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Assessment of Flexible Thermochemical Energy Conversion and Storage System based on Chemical Looping Combustion

Calin-Cristian Cormos*, Simion Dragan, Ana-Maria Cormos, Letitia Petrescu

Babes - Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos, Postal code: RO-400028, Cluj - Napoca, Romania
calin.cormos@ubbcluj.ro

Today, conventional heat and power production systems are facing significant operational challenges due to the integration of time-variable renewable energy sources (e.g., wind, solar). In addition, the transition to a low-carbon economy requires the deployment of innovative energy production systems with low CO_2 emissions. The chemical looping combustion technology is a promising option to provide a system with, simultaneously, high energy efficiency and low carbon emissions. This work assesses the natural gas-based chemical looping combusting system for time-flexible production of power with almost total decarbonization (carbon capture rate > 99 %). The iron oxide looping system was assessed as an illustrative thermo-chemical process for energy conversion and storage. The size of investigated concept generates 100 MW net power. Two chemical looping combustion configurations were evaluated as follow: a base-load option and a time flexible one using the feature of oxygen carrier storage (in both reduced and oxidized forms). As the overall evaluation of performance shows, the flexible operation of chemical looping combustion system improves the overall performance e.g., reduction of specific capital cost up to 3 %, reduction of power cost up to 2 %, reduction of CO_2 capture cost up to 8 %.

1. Introduction

Currently, the energy production sector is facing multiple challenges due to several elements e.g., increased penetration of renewable energy sources (most of them being highly time dependent such as solar and wind), volatile market in term of prices, tight environmental regulations aiming to reduce pollution (for instance, in term of CO_2 emission) etc. The transition to future low-carbon economy requires significant modifications to the existing energy systems, for instance, developing innovative technologies able to cope with the time variability of solar and wind-based processes, enhancing energy storage feature as well as enforcing a high energy efficiency coupled with a deep reduction of CO_2 emissions. The chemical looping technology (in its different variants such as: Chemical Looping Combustion - CLC, Chemical Looping Reforming - CLR, calcium-based sorbent looping - CaL) is a promising energy conversion method which has high energy efficiency combined with CO_2 capture (Fan, 2010). Even further, the chemical looping systems have high prospects of thermo-chemical energy storage capabilities (Yan et al., 2020). For the CLC systems, various Oxygen Carriers (OC) can be used e.g., metallic oxides of iron, manganese, nickel, copper, cobalt etc. (Abuelgasim et al., 2021).
This analysis evaluates the main techno-economic performances of iron-based chemical looping combustion system for power generation. The size of investigated concept is 100 MW net power output with a carbon capture rate higher than 95 %. As fuel, natural gas was considered. Two CLC options were assessed: a base-load option and a time flexible one using the feature of oxygen carrier storage (in both reduced and oxidized forms). Detailed mathematical modelling, simulation and thermal integration analysis were performed to cover the following aspects: conceptual designs, characterization of mass and energy balances of both chemical looping combustion cycles, energy integration issues, detailed calculation of techno-economic and environmental performance indicators, development issues etc. The key novelty element of this analysis, in respect to available state-of-the-art literature sources (Wu et al., 2018), represents the detailed techno-economic evaluation of an industrial-relevant iron-based chemical looping combustion (CLC) system for flexible thermo-chemical energy conversion and storage. For instance, the assessment of energy storage feature for an iron-based looping cycle was not yet reported in the literature compared to the calcium looping cycle case (Cormos et al., 2021).

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2. Process description, key design assumptions and thermal integration analysis

The natural gas-based chemical looping combustion cycle is based on the utilization of two separate reactors: (i) fuel reactor in which the natural gas is fully oxidized by the oxygen carrier (Fe_2O_3) to carbon dioxide and water with simultaneous reduction of oxygen carrier to FeO; (ii) air reactor in which the reduced form of the oxygen carrier (FeO) is re-oxidized back to Fe_2O_3 using air. This arrangement with two separate reactors ensures that the captured carbon dioxide is not impurified by nitrogen from air. The reactions are the following:

- Fuel reactor:

$$CH_4 \quad + \quad 4Fe_2O_3 \quad \leftrightarrow \quad CO_2 \quad + \quad 2H_2O \quad + \quad 8FeO \quad \Delta H = +\,307.2\; kJ/mol \tag{1}$$

- Air reactor:

$$2FeO \quad + \quad 1/2O_2 \quad \leftrightarrow \quad Fe_2O_3 \quad \Delta H = -\,517.85\; kJ/mol \tag{2}$$

There are several proposed configurations for the chemical looping reactors (Mattisson et al., 2018). The most evaluated option (also used in this analysis) involves the utilization of inter-connected circulating fluidized bed (CFB) reactors with the solid oxygen carrier circulating among the two reactors. Other potential option can use a fixed bed reactor and the reduction and oxidation steps are done by modification of the gaseous streams (natural gas for reduction, followed by inert gas purge and then by oxidation with air) entering the reactor. The conceptual design of iron-based chemical looping combustion (CLC) cycle is presented in Figure 1.

