

Design of an Integrated CSP-Calcium Looping for Uninterrupted Power Production Through Energy Storage

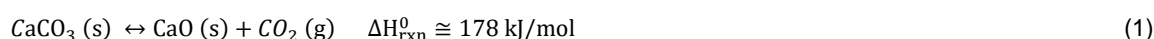
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Solar driven large scale uninterrupted power production can be accomplished with a combination of Concentrated Solar Power (CSP) plant and a Thermochemical Energy Storage (TCES) based on a Calcium Looping (CaL) process. Thermal energy can be stored in the form of chemical energy due to calcination reaction and released back as thermal energy during the carbonation reaction ($\text{CaO} + \text{CO}_2 \leftrightarrow \text{CaCO}_3$). This paper presents the preliminary design, integration, and simulation of such process plant in AspenPlus™ by considering solar energy in the system. This includes indirect solar heated calcination by explicitly heating up CO_2 at high temperatures at a concentrated solar heat exchanger (receiver), where CO_2 is directly imported into the calciner not only to preheat solids, but to provide the appropriate energy for the highly endothermic calcination reaction. The global efficiency of the integrated system reaches 31.5 %. A parametric analysis is presented on the effects of key parameters, such as the carbonation pressure, the CO_2 inlet temperature to calciner, and CaO storage temperature.

1. Introduction

Global warming is a growing social and political issue. High levels of CO_2 concentration in the atmosphere require a reduction in the use of fossil fuels and uptake renewable energy technologies. Currently, fossil fuels are used on a great amount for power production, in both base load and peak load plants amplifying greenhouse effect (Edwards and Materic, 2012). Among several types of renewable technologies, solar energy constitutes an attractive, free, and endless source that can be converted into electricity by means of a Concentrated Solar Plant (CSP) (Pardo et al., 2014). The technology alone can only provide energy during the day light hours. Thermal Energy Storage (TES), Phase Change Materials (PCM), and Thermochemical Energy Storage (TCES) systems constitute the most interesting and applicable energy storage technologies for CSP (Chacartegui et al., 2016). TCES uses an external source of heat to drive an endothermic chemical reaction. The products of this reaction are separately stored, and when energy is needed, the reversible exothermic reaction is performed, which releases the previously chemical stored energy in the form of high temperature heat, readily available for power production. One of the most promising chemical system for TCES at large scales according to Miccio et al. (2015) is a Calcium Looping (CaL), which relies on the calcination-carbonation reaction (Eq(1)) of CaCO_3/CaO .



Several publications refer to CaL technology both for TCES applications with a CSP plant and for CO_2 post-combustion capture processes (Cormos and Cormos, 2015). A first detailed venture for an integrated CSP-CaL plant has been presented by Edwards and Materic (2012) with a solar tower receiver as a calciner and a pressurised fluidised bed carbonator implementing an open-air Brayton power cycle for energy production. More recently, Alovio et al. (2017) performed a detailed optimised CSP-CaL study considering three different configuration schemes using a potential solar heat receiver as calciner and a fluidised bed reactor as carbonator and a closed CO_2 Brayton cycle for power production. In addition, Ortiz et al. (2017) presented a detailed

analysis of potential power cycles configurations including directly power production, such as closed CO₂ Brayton power cycle, or indirectly, such as steam reheat Rankine cycle or a supercritical CO₂ cycle. However, no commercial plant exists and not even integrated units in research.

The aim of this study is to develop an integrated CSP plant that stores energy storage and produces power during the day and the night. This study comprises a preliminary design analysis of such a system and conducts several parametric process simulations seeking for a sustainable operation region with the maximum working efficiency.

