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Evaluation of Calcium Looping Cycle as a Time-flexible CO_2 Capture and Thermo-Chemical Energy Storage System

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Currently, the time flexibility of energy conversion systems is an issue of great operational importance considering the high integration of time-irregular renewable energy sources (e.g., solar, wind) which put an additional pressure on the conventional fossil-based systems. In addition, the reduction of fossil CO_2 emissions from various energy-intensive industrial sectors needs to be addressed considering the issues of global warming and climate change. This paper evaluates the innovative Calcium Looping (CaL) cycle both as an energy-efficient post-combustion CO_2 capture option and as a time-flexible thermo-chemical energy storage system. As illustrative energy conversion system to which the calcium looping cycle will be applied, a natural gas-based combined cycle power plant was considered. The net power output was about 400 - 500 MW with a 90 % CO_2 capture rate. Corresponded non-decarbonized case was also considered to calculate the CO_2 capture penalty. In-depth modelling, simulation and thermal integration evaluations were done to cover the following relevant operational elements: characterization of decarbonized combined cycle power plants with CaL cycle with / without solid sorbent storage; mass and energy integration issues; detailed techno-economic and environmental calculations of main performance indicators; flexible part load operation of the power plant to take advantages of CaL thermo-chemical energy storage characteristics etc. As the results show, the flexible time-operation of the decarbonized power plant integrated with CaL cycle using sorbent storage option improves the overall performances e.g., capital cost reduction up to 10 %, lower electricity production cost up to 5 % etc.

1. Introduction

Cutting down the CO_2 emissions from energy intensive sectors (e.g., heat and power, metallurgy, petro-chemistry, cement etc.) is a paramount important element for developing a sustainable low carbon future. The carbon footprint can be reduced by several methods e.g., increasing the share of renewable energy sources (e.g., solar, wind, biomass), improving the energy efficiency for both conversion and utilization steps, large-scale deployment of Carbon Capture, Utilisation and Storage (CCUS) technologies (European Commission, 2019). The renewables are seen as a promising low carbon energy source but the time-dependence of solar and wind is a key element that has to be considered for future modern energy systems. To overcome the time-variability of renewable energy sources, the backup power capacity with high cycling capabilities needs to be developed. These backup capacities are based on fossil fuels eventually being fitted with carbon capture feature. This work evaluates the techno-economic implications of the calcium looping as an innovative carbon capture technology which can be used also as an energy-storage system. This CO_2 capture technology was implemented in a natural gas-fuelled combined cycle power plant (400 - 500 MW net output with 90 % CO_2 capture rate) for flexible operation. The key innovative element of this analysis against the literature represents the techno-economic assessment of dynamic operation of calcium looping cycle both as post-combustion CO_2 capture system as well as energy-storage using sorbent storage (Yan et al., 2020). A wide range of process system engineering tools were used: modeling and simulation, thermal integration by Pinch Analysis, dynamic operation of decarbonized power plant, assessment of the overall techno-economic performance indicators.

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2. Process description, design assumptions and energy integration elements

The calcium looping technology is based on the following reversible chemical reaction (Fan, 2010):

$$CaO \quad + \quad CO_2 \quad \leftrightarrow \quad CaCO_3 \qquad \Delta H_r^0 = -178\ kJ/mol \qquad (1)$$

The carbonate looping cycle includes two circulated fluidized bed reactors: the carbonator in which the flue gases are decarbonized by reaction with the regenerated sorbent (see reaction 1) followed by the calciner in which the carbonated sorbent is thermally decomposed back to carbon dioxide and regenerated sorbent. Additional heat (usually by oxy-combustion fashion) has to be supplied in the calcined to cover the carbonate decomposition reaction. Figure 1 presents the conceptual layout of Natural Gas Combined Cycle (NGCC) power plant fitted with post-combustion CO_2 capture based on calcium looping technique (Berstad et al., 2014).