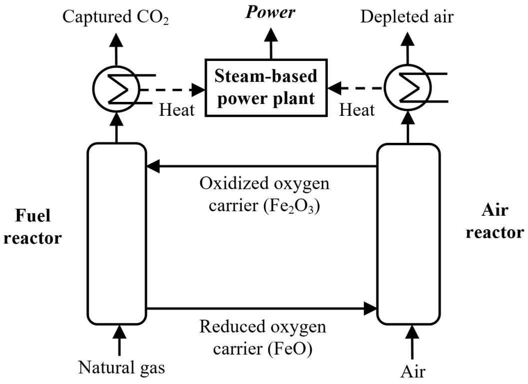

Figure 1: Conceptual design of iron-based chemical looping combustion cycle

Table 1 presents the key design assumptions of iron-based chemical looping combustion (CLC) cycle using natural gas as fuel for power generation (Lyngfelt et al., 2019).

Table 1: Key design assumptions

Plant sub-system	Design specifications
Natural gas composition and thermal properties	Composition (vol. %): 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
Fuel reactor	Operating temperature & pressure: 800 °C & 3 bar Fuel conversion rate: > 99 %
Air reactor	Operating temperature & pressure: 985 °C & 2.5 bar Oxygen carrier re-oxidation rate: 98 - 99 %
Steam cycle power plant	Net power output: 100.00 MW Steam conditions: 585 °C & 120 bar / 210 °C & 3 bar Steam turbine efficiency: 85 % Condenser pressure: 0.045 bar
CO_2 drying and compression unit	Final delivery pressure: 120 bar Compressor efficiency: 85 % Dehydration unit: TEG (Tri-ethylene-glycol) CO_2 composition (vol. %): > 95 % CO_2, < 2,000 ppm CO, < 250 ppm H_2O, < 100 ppm H_2S, < 4 % non-condensable gases
Heat exchangers	Pressure drops: 2 – 3 % of inlet pressure Minimum temperature difference: $\Delta T_{min.}$ = 10 °C

The natural gas-based chemical looping combustion cycle was modelled and simulated using ChemCAD software. The developed models were validated against experimental data (Mattisson et al., 2018). No significant differences are observed in term of key performance indicators (e.g., fuel conversion rate, CO_2 capture yield, chemical looping reactor operating parameters etc.). The design was subject of thermal integration analysis using Pinch methodology (Klemeš, 2013). To illustrate the thermal integration, Figure 2 presents the Composite Curves for the chemical looping combustion cycle. Following the simulation, the overall mass and energy balances were used for estimation of key performance indicators.

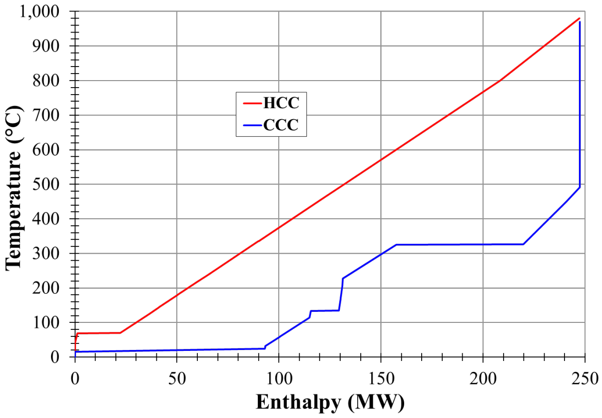

Figure 2: Composite Curves for the iron-based chemical looping combustion cycle

3. Flexible operation of iron-based chemical looping combustion cycle

Currently, the modern power plants have to be designed in a flexible operational regime due to high integration degree of time-dependent renewable energy sources (e.g., solar, wind). In order to keep the balance of electricity production - transportation and utilization system, flexible back-up power generation capacities (most of them based on fossil fuels but with a decarbonization feature) are to be developed and deployed. The proposed iron-based chemical looping combustion cycle can be operated in a flexible manner by exploiting the possibility of the oxygen carrier (OC) storage in both oxidized (Fe_2O_3) and reduced (FeO) forms. Figure 3 presents a flexible chemical looping combustion cycle in which both oxidized and reduced form of the oxygen carrier can be stored to be used when needed.