2. Process description of a CSP-CaL integration system for thermochemical energy storage

2.1 Process description

Figure 1 shows the concept of an integrated CSP-CaL plant for thermochemical energy storage and power production. The process begins with the CaCO₃ decomposition calcination reaction, which is carried out at high temperature under a high excess CO₂ environment. The overall process design assumes that the total heat uptake in the adiabatic calciner can be achieved with a realistic manner if CO₂ is also used as the working fluid. In particular the high CO₂ temperature (above 950 °C) can be attained in a solar heat exchanger and be introduced in the calciner to accomplish CaCO₃ calcination at 950 °C and 1 bar. In this way, both original CO₂ and the surplus produced by the calcination reaction will be at high temperatures (950 °C) at the exit of the calciner and can be exploited for energy production during the process that takes place in the day. CSP with proper receiver materials can achieve even higher temperatures (Ho and Iverson, 2014).

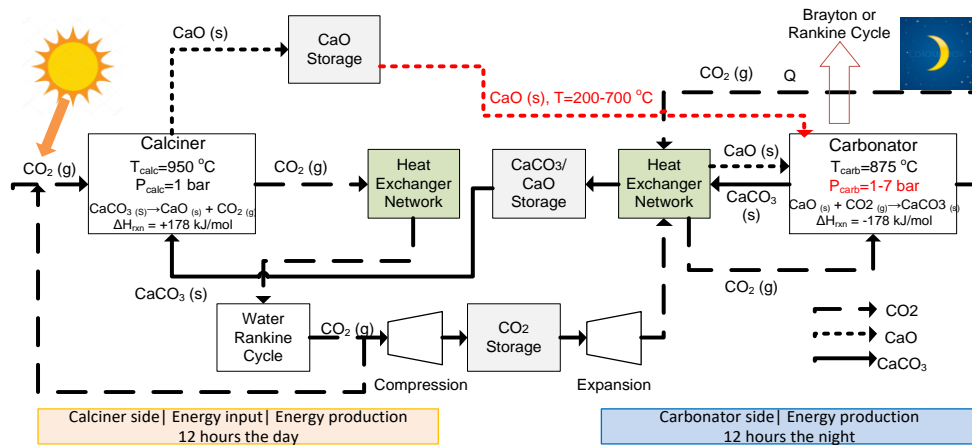


Figure 1: Concise conceptual CSP-CaL integration scheme

As shown in Figure 1, a solar preheated CO₂ stream is entering the calciner, whereas CaCO₃ and unreacted CaO particles are also entering the reactor at high temperature. The hot CO₂ released at 950 °C after calcination is later used in a Water Rankine Cycle (WRC) for energy production after being used in a heat exchanger for preheating the solids. The CO₂ amount equal to the produced CO₂ from calcination is cooled down and compressed, while the remaining recirculates back to the calciner. The produced CaO with the unreacted CaCO₃ hot stream at 950 °C is circulated to an insulated storage reservoir to be used later for carbonation. The carbonation reaction occurs at high temperature (875 °C) at night, where the previously stored amount of CaO/CaCO₃ is entering the reactor. The previously compressed CO₂ is also entering the carbonator after being expanded and preheated yielding useful work. From the carbonation reaction, the excess of CO₂ used as a heat fluid carrier is delivered to a power block (CO₂ closed Brayton cycle or WRC) for power generation and then is recycled and mixed with the cool CO₂-stream generated in the calciner.

2.2 Modelling methodology and model assumptions

The main assumptions made to model the integrated CSP-CaL plant are summarised in Table 1. As a base for the calcination section, a 100 MW_{th} net solar flux is considered to heat up a CO₂ stream in a concentrated solar heat exchanger at high temperatures (above 1,000 °C) in order both to heat up an appropriate amount of input particles as to preserve the necessary amount of energy to achieve calcination reaction. An adiabatic calciner with 5% energy losses is considered, so the throughput of solids is proportional to the temperature of CO₂ entering the reactor. Almost total conversion (97 %) of CaCO₃ and calcination temperature and pressure of 950 °C and 1 bar is considered. Due to the operation of calciner at atmospheric conditions, a WRC is employed for

