produce decarbonised energy from coal as a primary energy source. The integrated system of CaL with MCFC presented in this paper, is fed with a raw syngas coming from coal gasification [1]. The raw syngas is decarbonised using calcium oxide as solid sorbent in the first reactor of CaL (carbonator), subsequently the clean syngas flowing out of the carbonator is used as anodic fuel for an MCFC. The thermal regeneration of solid sorbents occurs burning methane with air producing a CO2 reach gas, that feeds the cathodic compartment of MCFC.

This configuration allows to concentrate the CO2 from cathode side to anode side of the MCFC, using internal electrochemical reactions of the cell, producing electric power at the same time.

This work has been structured to tackle the coupling of CaL with MCFC using a combined numerical and experimental approach. Thus the investigation of the possible integration has been carried out starting with a lumped model simulating the whole calcium looping process. The model was used to investigate the behaviour of the CaL system when varying the amount of solid sorbent used in the process.

Data coming from the model in terms of gas composition flowing out from CaL reactors were subsequently validated experimentally simulating different operating conditions in a MCFC single cell (81 cm2). Performance of the MCFC was monitored with polarisation curves and power density curves, aiming to integrate experimentally the electric behaviour of the whole system, in order to have a first validation of the two systems working together.

1. Introduction

1.1. The CaL process for CCS applications

Carbon Capture and Storage (CCS) is a technology for trapping carbon dioxide (CO_2) emissions produced from the use of fossil fuels in electricity generation and industrial processes, preventing the carbon dioxide from entering the atmosphere. This technology has significant potential to help mitigate climate change and to meet greenhouse gas emissions reduction targets as highlighted during the international conference of climate changing COP 21 [27]. The calcium looping process (CaL) is one of the most promising technique for carbon capture, exploitable in pre and post combustion configuration.

CaL process is based on the use of calcium oxide as a regenerable sorbent in a loop made of carbonation and calcination cycles as shown in Fig. 1. CaL process involves the separation of CO_2, present in a raw syngas or in exhaust gas coming from a power plant, at high temperatures (600–700 °C) using carbonation reaction of CaO (Reaction (1)) at atmospheric pressure, that takes place in a fluidized bed reactor (carbonator). The reaction temperature ensures a low value of the equilibrium CO_2 concentration (around 1% vol), keeping the kinetic of the reactions fast enough to ensure a short residence time in the

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[*] Corresponding author at: ENEA R.C. Casaccia, Via Anguillarese 301, 00123, Rome, Italy.
E-mail addresses: max.dellapietra@gmail.com, massimiliano.dellapietra@enea.it (M. Della Pietra).

https://doi.org/10.1016/j.jcou.2018.03.002
Received 7 November 2017; Received in revised form 17 February 2018; Accepted 1 March 2018

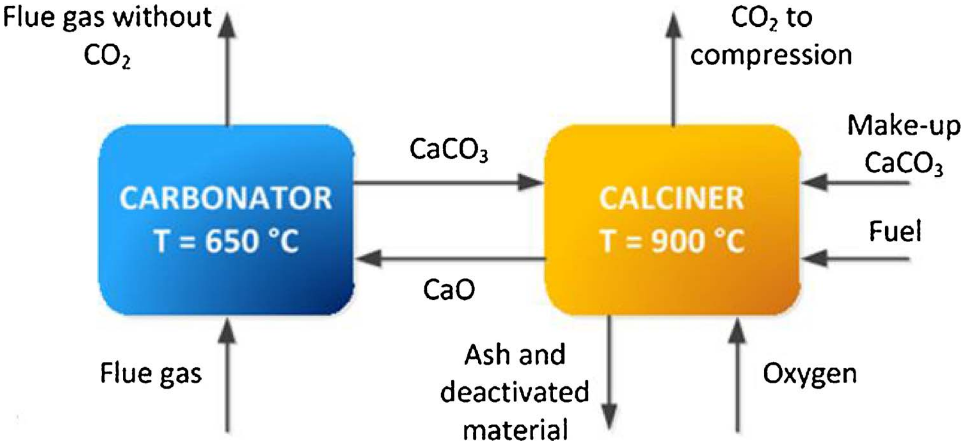

Fig. 1. Schematic overview of the working principles of calcium looping process. Flue gas entering the carbonator is impoverished of the CO2, while CaO solid sorbents go to the calciner reactor where occurs the regeneration. The CO2 released in the regeneration, can be sent to a compression stage.

carbonator.