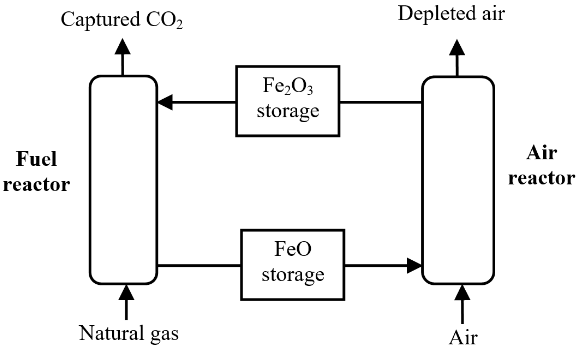

Figure 3: Flexible chemical looping combustion cycle with storage of oxygen carrier

To evaluated the main techno-economic indicators of flexible natural gas-based CLC cycle using oxygen carrier storage, a week-long power plant operation scenario was defined (see Table 2). This operational scenario takes into consideration the common situation in Europe as reported by Astolfi et al. (2019).

Table 2: Flexible operational scenario of CLC-based power plant

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 the above-mentioned pattern, for the flexible power plant, compared to the base-load case, the operational factor is about 73 % for the Monday to Friday period, 50 % for the weekend and about 66.5 % for the whole week. This variation of the operational factor was considered for the techno-economic assessment of flexible natural gas chemical looping combustion power plant.

4. Techno-economic assessment methodology

The following CLC-based power plant concepts were evaluated:

Case 1: Natural gas-based CLC power plant operated in base load conditions;
Case 2: Natural gas-based CLC power plant operated in flexible load conditions (OC storage);

The iron-based CLC power plant concepts with CO_2 capture were modelled and simulated using ChemCAD process flow modelling software. The Soave-Redlich-Kwong (SRK) model was used as thermodynamic package. The developed models were validated by comparison of the simulation results with available experimental data. In this respect, the key performance indicators were used e.g., natural gas / oxygen carrier conversion rates, CO_2 capture rate etc. (Chisalita and Cormos, 2018). For instance, the natural gas conversion rate within the fuel reactor is almost total (>99 %) in accordance to the relevant literature references in the field (Chen et al., 2021). Considering the available heat sources within the plant (e.g., hot gaseous effluent streams from both fuel and air reactors), the steam generation was considered which was further expanded in a steam turbine to produce power. The generated power was used to cover completely the ancillary electricity consumption, the remaining being considered for grid export.

Based on the mass and energy balances produced from mathematical modelling and simulation of assessed iron-based CLC power plant concepts, the key techno-economic and environmental plant performance indicators were calculated for both base load and flexible load operation regimes. For the techno-economic assessment, the overall methodology proposed by International Energy Agency - Greenhouse Gas R&D Programme (IEAGHG, 2012) was followed with the calculation of following performance indicators: net and gross power outputs; ancillary power consumption; net power efficiency to show the overall energy conversion yield of natural gas to power; CO_2 capture rate to show the overall power plant decarbonization yield; specific CO_2 emissions per each kW of generated power; specific investment cost to illustrate the investment required per each kW of net power; operational & maintenance (O&M) cost; levelized cost of electricity; CO_2 removal and avoidance costs etc. An in-depth characterization of calculated key performance indicators as well as the main economic assumptions are provided by previous authors studies (e.g., Cormos et al., 2021). The benchmark case used to calculate CO_2 capture costs was a natural gas combine cycle plant (IEAGHG, 2012).

5. Results and discussions

The key techno-economic and environmental performance indicators for iron-based CLC power plant with CO_2 capture operated in based load conditions are presented in Table 3.