power production. A maximum temperature and pressure of 600 °C and 75 bar of superheated steam and condenser pressure at 0.1 bar is considered for approaching high cycle efficiency (~35 %). On the other hand, the carbonator reactor could be a fluidised bed reactor (Cormos and Simon, 2013), or a drop tube reactor depending on particle size distribution (PSD). Carbonation under pressure is favourable for direct power-cycle integration and it allows carbonation at high temperatures with fast kinetics (Yu and Fan, 2011). This study examined an adiabatic carbonator with carbonation temperature to be predestined at 875 °C, which is a feasible value for an effective power block operation (Alovisio et al., 2017). In addition, a 50 % of CaO conversion is considered and an excess of CO₂ is entering the reactor as a fluid heat carrier to maintain the carbonator adiabatic and to deliver heat to a gas turbine. The carbonation reaction can take place both at atmospheric and under pressure conditions. For atmospheric carbonation, a WRC for power generation is considered, whereas a CO₂ closed Brayton cycle is employed for pressurised one. An Organic Rankine Cycle (ORC) is included in carbonation schemes with 15 % efficiency to exploit low temperature (~200 °C) streams. For both calcination and carbonation, minimum temperature approach (ΔT_{\min} °C) for gas-gas (GG), gas-solid (GS), and gas-liquid (GL) heat exchangers was of 50, 25, and 25 °C. Finally, daylight was assumed as 12 h/d (calcination) (the rest for carbonation).

Table 1: Summary of model assumptions.

Calcination Assumptions	Values	Carbonator Assumptions	Values
Net solar flux in solar HX (Q_{input}) (MW _{th})	100	-	-
Thermal losses in calciner (%)	5	Thermal losses in carbonator (%)	0
Calciner Temperature (°C)	950	Carbonator temperature (°C)	875
Calciner pressure (bar)	1	Carbonator pressure (bar)	1,3,5,7
Ambient Temperature (°C)	25	Ambient temperature (°C)	25
CaCO ₃ conversion (%)	97	CaO conversion (%)	50
max Rankine temperature (°C)	600	Brayton outlet pressure (bar)	1 bar
max Rankine Pressure (bar)	75	-	-
min temperature approach for GG, GS, GL HX (°C)	50, 25, 25	-	50, 25, 25
Intercoolings in CO ₂ storage compression	3	-	-
Intercoolings in CO ₂ cycle compression	1	-	1
CO ₂ storage conditions (bar, ambient)	75	-	-
Daylight hours (h)	12	Night hours (h)	12
Isentropic efficiencies (compression/expansion)	0.89	-	0.89
Organic Rankine Cycle (ORC) efficiency (%)	-	-	15

At the calciner side, three parametric simulations were performed regarding the CO₂ inlet temperature (1,000 °C; 1,050 °C; 1,100 °C). On the other hand, at the carbonator side, thirty parametric simulations were conducted. The pressure of carbonator was studied ranging from 1 - 7 bar. In the case of 1 bar, a WRC was employed for power production, whereas in higher pressures a CO₂ closed Brayton cycle one. The incoming temperature of previously produced solids (CaO/CaCO₃) for carbonation was parametrically studied ranging from 200-700 °C. For these simulations, a general chemical process simulator (AspenPlus™) was utilised for the calculation of mass and energy balances and thermodynamic properties. The developed model uses basic AspenPlus™ unit operation blocks to simulate the devices that are used in the process flow diagrams (Figure 2). Several Fortran calculator blocks and design-specs were employed to regulate the minimum temperature approach in heat exchangers and to calculate the appropriate CO₂ mass flow needed for approaching high inlet temperatures (above 1,000 °C) in the calciner side by a fixed solar input flux (100 MW_{th}). The particles throughputs in the calciner side and the mole ratio of CO₂/CaO in the carbonator were calculated to maintain adiabatic operation of both reactors.