Once the CaO has reached its ultimate conversion to $CaCO_3$ by reacting with the CO2, it can be thermally regenerated by heating beyond its calcination temperature (850–900 °C) in second reactor (calciner), according to the Reaction (2).

$$CO_2(g) + CaO(s) \rightarrow CaCO_3(s) \quad (1)$$

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \quad (2)$$

The CO_2 gas exiting the calciner is thus ready for sequestration or utilisation. The high temperatures, needed for the regeneration of CaO, are achieved by burning fuel in the calciner under a flow of pure O_2 (oxycombustion) in order to avoid CO_2 dilution [2–5].

The process is typically initiated by precalcining a batch of limestone (CaCO3) under air in the calciner, where the net production of CO2 is only due to this initial calcination step. Calcium Looping (CaL) was originally proposed to be carried out in fluidized bed reactors at ambient pressure by using Calcium-based natural materials as CO2-sorbents (Shimizu et al., 1999).

Among different sorbents, metal oxides contained in naturally osccurring minerals represent the cheapest option for the CO2 capture process; limestone and dolomite (in their calcined form). In this process, CaO is converted into CaCO3 during the CO2 uptake (carbonation). It is desirable to produce a concentrated CO2 stream during regeneration and in this case the calcination will often be carried out in an atmosphere rich in CO2. This puts requirements on the sorbent, e.g. the sorbent must withstand a high CO2 concentration during its regeneration for an extended number of cycles. However, the presence of CO2 during the regeneration step has been shown to decrease the calcination rate of the solid sorbent, and also to cause sintering of CaO grains with associated negative effects on the CO2 uptake capacity after multiple cycles [21,22]. The sorbent must show a high stability and stable sorption capacity throughout multiple CO2 uptake–regeneration cycles. Further important properties of a high performance sorbent are: low–cost manufacture, fast reaction kinetics, and mechanical stability and sintering resistance. Although natural carbonates, e.g. limestone (CaCO3) or dolomite ([Ca,Mg]CO3) seem to be the best candidates given their low cost and its high availability, they show a pronounced decay in CO2 sorption capacity during repeated cycling [23–25]. The carbonation of these materials is characterized by an abrupt transition from the rapid initial reaction rate, most likely kinetically controlled, to a slower reaction rate, which is most likely diffusion controlled. The enhancement of the chemical stability can be assured by the CO2 capture on CaO based sorbent impregnated on mayenite phase (Ca12Al14O33) [26]. Most of the new developed sorbents use calcium aluminate compounds as support and show improved mechanical stability resulting in a better resistance to attrition when used in fluidized bed reactor systems, and therefore reducing the loss of material in the process.

1.2. The MCFC as CCS device

Pre-, post-,and oxyfuel-combustion capture can be considered as passive CO_2 separation technologies, as the process consumes a fraction of the power output. In contrast, the MCFC can be categorized as an "active" CO_2 separation technology [9], as the MCFC produces electricity from an addition of fuel, which adds to the power plant output and separates CO_2 from flue gas to the anode exhaust simultaneously. MCFCs are being extensively studied for post-combustion Carbon Capture and Storage (CCS) applications [17,18] and many studies has been performed to investigate about technical feasibility of this application [13,14].

The electrolyte of the molten carbonate fuel cell is a molten mixture of alkali metal carbonates – usually a binary mixture of lithium and potassium carbonates, or lithium and sodium carbonates, which is retained in a ceramic matrix of $LiAlO_2$. At the high operating temperatures (typically 600–700 °C) the alkali carbonates form a highly conductive molten salt, with carbonate ions ($CO_3{}^{2-}$) providing ionic conduction. In MCFCs carbon dioxide needs to be supplied to the cathode as well as oxygen, and this becomes converted to carbonate ions, which provide the means of ion transfer between the cathode and the anode. At the anode, the carbonate ions are converted back into CO_2. There is therefore a net transfer of CO_2 from cathode to anode (Reactions (3) and (4)).

$$\frac{1}{2}O_2 + CO_2 + 2e \rightarrow CO_3^{2-} \quad (3)$$

$$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e \quad (4)$$

It is usual practice in an MCFC system that the CO_2 generated at the cell anodes is recycled externally to the cathodes where it is consumed. This might at first seems an added complication and a disadvantage for this type of cell, but this can be done by feeding the anode exhaust gas to a combustor (burner), which converts any unused hydrogen or fuel gas into water and CO_2. The exhaust gas from the combustor is then mixed with fresh air and fed to the cathode inlet. This process is no more complex than for other high temperature fuel cells, as the process also serves to preheat the reactant air, burn the unused fuel, and bring the waste heat into one stream for use in a bottoming cycle or for other purposes. Another less commonly applied method is to use some type of device, such as a membrane separator, that will separate the CO_2 from the anode exit gas and will allow it to be transferred to the cathode inlet gas. The advantage of this method is that any unused fuel gas can be recycled to the anode inlet or used for other purposes. Another