

A FLUIDIZED BED AUTOTHERMAL REACTOR FOR SOLAR-POWERED SUSTAINABLE PROCESSES

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Abstract

In the last decades Concentrating Solar Thermal (CST) technologies have been successfully employed in the power sector and might prove a viable solution to decarbonize heavy industry and transportation in future years. Solar-driven chemical processes can be targeted to produce sustainable fuels and commodities, but this advancement will require the development of innovative chemical reactors. The present study advances the concept of a Directly Irradiated Fluidized Bed Autothermal Reactor (DIFBAR). This novel reactor incorporates an internal solid-solid heat exchanger that allows to preheat the reactants, by recovering the sensible energy of the products. This paper presents new experimental results, considering the Calcium Looping (CaL) process as a reference case-study. Cold flow and high temperature experiments are carried out, testing a natural calcarenite (a CaCO_3 -based sand) as reactant, mixed with black proppants particles to enhance the absorption of solar radiation.

Introduction

Concentrated solar thermal (CST) technologies are based on a set of sun-tracking mirrors (heliostats), that focus solar rays on a receiver. In the last twenty years the production of electricity by CST-powered plants has reached commercial maturity [1]. The development of large scale CST plants has catalyzed the interest toward the application to the chemical and fuel industry, that is today a wide and diverse field of research. Many applications involve gas-solid processes, that can be carried out at temperatures compatible with the most advanced solar receivers [2]. These processes can produce solar fuels and chemicals by the thermochemical conversion of biomasses or the chemical looping of metal oxides [3]. Another field of interest is the thermochemical energy storage (TCES): solar energy drives an endothermic reaction, whose products are stored and employed to release heat through the reverse exothermic reaction [4]. Calcium looping (CaL) is one of the most promising

processes because of the combination of high operating temperatures, energy density and low cost. It based on the reversible reaction:



Solar energy is used to drive the endothermic decomposition (calcination) of calcium carbonate (CaCO_3), that produces calcium oxide (CaO) and carbon dioxide (CO_2). Then, the reverse reaction (carbonation) is conducted to release energy.

As no limitations occur on the side of heliostat engineering, major efforts must be directed to the development of reactor technologies [5]. Fluidized bed reactors have been widely recognized as an adequate solution for the deployment of CST-driven thermochemical processes [6], thanks to their excellent heat transfer properties and flexibility. This paper is dedicated to the study of a Directly Irradiated Fluidized Bed Autothermal Reactor (DIFBAR) [7]. This innovative reactor type recovers the sensible energy of reaction products to preheat the reactants in an internal solid-solid heat exchanger, following the principle of autothermal reactors. In this way the conversion of solar to chemical energy is maximized. Recently a lab-scale prototype has been set up for the proof of concept [8]: the study characterized the experimental apparatus with inert sand as bed inventory and went on to demonstrate the operation as chemical reactor by performing the calcination of magnesium carbonate particles at 600-750°C.

On the other hand, the selection of suitable materials is crucial for the success of any solar-driven process. This study studies the application of the DIFBAR to the CaL processes, testing a natural calcarenite (a CaCO_3 -based sand) as reactant. In order to compensate their poor absorptivity of solar radiation, reactant particles are mixed with black proppants with a 1:3 mass ratio. A calcination test at temperatures between 700-800°C was performed by irradiating the lab-scale prototype with a 10 kW_e solar simulator, followed by a carbonation test with a CO_2 -rich stream at 550-600°C under non-irradiated conditions.

Experimental set up

Figure 1 pictures the DIFBAR prototype. The prototype is made of stainless steel and insulated with rock wool blankets and ceramic shells. It is equipped with four mass flow controllers, eight pressure transducers and sixteen K-type thermocouples at various heights. Setpoints and measuring signals are handled by a LabView application.