The schematics layouts proposed in the next section were simulated to calculate the global plant efficiency, which is defined by the following mathematical formulation:

$$\eta_{global} = \frac{\dot{W}_{net,day} \cdot 12 \text{ h} + \dot{W}_{net,night} \cdot 12 \text{ h}}{\dot{Q}_{input} \cdot 12 \text{ h}} \quad (2)$$

where $\dot{W}_{net,day}$ and $\dot{W}_{net,night}$ are the net power produced during the day at calciner section and at night at carbonator section. \dot{Q}_{input} represents the input solar flux in solar heat exchanger. The net power production terms are defined by the following expressions, where $\dot{W}_{turb,rank}$, \dot{W}_{comp} , $\dot{W}_{comp1,2,3}$ and \dot{W}_{pump} perform the power produced from Rankine turbine, the power consumed from different compression stages and pump 100

consumption as shown in Figure 2. Similarly, $\dot{W}_{turb,main}$, \dot{W}_{turb} and \dot{W}_{ORC} terms present the power produced from the main turbine, the CO₂ expansion turbine and the ORC, while \dot{W}_{comp} refers to the compression stage.

$$\dot{W}_{net,day} = (\dot{W}_{turb,rank} - \dot{W}_{comp} - \dot{W}_{comp1} - \dot{W}_{comp2} - \dot{W}_{comp3} - \dot{W}_{pump}) \quad (3)$$

$$\dot{W}_{net,night} = (\dot{W}_{turb,main} + \dot{W}_{turb} + \dot{W}_{ORC} - \dot{W}_{comp}) \quad (4)$$

3. CSP-CaL integration scheme

3.1 Calcination–Carbonation layout

In the proposed AspenPlus™ simulation (Figure 2a), a comprehensive layout of the calcination process is presented. In the calcination process, both calcium oxide (CaO) and electrical energy can be produced the day. A solid stream (S-01) is coming by the CaCO₃ storage through a heat exchanger (HXA) into the calciner. At the outlet, the produced particles (S-05) are conveying to an insulated storage vessel to maintain as much as possible their heat while stored. A recycled stream of CO₂ (S-11) after being heated in a solar heat exchanger (Solar HX) passes through calciner, not only to accomplish calcination, but also to give the essential thermal energy to heat up solids. The excess CO₂ (S-06) exiting the reactor, after heating partially the incoming solids, is used as an input thermal energy in a WRC for power production. The cooled CO₂ stream (S-08) is then compressed, cooled, and split to a stream (S-11) back to the reactor, and a stream (S-12) following three stages of compression and intercooling reaching CO₂ storage conditions (25 °C, 75 bar).

