DYNAMIC OPTIMIZATION OF FIXED BED CHEMICAL-LOOPING COMBUSTION PROCESSES

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Abstract

The feasibility of incorporating chemical-looping combustion (CLC) into a combined cycle power plant is explored. We propose a model-based framework to optimally design the cycle strategy for a CLC system, composed of multiple fixed bed reactors. The CLC reactor system is optimally integrated with the downstream gas turbine of a combined cycle power plant, by solving a dynamic program to optimize the temperature profile of the heat removal step out of each reactor, with constraints on the system performance during reduction and oxidation. We demonstrate the feasibility of fixed bed CLC systems to achieve different exhaust temperatures, using synthetic Cu- and Ni-based oxygen carriers. The optimal operating strategy is scaled-up to a system of fixed bed reactors operating in parallel. We show that through process optimization, the batch-operation of fixed bed CLC reactors is void of significant exhaust gas temperature fluctuations and can reach high thermal efficiencies with in-situ CO₂ capture.

Keywords: *chemical-looping combustion, dynamic optimization, power plant, fixed bed reactor*

1. Introduction

The increasing concentration of CO₂ in the atmosphere is a major contributor to global climate change.¹ Carbon capture and sequestration (CCS) is a promising, short-term solution to control CO₂ emissions from fossil-fueled power generation, often with a high energy penalty.²⁻⁴ Chemical-looping combustion (CLC) is a promising option to reduce the cost of CO₂ capture from oxidation of hydrocarbon fuels, in a two-step process that produces a pure stream of CO₂, ready for compression and sequestration.^{3,5-9} In CLC, a solid oxygen carrier, in the form of metal oxides, is used to transfer oxygen from air to combust the fuel. Since the fuel is not mixed with air, separation of CO₂ is inherent to the process.

The main application of CLC will be in the power generation sector. Among the most energy efficient power cycles is the combined cycle power plant (CCPP), which is an arrangement of a gas turbine with a steam cycle. Combined cycles offer the advantage of high efficiencies, reduction in pollutant emissions, low capital and maintenance costs, and compatibility with natural gas and coal feedstocks.¹⁰⁻¹³ In the natural gas fired combined cycle (NGCC), clean natural gas is combusted with air at high temperature and pressure in a gas turbine, producing electricity. Waste heat from the exhaust is then recovered through generation of high pressure steam, which powers steam turbines to produce more electricity. The exhaust gas contains CO₂ and steam, diluted in N₂ from the combustion air. To separate the CO₂ from the N₂, solvent-based absorption methods are usually preferred and afterward, the CO₂ is cooled and compressed to supercritical conditions.^{13,14} Coal fired processes use the integrated gasification combined cycle (IGCC), wherein a synthesis gas mixture is produced through gasification of the

coal at high pressure with oxygen. After cleaning, the syngas is burned in the gas turbine and the exhaust gases are sent to the steam cycle. CO₂ removal from IGCC systems entails the addition of a shift converter unit (to convert the syngas into CO₂ and H₂) and/or a CO₂ separation and compression unit. The net power efficiency of conventional combined cycles without CO₂ capture is approximately 58%¹⁰ using natural gas and 40-42%^{12,13} using coal. Carbon capture by means of chemical absorption from the flue gases of the NGCC reduces the net plant efficiency and power output of the NGCC systems by about 10%.¹⁵ The efficiency of IGCC with pre-combustion decarbonization by physical absorption decreases the efficiency of the plant to 35%.¹⁶ To reduce the energy expenditure of the CO₂ capture step, CLC can be used in these combined cycle plants.⁸

One of the challenges in the commercialization of CLC technology is the integration of the CLC reactor with an existing power plant, from the process design perspective. The CLC unit can be integrated with a combined cycle by replacing the combustor of the gas turbine. In conventional syngas-fed and natural gas-fed gas turbines, the gas turbine pressure ratio is in the range of 10-20 with turbine inlet temperatures of 1100-1300°C.^{15,17,18} The thermal efficiency of the gas turbine increases with the inlet temperature and pressure,¹⁹ which also benefits the steam cycle because the gas exiting the gas turbine is at higher temperatures. Therefore, CLC needs to be operated at elevated pressures, if integrated in a combined cycle power plant. From the efficiency perspective, the pressure drop across the CLC reactor should be low ($\Delta P/P < 8\%$),²⁰ in order to conserve the energy spent in gas compression. In summary, high-pressure operation with low pressure drop is a requirement for high efficiency CLC integrated with a combined cycle.