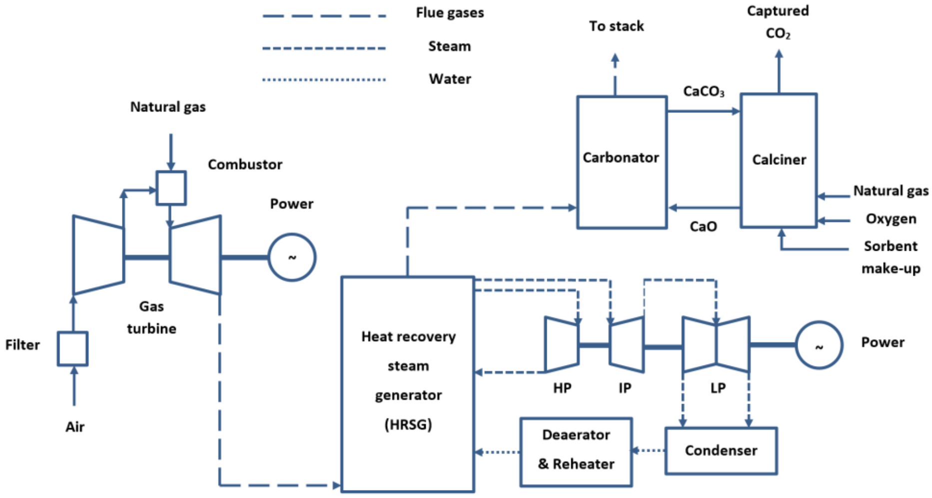

Figure 1: Layout of decarbonized natural gas combined cycle power plant

The most important design elements of decarbonized NGCC power plant using calcium looping cycle are presented in Table 1 (Berstad et al., 2014; Cormos, 2020). The correspondent NGCC benchmark case without carbon capture was also considered to quantify the CO_2 capture energy and cost penalties.

Table 1: Key design assumptions

Plant sub-system	Design specifications
Natural gas composition and thermal properties	Composition: 89 % methane, 7 % ethane, 1 % propane, 0.1 % butanes, 0.01 % pentanes, 2 % carbon dioxide, 0.89 % nitrogen Lower heating value: 46.73 MJ/kg
Natural gas combined cycle (NGCC) power plant	Gas turbine type: 1 x M701G2 Net power output: 334.00 MW Pressure ratio: 21.00 Net electrical efficiency: 39.50 % Steam conditions: 585 ^oC & 120 bar / 425 ^oC & 34 bar / 210 ^oC & 3 bar
Calcium looping (CaL) cycle	Sorbent: natural calcium-based sorbent (limestone) Carbonation reactor: 575 - 625 ^oC / Calcination reactor: 850 – 980 ^oC CO_2 capture rate: 90 %
Cryogenic air separation unit (ASU)	Oxygen composition (% vol.): 95 % O_2, 2 % N_2, 3 % Ar ASU ancillary consumption: 200 kWh/t O_2
CO_2 processing unit (CPU)	Plant gate delivery pressure: 120 bar Compressor efficiency: 85 % TEG (Tri-ethylene-glycol) dehydration unit CO_2 quality specification (vol. %): >95 % CO_2, <2,000 ppm CO, <250 ppm H_2O, <100 ppm H_2S, <4 % non-condensable gases
Heat recovery & steam cycle	Steam turbine efficiency: 85 % Steam wetness: max. 10 % Minimum approach temperature: $\Delta T_{min.}$ = 10 ^oC

To optimize the overall energy utilization, detailed thermal integration analysis was performed using Pinch method (Klemeš, 2013). Figure 2 shows Composite Curves for the combined cycle and the carbonation cycle considering 10 °C as minimum temperature difference. As can be noticed, the CaL cycle has a relevant high-temperature heat recovery potential which has a positive influence on the overall energy efficiency of the plant. In comparison to CO_2 capture by reactive gas-liquid absorption which operates around ambient conditions, the calcium looping cycle can generate heat at higher temperatures which can be used for steam generation (about 125 MW_{th} as HP steam and 52 MW_{th} as LP steam).