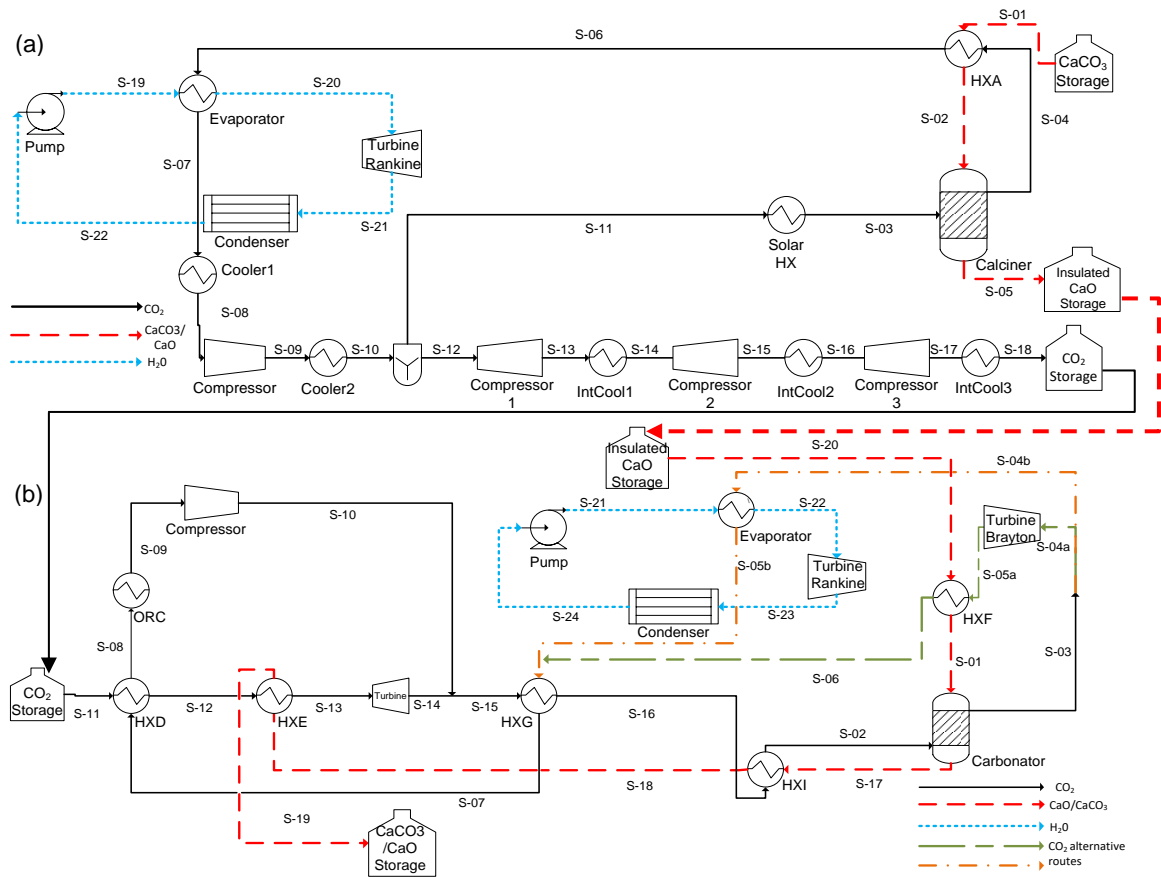


Figure 2: Process flow diagram of (a) calcination and (b) carbonation section of CSP-CaL plant.

The proposed carbonation process flow diagram in AspenPlus™ is presented in Figure 2b. In this layout, the previously produced CaO along with unreacted CaCO₃ are conveyed towards carbonator. The particles potentially can pass through a heat exchanger (HXF) for preheating or enter the reactor directly. This depends on the temperature that solids are maintained at the insulated storage. Alovio et al. (2017) stated that a temperature of ORC of 650 - 700 °C is acceptable and does not need supplementary preheating. The CaO inlet

temperature (200 - 700 °C) was parametrically studied and a parametric study of carbonation pressure (1 - 7 bar) was conducted. In the case of atmospheric carbonator conditions, a WRC is chosen for power generation as shown with orange lines, whereas for pressures above atmospheric, a closed CO₂ Brayton cycle is employed as shown with green lines. These two decisions are independent and cannot co-exist. Consequently, CO₂ passes through several heat exchangers (HXG, HXE, HXD) to transfer the latent heat to input stream, and the residual low thermal energy (~200 °C) stream (S-08) is exploited by an ORC. The CO₂ mass flow rate of stream S-11 of Figure 2b is matched with stream S-18 of Figure 2a and is equal to the amount of CO₂ consumed in the carbonator.