During calcination experiments, a fluidizing air stream (Q_1) entrains the solids through the riser (a) to the solar receiver (b). There, the particles are exposed to a concentrated solar radiation passing through a circular aperture of 100mm and sealed by a quartz window. Then the solids flow through the annulus tube (c) and are returned to the storage reservoir (d). The particles in the annulus and in the riser exchange heat counter-currently. The reservoir can be fluidized by a secondary air stream (Q_{res}) fed through a sparger. Two additional air streams can be fed (Q_3 and

Q_4), to provide a gas-sealing for the reservoir and the receiver. The Q_3 stream also regulates the solid discharge rate from the annulus into the reservoir and is set so as to keep constant the bed level inside the annulus for any circulation rate. During carbonation experiments, the solar receiver is not operated, whereas the reservoir is operated as a FB reactor with a 15% CO_2 -air mixture stream. Concentrated solar radiation is simulated with a 10kW_e Xenon arc lamp and an elliptical reflector (high-flux solar simulator). Electric heaters are used to heat up the reservoir during start-up phase (max. power 1.5kW) and to keep its temperature during the carbonation test.

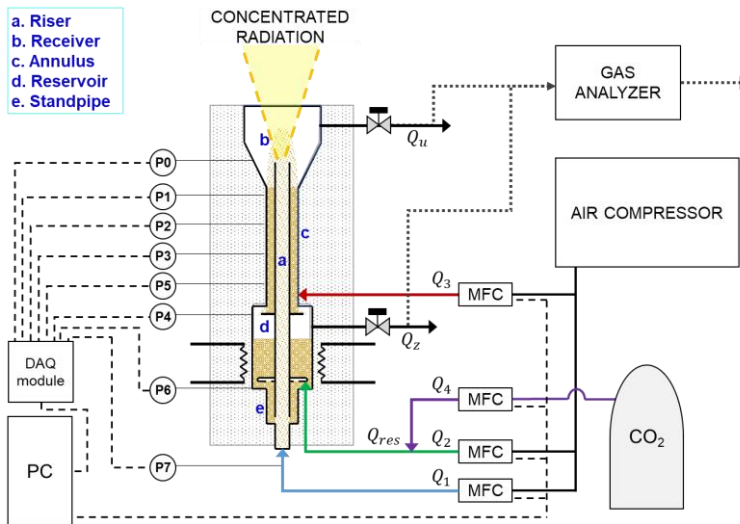


Figure 1. Experimental set-up: (a) prototype scheme and (b) photograph.

A mixture of calcarenite sand and black proppants with 1:3 mass ratio and a total mass of 1.4 kg was used as bed inventory. The calcarenite is a natural rock from Apulia (Italy), composed by 91%_w of CaCO_3 , as estimated from thermogravimetric experiments. The two solids were sieved in different size ranges in order to separate the reactant after the experiments for subsequent analysis. Size ranges were selected to ensure desired fluidization conditions in the reactor.

Table 1. Materials properties

Material	Size range [μm]	Bed density [kg/m ³]	Minimum fluidization velocity [cm/s]
Black proppants	90-300	1830	3.5
Calcarenite	300-420	1175	11.8
Mixture	-	1664	4.8

The steady temperature profile proves the efficiency of the heat exchanger during calcination. Outlet CO₂ concentration were measured with an online gas analyzer to monitor the course of the reactions. After the carbonation experiment the reactant was sampled and analyzed to assess the final conversion.

Results

Figure 2 shows the mass flux of the calcarenite-black proppant mixture through the riser (G_r) obtained by cold flow experiments. The solids mass flux linearly increases from 0 to 40 kg/(m²s) for gas velocities between 1.8 and 2.0 m/s. The figure also reports the fraction of calcarenite particles fed to the receiver (α). This measure shows a slight increase with the fluidizing velocity, but is in general quite close to the value 25%. This demonstrates that the particles are well-mixed inside the riser and no segregation occurs inside the reservoir.

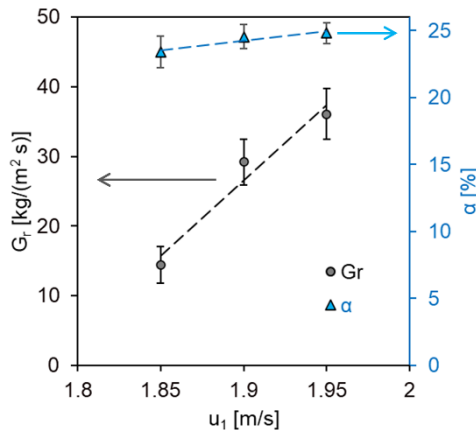


Figure 2. Solids mass flux (G_r) and calcarenite fraction (α) in the riser.