Table 3: Key performance indicators for natural gas CLC power plant (base load operation)

Plant indicator	Units	Base load
Input natural gas flowrate	t/h	17.60
Natural gas lower calorific value	MJ/kg	46.73
Input natural gas thermal energy	MW_{th}	228.45
Expander output	MW_e	58.23
Steam turbine output	MW_e	78.48
Gross power output	MW_e	136.71
Ancillary power consumption	MW_e	36.71
Net power output	MW_e	100.00
Net electrical efficiency	%	43.77
CO_2 capture rate	%	99.85
Specific CO_2 emissions	kg/MWh	0.25
Specific investment cost	€/kW	884.00
Operational & maintenance (O&M) cost	€/MWh	45.61
Levelized cost of electricity (LCOE)	€/MWh	68.57
CO_2 removal cost	€/t	44.16
CO_2 avoided cost	€/t	54.88

As can be noticed, the iron-based CLC power plant has a high energy efficiency (about 44 %) coupled with an almost total decarbonization rate (> 99 %). The specific CO_2 emissions are almost negligible (about 0.25 kg/MWh). For comparison reason, a Natural Gas Combined Cycle (NGCC) power plant without CO_2 capture feature has an efficiency of about 56 - 58 % with specific CO_2 emissions of about 375 kg/MWh (IEAGHG, 2012). The key economic indicators of NGCC power plant without carbon capture were: 686 €/kW net power as specific investment costs; 36 €/MWh as Operational & Maintenance (O&M) cost and 48 €/MWh as levelized cost of electricity (Cormos et al., 2021). One can see that decarbonization implies significant energy and cost penalties.
The flexible iron-based CLC power plant uses the oxygen carrier storage option to improve the power plant cyclability. For both oxygen carrier forms (reduced and oxidized), high temperature storage facilities were considered. These high-temperature solid storage facilities are similar with the ones used in cement industry but still requiring further developments. Considering the flexible operation scenario (presented in Table 2), the variations of oxygen carrier storages and power plant load over a week time cycle are presented in Figure 4.

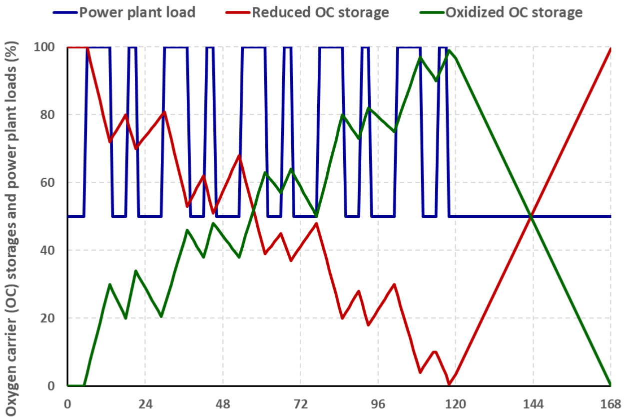

Figure 4: Flexible chemical looping combustion cycle with storage of oxygen carrier

During peak time, when the CLC power plant operates at full capacity (100 %), the oxidized oxygen carrier (OC) storage is gradually filling up and the reduced oxygen carrier storage is discharged. When the power plant load is reduced (e.g., during the night or in weekend), the overall process is reversed: the oxidized OC storage is discharged and the reduced OC storage is filling up. In these conditions, at the end of the weekend, the reduced OC storage is completely full and the oxidized OC storage is completely emptied for the next week cycle.
In term of economic analysis, the flexible iron-based CLC power plant (Case 2) requires an additional positive investment for the high-temperature OC storage facilities but it induces also a size reduction of CLC unit which reduces the investment cost. Considering that the oxygen carrier storage facilities require a reduced capital cost than the interconnected CFB-CLC unit (due to design complexity and operational parameters), an overall investment reduction is expected. Table 4 shows the main techno-economic performances for both base load and flexible iron-based CLC power plant concepts. It can be observed that the flexible CLC power plant concept with oxygen carrier storage facilities shows improved techno-economic performances. In this respect, the specific investment cost is reduced by about 3 %, the operation & maintenance (O&M) cost is also reduced by about 2 %, the power production cost is reduced by about 2 %. As can be observed, the flexible operation of CLC power plant using the OC storage facilities induced improved power plant economic performance.

Table 4: Key performance indicators for CLC power plants with and without oxygen carrier storage

Plant indicator	Units	Base load	Flexible load
Air reactor operational factor	%	100.00	73.00
Gross power output	MW_e	136.71	120.78
Ancillary power consumption	MW_e	36.71	35.90
Net power output	MW_e	100.00	84.88
Specific investment cost	€/kW	884.00	858.00
Operational & maintenance cost	€/MWh	45.61	44.80
Levelized cost of electricity	€/MWh	68.57	67.20
CO_2 removal cost	€/t	44.16	40.89
CO_2 avoided cost	€/t	54.88	50.45

In term of technological implementation to large scale, the CLC-based power generation with carbon dioxide capture still requires significant development efforts for both process optimization (e.g., reduction of deactivation rate of oxygen carrier, improve the kinetic and hydrodynamic aspects, reduce the oxygen carrier costs, reactor design issues, high temperature oxygen carrier storage) and the scale-up issues from current laboratory scale up to 1 MW thermal size (Osman et al., 2021) to tens and hundreds of MW required for industrial systems.