4. Results and discussion

Table 2 summarises the calciner results. Three different CO₂ inlet temperatures (1,000 °C; 1,050 °C; 1,100 °C) were studied and the influence of them was examined in some critical process parameters. It can be illustrated that by increasing CO₂ inlet temperature, a significant decline in produced power (28 - 33 MW_e) from the Rankine turbine and a subsequent reduction in the total network (25 - 30 MW_e) is resulted. This can be justified as for a fixed solar input flux (100 MW_{th}), less amount of CO₂ (81 - 91 kg s⁻¹) can be heated up as inlet temperature arises, resulting in less amount of CO₂ passes through Rankine cycle producing less power. As temperature increases, less mass flow of water (21 - 26 kg s⁻¹) constitutes the working medium of the Rankine cycle due to less CO₂ recycle. It is important that by increasing temperature, larger amounts of CaCO₃ (1 - 9 kg s⁻¹) particles are handled in the calciner, leading to well over produced CaO for carbonation.

Table 2: Summary of calciner results.

Calcination Temperature (°C)	Parameter	1,000	1,050	1,100
Solar heat exchanger Duty (MW _{th})	Solar HX-12 h	100	100	100
Power Produced (MW _e)	Turbine Rankine	33.31	30.64	28.08
Power Consumed (MW _e)	Compressor	2.22	2.12	2.04
	Compressor1	0.03	0.12	0.24
	Compressor2	0.04	0.15	0.29
	Compressor3	0.03	0.15	0.27
	Pump	0.22	0.20	0.19
$\dot{W}_{net,day}$ (MW _e)	-	30.77	27.90	25.00
Critical operational throughputs (kg s ⁻¹)	CO ₂ recycle	90.95	85.87	81.30
	H ₂ O circulate	25.74	23.86	21.66
	CaCO ₃ /CaO	1.16	3.18	9.32

Table 3 and Figure 3 show the carbonator section results. The parametric analysis of the carbonation pressure and incoming CaO temperature inferred to a wide value range of some critical parameters and efficiencies. A constantly meaningful increase of network ($\dot{W}_{net,day}$) is observed by increasing carbonation pressure by preserving the incoming CaO temperature as high as possible. This ranges between 0.45 MW_e (690 °C, 1 bar) for low CaO temperatures and pressures, and to 5.75 MW_e for high (690 °C, 7 bar). Moreover, a slight increase of global efficiency (η_{global}) is succeeded with increasing CaO temperature and with carbonation pressure. Particularly, a maximum efficiency of 31.5 % is achieved if carbonation occurs at 7 bars and 690 °C incoming CaO temperature, whereas a minimum efficiency of 28.6 % achieved with the scenario of atmospheric operation pressure and same CaO temperature.

Table 3: Carbonation section results.

Calc. CO ₂ inlet T (1,050 °C)	Parameter	1bar			3 bar			5 bar			7 bar			
		690	200	500	690	200	500	690	200	500	690	200	500	690
η_{global} (%)	-	29.8	30.1	30.5	30.8	30.3	30.6	30.9	30.3	30.6	30.9	30.3	30.6	30.9
$\dot{W}_{net,day}$ (MW _e)	-	1.92	2.25	2.63	2.88	2.36	2.72	3.00	2.41	2.75	3.03	2.41	2.75	3.03
Critical operational throughputs (kg s ⁻¹)	CO ₂ recycle	14.4	14.2	16.7	18.53	12.2	14.1	15.6	11.2	12.8	14.2	11.2	12.8	14.2

There is a strong relationship of the input CO₂ inlet temperature in the calciner and the hourly % contribution of the night carbonation operation to the total produced energy. As shown in Figure 3, a substantial percentage (~18.5 %) of the carbonation operation contribution is attained only with an increase in CO₂ temperature (value

for an average carbonation pressure is 5 bar and input CaO inlet temperatures is 690 °C). From these simulations, a range of 2.6 - 35.1 kg s⁻¹ of CO₂ runs through the carbonation section.