Figure 3 shows the results of a calcination experiment. The internal heat exchanger allows to preheat the reactants from 550°C to 750°C (Fig. 1a).

To increase the residence time of the reactants in the receiver and allow calcination, a fill-and-empty strategy was adopted, resulting in oscillating receiver temperature (T11) and CO₂ concentration (Fig. 1b). The outlet CO₂ concentration is close to reaction equilibrium conditions (9% CO₂ at 750°C).

Figure 4 reports the reservoir temperature and CO₂ concentration during the carbonation test, carried out right after the end of calcination. The final carbonation degree was 55% after a total reaction time of 1.5h at 550-600°C. This results are in line with similar experiments carried out with Sardinian limestone [9].

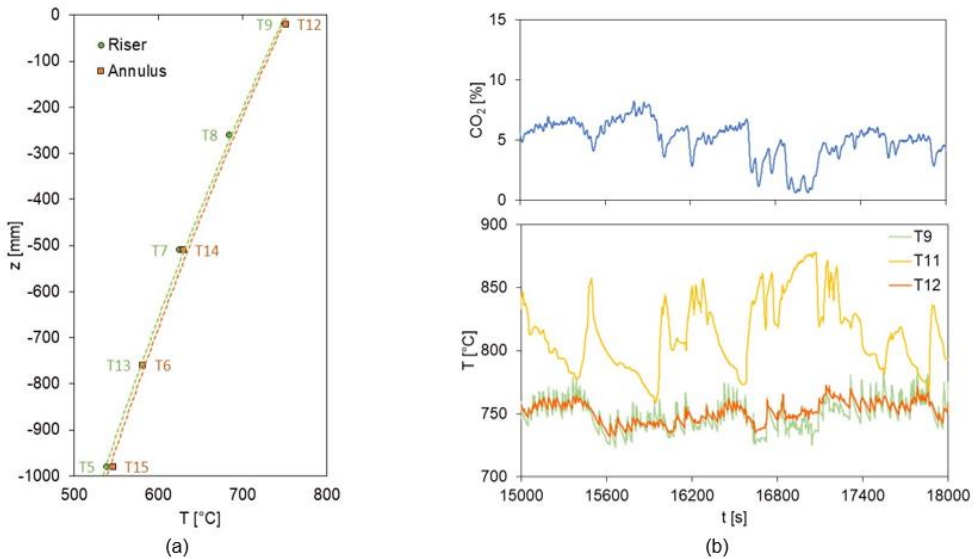


Figure 3. Calcination results: (a) temperature profile of the internal heat exchanger, (b) CO_2 outlet concentration and receiver temperatures.

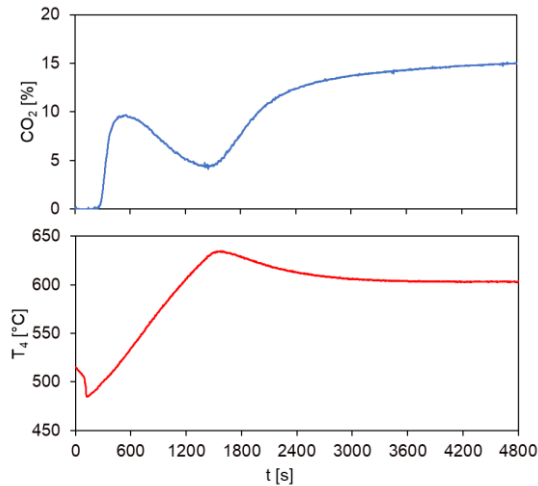


Figure 4. Carbonation results: CO_2 outlet concentration and reservoir temperature.

Conclusions

Altogether these experiments show the potentiality of the DIFBAR as a solar reactor and its key operating variables. In particular the results highlighted that the calcarenite is a valid material for TCES with results comparable to limestone and that mixing it with black proppants is a viable strategy to compensate its poor absorptivity in a directly irradiated reactor. Next experiments will scrutinize the effect of the mass ratio of the solids mixture.

Acknowledgements

The study has been supported by the Ministry of University and Research (MUR) - Italy, in the frame of the project PRIN 2022 PNRR – P202224CPL - REchargeable THERmochemical Energy Battery for Energy Storage from renewable sources (reThebes).

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