6. Conclusions

This paper assesses the techno-economic and environmental performance of flexible iron-based CLC power plant considering the oxygen carrier storage. As illustrative fuel, natural gas was considered. A similar based load CLC power plant was considered for comparison reason. An integrated assessment methodology was used covering modelling and simulation, thermal integration, techno-economic and environmental evaluation. The results show that the flexible iron-based CLC power plant with oxygen carrier storage feature has relevant economic advantages (beside the overall power plant flexibility) in comparison to the base-load system: about 3 % reduced specific capital investment cost, about 2 % lower levelized cost of electricity, about 8 % lower CO_2 capture costs. The CLC-based systems for energy conversion and storage still require further development for process optimization (e.g., oxygen carrier refinement and cost reduction, high temperature oxygen carrier storage facilities etc.) and scale-up from current less than 1 MW size to relevant industrial sizes. The above-mentioned key performance indicators show the promising potential of iron-based chemical looping combustion to deliver innovative energy and cost-efficient solution with lower environmental impact and safety issues than other oxygen carriers for thermo-chemical energy storage to be integrated in future flexible energy systems.

Acknowledgements

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References

Abuelgasim A., Wang W., Abdalazeez A., 2021, A brief review for chemical looping combustion as a promising CO_2 capture technology: Fundamentals and progress, Science of The Total Environment, 764, 142892.

Astolfi M., De Lena E., Romano M.C., 2019, Improved flexibility and economics of Calcium Looping power plants by thermochemical energy storage, International Journal of Greenhouse Gas Control, 83, 140–155.

Chen W.H., Chen K.H., Ubando A.T., Lee W.J., Chio M.H., 2021, Redox degrees of iron-based oxygen carriers in cyclic chemical looping combustion using thermodynamic analysis, Chemical Engineering Journal, 426, 130834.

Chisalita D.A., Cormos A.M., 2018. Dynamic simulation of fluidized bed chemical looping combustion process with iron based oxygen carrier, Fuel, 214, 436–445.

Cormos C.C., Dragan S., Cormos A.M., Petrescu L., Dumbrava I.D., Sandu V.C., 2021, Evaluation of calcium looping cycle as a time-flexible CO_2 capture and thermo-chemical energy storage system, Chemical Engineering Transactions, 88, 19–24.

Fan L.S., 2010, Chemical looping systems for fossil energy conversions, Wiley-AIChE, New Jersey, USA.

International Energy Agency - Greenhouse Gas R&D Programme (IEAGHG), 2012, CO_2 capture at gas fired power plants, Report 2012/8, Cheltenham, UK.

Lyngfelt A., Brink A., Langørgen Ø., Mattisson T., Rydén M., Linderholm C., 2019, 11,000 h of chemical-looping combustion operation - Where are we and where do we want to go? International Journal of Greenhouse Gas Control, 88, 38–56.

Klemeš J.J. (Ed), 2013, Handbook of Process Integration (PI): Minimisation of Energy and Water Use, Waste and Emissions, Woodhead Publishing Limited, Cambridge, UK.

Mattisson T., Keller M., Linderholm C., Moldenhauer P., Rydén M., Leion H., Lyngfelt A., 2018, Chemical-looping technologies using circulating fluidized bed systems: Status of development, Fuel Processing Technology, 172, 1–12.

Osman M., Khana M.N., Zaabout A., Cloete S., Amini S., 2021, Review of pressurized chemical looping processes for power generation and chemical production with integrated CO_2 capture, Fuel Processing Tehnology, 214, 106684.

Yan Y., Wang K., Clough P.T., Anthony E.J., 2020, Developments in calcium/chemical looping and metal oxide redox cycles for high-temperature thermochemical energy storage: A review, Fuel Processing Technology, 199, 106280.

Wu S., Zhou C., Doroodchi E., Nellore R., Moghtaderi B., 2018, A review on high-temperature thermochemical energy storage based on metal oxides redox cycle, Energy Conversion and Management, 168, 421–453.