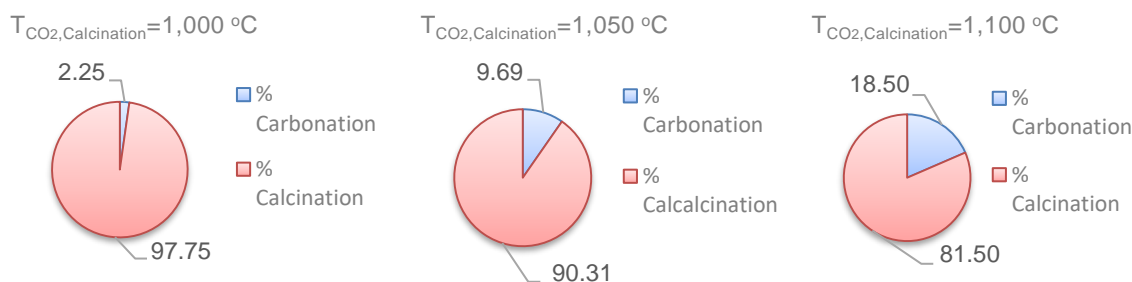


Figure 3: The carbonation contribution to the total produced work for three CO₂ calcination temperatures.

5. Conclusions

A preliminary study of an integrated Concentrated Solar Power plant (CSP) by an alternative solar energy exploitation using a Calcium Looping process (CaL) with thermochemical energy storage for power production was performed. Calcination reaction and power production occur during the day, while at night stored calcium oxide is carbonated and power is generated. Parametric studies have shown that process performance improves, and global efficiency can reach a maximum (31.5 %) when CO₂ inlet temperature at calciner increases (1,100 °C). Also, global efficiency enhances when carbonation pressure and CaO storage temperature increase to 7 bar and 690 °C respectively. CO₂ and H₂O mass flow recirculation in the process, as well as the total heat exchanger surface are critical parameters that affect process performance. A feasibility study can calculate the impact of the above parameters and will be the next scope for future work.

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References

- Alovisio A., Chacartegui R., Ortiz C., Valverde J.M., Verda V., 2017, Optimizing the CSP-Calcium Looping integration for Thermochemical Energy Storage, *Energy Conversion and Management*, 136, 85-98.
- Chacartegui R., Alovisio A., Ortiz C., Valverde J.M., Verda V., Becerra J.A., 2016, Thermochemical energy storage of concentrated solar power by integration of the calcium looping process and a CO₂ power cycle, *Applied Energy*, 173, 589-605.
- Cormos C.C., Cormos M.A., 2015, Assessment of CO₂ Capture by Calcium Looping from Natural Gas Combined Cycle (NGCC) Power Plants, *Chemical Engineering Transactions*, 45, 277-282.
- Cormos M.A., Simon A., 2013, Dynamic Modelling of CO₂ Capture by Calcium-Looping Cycle, *Chemical Engineering Transactions*, 35, 421-426.
- Edwards S.E.B., Materic V., 2012, Calcium looping in solar power generation plants, *Solar Energy*, 86, 2494-2403.
- Ho K.C., Iverson D.B., 2014, Review of high-temperature central receiver designs for concentrating solar power, *Renewable and Sustainable Energy Reviews*, 29, 835-846.
- Miccio F., Doghieri F., Landi E., 2015, Insights into High Temperature Sorbents for Carbon Dioxide, *Chemical Engineering Transactions*, 43, 901-906.
- Ortiz C., Chacartegui R., Valverde J.M., Alovisio A., Becerra J.A., 2017, Power cycles integration in concentrated solar power plants with energy storage based on calcium looping, *Energy Conversion and Management*, 149, 815-829.
- Pardo P., Deydier A., Anxionnaz-Minvielle Z., Rouge S., Cabassud., Cognet P., 2014, A review on high temperature thermochemical heat energy storage, *Renewable and Sustainable Energy Reviews*, 32, 591-610.
- Yu F.C., Fan L.A., 2011, Kinetic study of high-pressure carbonation reaction of calcium-based sorbents in the Calcium Looping Process (CLP), *Industrial & Engineering Chemistry Research*, 50, 11528-11536.