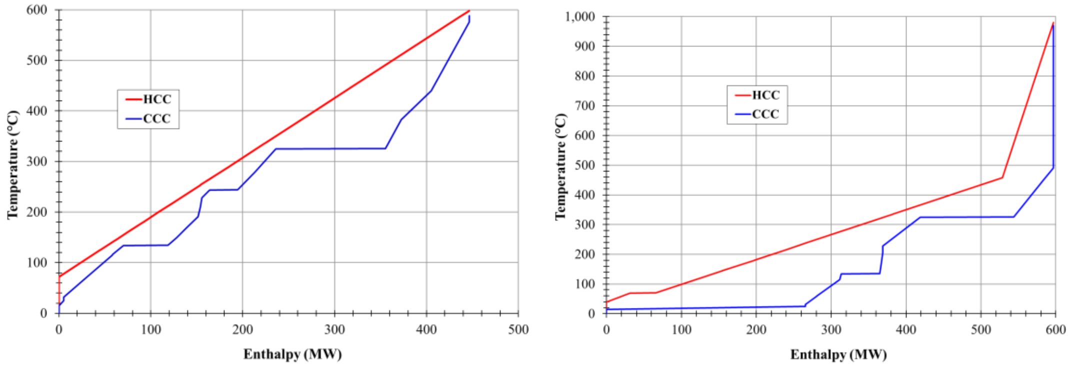

Figure 2: Composite Curves for NGCC plant (Figure 2.a - left) and calcium looping cycle (Figure 2.b - right)

3. Flexible operation of the decarbonized combined cycle power plant

The flexibility characteristic of modern power plants is very important considering the constraints imposed by the integration of time-variable renewable sources (Al-Shetwia et al., 2020). From this point of view, the backup power generation capacities (most of them being fossil-based such as investigated natural gas plant) gas to cycle more frequent. The investigated decarbonized NGCC power plant can be designed in a flexible manner by exploiting the energy storage potential of the carbonate looping cycle (Prasad, 2019). A flexible NGCC – CaL plant with sorbent storage facilities has promising potential for further reduction of energy and cost penalty for CO_2 capture. In such a flexible this design (see Figure 3), both carbonated and calcinated sorbent can be stored during the peak-period to be processed when electricity consumption is lower.

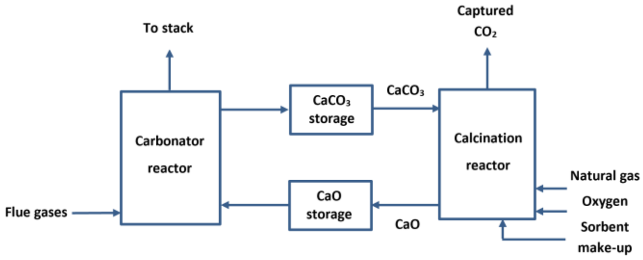

Figure 3: Flexible carbonate looping cycle with sorbent storage facilities

To assess the potential benefits of flexible plant by exploiting the sorbent storage design, an average variation of NGCC power plant capacity factor vs. time for a whole week was defined based on current operational pattern in Europe (Astolfi et al., 2019). Table 2 presents the evaluated flexible operation scenario of NGCC – CaL plant.

Table 2: Weekly variation of NGCC – CaL power plant capacity

Monday – Friday		Saturday – Sunday
6 AM to 1 PM 7 PM to 9 PM	10 PM to 5 AM 2 PM to 6 PM	0 AM to 12 PM (all day)
100 %	50 %	50 %

Considering this time variation of decarbonized NGCC power plant capacity, the flue gases flow in a flexible operation scenario compared to the base-load operation is about 73 % for the Monday to Friday period, 50 % for the weekend and about 66.5 % for the whole week. The nominal base-load flue gases flow for decarbonized power plant is about 2,662 t/h with 4.21 % vol. carbon dioxide and the corresponding plant capacity is 90 %.

4. Assessment methodology

The evaluated natural gas-fuelled combine cycle plants with and without CO_2 capture feature were modelled and simulated using ChemCAD software. As thermodynamic package, Soave-Redlich-Kwong (SRK) model was used for gas processing and calcium looping cycle. The carbonation and calcination reactors were modelled as Gibbs units (Cormos, 2020). The model of calcium looping cycle was validated by comparison the simulation results to the experimental data (see Figure 4). One can noticed a good correlation (Cormos and Simon 2015).