The high-pressure requirement imposes constraints in the design and cycling sequence of CLC reactors. The most widely recognized design for CLC consists of interconnected fluidized bed reactors.^{8,21} In this configuration, the solid oxygen carrier is physically transported between the so-called air and fuel reactors. This concept was successfully demonstrated in different prototypes with various oxygen carriers at atmospheric pressure.^{22–30} The high-pressure fluidized bed concept is still under development,^{31–33} due to the technical difficulties in gas/solid separations and the inherent challenges in achieving stable circulation of solids. Additionally, a high temperature and high pressure solids filtering system is required to remove the fines that result from the unavoidable particle attrition in fluidized bed systems.³⁴ The presence of particles in the outlet stream can negatively impact the performance of the gas turbine, as well as damage the thermal-barrier coatings on the surfaces of the gas turbine.³⁵ Alternatively, the fixed bed reactor configuration appears as a more practical option to accomplish high-pressure CLC. This concept was studied in several works for power generation and hydrogen production.^{34,36–42} In the fixed bed design, the gas/solid separation problem is inherently avoided and no fines are sent to the gas turbine. The control and operation of fixed bed reactors under high-pressure operation is more straightforward than in the fluidized bed design. Due to its simplicity, the fixed bed design concept might serve well as an intermediate-scale technology deployment option for CLC.

In principle, the fixed bed CLC system is a batch process (**Figure 1**), that dynamically switches between consecutive reduction, oxidation, and heat removal phases. During the reduction phase, a hydrocarbon fuel is oxidized into CO₂ and steam, by reduction of the oxygen carrier.

The reactor is briefly purged with an inert gas and the gas flow is switched to air to commence the oxidation step. Regeneration of the oxygen carrier is exothermic and produces a hot gas stream, which can be converted to electricity in a combined cycle power plant. Typically, oxidation and heat removal occur in succession without change of input parameters. In this cyclic process, the conversion and temperature profiles of the previous cycle influence the performance of the next. This, in addition to the effect of temperature on the oxygen carrier reactivity, impacts the switching scheme of the CLC process.

Conventional approaches to optimization of power plants aim at increasing efficiency during full load and partial-load plant operation and determining procedures to reduce start-up time, while keeping mechanical and thermal stress under control.^{43–48} The aim of this work is to showcase a model-based approach to optimally design and control such a batch process for power generation applications. We explore high-pressure fixed bed CLC reactors as a case study for this approach, where the process is heavily constrained in terms of performance and heat management. First, we discuss the formulation of a dynamic optimization problem for this batch heat generation process. The conditions of the CLC reactor that allow for seamless integration with a combined cycle are expressed as process constraints within the optimization problem. Optimal cycle strategies for fixed bed CLC with methane and syngas are presented and compared against a baseline design. We assess the feasibility of batch CLC processes utilizing synthetic Cu and Ni oxygen carriers, due to the availability of their kinetic data at high-pressure and their intrinsic differences in melting points, both of which impact the CLC performance and the efficiency of the power plant. The CLC process is evaluated on the basis of

its compatibility with the combined cycle power plant, at different temperature set-points to feed the downstream gas turbine. Finally, the operation of a system of a series of fixed bed reactors working in parallel is calculated for a full-scale power plant.

Figure 1: Schematic of a cycle strategy for a fixed bed CLC reactor.

2. Problem formulation

2.1. Process description

The CLC cycle in a batch fixed bed reactor consists of reduction, oxidation, and heat removal steps. To control this transient switching, a practical approach is to use the temperature and gas selectivity measurements of the exhaust stream to decide when to alternate the gas flow,³⁷ as shown in **Figure 1**. **Figure 1** is not a real and complete controls diagram, but an illustration of a conceptual design strategy. In this strategy, the reduction cycle is stopped when: (a) fuel slip is detected or (b) the CO₂ capture efficiency is too low. Then the reactor switches to purging mode.