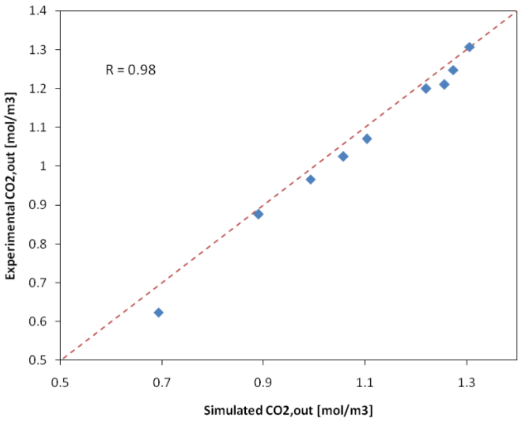

Figure 4: Calcium looping cycle model validation

The mass and energy balances derived from simulation were used to quantify the key techno-economic and environmental performance indicators. As relevant plant indexes the following elements were considered (IEAGHG, 2012): Net power efficiency to show the net energy conversion yield from fuel (natural gas) to net generated power; Carbon capture rate which quantify the CO_2 emission reduction ratio of the power plant (ratio of fuel carbon which was captured); Specific CO_2 emissions to illustrate the amount of emitted CO_2 per each MWh net generated power; Specific investment cost to show the capital cost per each kW of net installed power capacity; Operational & maintenance (O&M) cost which illustrates production cost of each MWh net generated power; Levelized cost of electricity (LCOE) to quantify the overall production cost of electricity; CO_2 capture costs to illustrate the economic penalty of carbon capture feature. An in-depth presentation and definition of these performance indicators as well as the key economic assumptions is provided by Cormos (2020)

5. Results and discussions

First, the decarbonized NGCC power plant integrated with calcium looping unit was evaluated in a base load scenario without sorbent storage. Table 3 presents the key techno-economic and environmental indicators for conventional NGCC power plant without carbon capture (Case 1) and decarbonized NGCC - CaL concept without sorbent storage (Case 2.a).

One can observe that introduction of carbon capture unit by calcium looping cycle implies an important energy and cost penalties for CO_2 capture as follow: reduction of overall plant efficiency by about 10.4 net percentage points, increasing the specific investment cost by about 41 %, increasing the operational & maintenance cost by about 26 % as well as increasing the levelized cost of electricity by about 25 %. In term of environmental impact, introduction of carbon capture feature induces a significant reduction of specific CO_2 emissions by about 91 %. Considering the current CO_2 price in European Union (EU) emission trading scheme (about 40 €/t according to Sandbag carbon price viewer, 2021) in comparison to the value of CO_2 avoided cost of this analysis, the decarbonized NGCC power plant show a promising economic perspective. The impact of natural gas extraction and transportation on the plant performance was not evaluated in the present analysis.

The second evaluated operation scenario of NGCC – CaL power plant was a flexible one which uses the sorbent storage facilities to overcome the issues related to plant cycling. For both sorbent forms, the regenerated one produced by the calciner and the carbonated one produced by the carbonator were considered storage facilities. Solid storage facility at high temperature as in this work could be similar with industrial concepts used in cement plants but there is a need for further research and demonstration. In this flexible operational scenario of the power plant, the calcium looping cycle was designed at about 74 % from the situation without sorbent storage (see Case 2.a from Table 3). According to the weekly time-operating scenario presented in Table 2, the variations of sorbent storages and power plant load over a week time cycle are presented in Figure 5.

Table 3: Key performance indicators for NGCC power plants

Plant indicator	Units	Case 1	Case 2.a
Input natural gas flowrate	t/h	65.35	92.25
Natural gas lower calorific value	MJ/kg	46.73	
Input natural gas thermal energy	MW_{th}	848.28	1,197.45
Gas turbine power output	MW_e	334.00	334.00
Steam turbine power output	MW_e	168.62	297.50
Gross power output	MW_e	502.62	631.50
Ancillary consumption	MW_e	2.62	50.45
Net power output	MW_e	500.00	581.05
Net electrical efficiency	%	58.94	48.52
CO_2 capture rate	%	0.00	90.00
Specific CO_2 emissions	kg/MWh	350.95	31.10
Specific investment cost	€/kW	686.00	970.00
Operational & maintenance cost	€/MWh	34.00	43.00
Levelized cost of electricity	€/MWh	44.60	55.90
CO_2 removal cost	€/t	-	28.70
CO_2 avoided cost	€/t	-	33.85

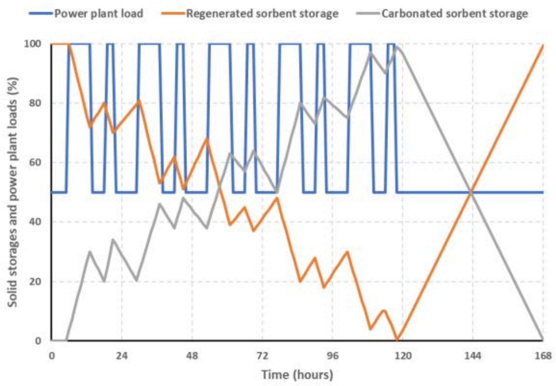

Figure 5: Carbonated / regenerated sorbent storage and power plant load validations over a week cycle

As can be observed from Figure 5, when the plant operates at full capacity (100%) during peak time in the week, the carbonated solid storage is gradually filling up and the regenerated solid storage is discharged. During the period with reduced power plant loads (50%), the overall sorbent storage process is reversed (the regenerated sorbent storage is gradually filling up and the carbonated sorbent storage is discharged). Over the weekend, the regenerated sorbent facility is filling up to 100% (Sunday night) to make available enough sorbent for the next week power plant operation.

The flexible NGCC - CaL power plant (noted as Case 2.b) induces a supplementary investment for the sorbent storage facilities but also a reduction of investment for the calcium looping unit. Considering that solid storage facilities have lower investment costs than interconnected fluidized bed CaL unit, it results an overall reduction of the capital cost. Table 4 presents the comparative performances of base-load decarbonized NGCC plant (Case 2.a) and flexible decarbonized NGCC plant (Case 2.b). The sorbent storage was sized based on the nominal flue gases flow, the size ratio of calcination line as well as the dynamic profile of the power generation. One can noticed that the flexible NGCC – CaL with sorbent storage facilities has better techno-economic performances than the similar base-load concept without sorbent storage. For instance, the specific capital investment was reduced by about 9.5 %, the operational & maintenance (O&M) cost by about 1.4 % and the levelized cost of electricity (LCOE) by about 5 %. Also, the CO_2 capture costs show a reduction for time-flexible calcium looping case by about 8 %. All these elements come to underline the promising potential of flexible calcium looping cycle with sorbent storage facilities to deliver improved energy and cost performances.

Table 4: Key performance indicators for NGCC - CaL power plants with and without sorbent storage

Plant indicator	Units	Case 2.a	Case 2.b
Calciner factor	%	100.00	74.00
Gas turbine power output	MW_e	334.00	334.00
Steam turbine power output	MW_e	297.50	264.00
Gross power output	MW_e	631.50	598.00
Ancillary consumption	MW_e	50.45	76.50
Net power output	MW_e	581.05	521.50
Specific investment cost	€/kW	970.00	878.00
Operational & maintenance cost	€/MWh	43.00	42.40
Levelized cost of electricity	€/MWh	55.90	53.15
CO_2 removal cost	€/t	28.70	26.40
CO_2 avoided cost	€/t	33.85	31.20

6. Conclusions

This work evaluates the techno-economic and environmental implications of time-flexible operation of calcium looping cycle considering sorbent storage as a method for both carbon capture and thermo-chemical energy storage. This promising energy-efficient CO_2 capture method was integrated in a natural gas combined cycle power plant. Similar power plant without CO_2 capture feature was considered to assess the energy and cost penalties for carbon sequestration. A wide range of process engineering tools were used (modelling and simulation, validation, thermal integration, techno-economic evaluation). As the results show the time-flexible NGCC – CaL design with sorbent storage has important benefits in comparison to the base-load design without sorbent storage e.g.,10 % lower investment cost, 5 % lower electricity production cost, 8 % lower CO_2 capture costs etc. These positive elements of calcium looping technology show a promising potential of this CO_2 capture and thermo-chemical energy storage method to be integrated in future energy systems.

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