After a brief purge, the oxidation cycle is initiated by feeding air into the reactor. When the front of the heat generated by the exothermic oxidation reaction reaches the reactor exit, the temperature of the exhaust stream rises and the exhaust gas is sent to the gas turbine. This is the heat removal stage and proceeds until the exhaust temperature reaches a temperature that is too low for the gas turbine. Some of the heat generated in the oxidation step is left in the bed and produces a moderate-temperature gas that can be used for heat recovery within the plant. After this, the reactor is purged and the cycle returns to the reduction step.

Temperature fluctuations occur in the reactor exhaust stream during the transient heat removal stage, which can negatively impact the operation of a downstream gas turbine. In particular, changes in turbine temperature can lead to thermal/mechanical cycling stress and differential expansion between stationary and rotating parts.^{40,49} Both phenomena cause fatigue damage and reduce the lifetime of the turbine if they are not properly handled. Therefore, adequate heat management of the CLC reactor is needed for the gas turbine to operate efficiently and safely. In addition, it is best to maximize the solid conversion in the reduction and oxidation cycles to fully utilize the oxygen carrier, while maintaining high CO₂ capture efficiency. Due to these strict requirements and constraints, the design and operation of the batch CLC reactor is complex and requires a formal methodology that ensures system safety and reliability. In the following section, we propose a generic model-based formulation for the design and tuning of the switching strategy, with the objective of seamlessly integrating CLC into a combined cycle power plant.

2.2. Optimization problem formulation

The unit operations for the batch reactor are formulated as an optimal control problem, with the objective of maximizing the energy extracted from the CLC reactor to produce a gas steam suitable for power generation in the gas turbine. The control variables considered in this study are the flow rate and temperature of the feed air, time interval for the reduction, oxidation, and heat removal steps, and loading of the metal oxide in the oxygen carrier, listed in **Table 1**. Overall, this is a first-level exploratory work focused on the optimality of operation from the safety and turbine stability perspective. For a given reactor size and specific turbine inlet temperature, TIT , we explore the feasibility of operating a fixed bed CLC upstream a gas turbine, by manipulating all the controls available in **Table 1**. The composition of the feed gas is fixed to fuel during reduction (100% CH_4 or a syngas mixture), N_2 during purge and air during oxidation and heat removal. The control profile for the feed gas is modeled with piecewise constant functions, represented as $\mathbf{u}(\tau_i) = \mathbf{u}_i$, where $\mathbf{u}$ is the vector of temperature, flow, and composition of the gas stream and i is the index for the CLC step, *i.e.*, reduction, purge, oxidation, and heat removal. The duration for reduction, oxidation, and heat removal is τ_i and is considered as a control variable. The metal oxide content in the oxygen carrier, ω , is a time-invariant control variable, which can be tuned to achieve different exhaust temperatures during heat removal. The set of control variables is summarized in the design vector, ϕ , shown in Eq.(1), which is constrained by upper and lower limits permitted in the design space, Φ :

$$\boldsymbol{\varphi} = [\mathbf{u}_i, \tau_i, \omega] . \quad (1)$$

Table 1: Design variables in the dynamic operation of fixed bed CLC.

Design variables	Notation
Air feed rate	$\mathbf{u}_i$
Air temperature	
Reduction time interval	τ_i
Oxidation time interval	
Heat removal time interval	
Metal oxide content in oxygen carrier	ω

The objective of the presented problem is to increase the efficiency of the combined cycle by manipulating the design and operating variables of the fixed bed CLC reactor. Since the gas turbine contributes to over 60% of the power of a combined cycle power plant,²⁰ the goal of this work is to make the heat removal phase of the CLC reactor as long as possible, so that the gas turbine has the maximum thermal input. The objective function to be maximized is the time-integral of the temperature of the exhaust gas stream produced during heat removal, $T_{HR,out}(t)$. This can be interpreted as maximizing the time interval in which a high-temperature gas is generated for electricity production in the gas turbine. A normalization factor is used in the objective, $\alpha = \frac{1}{273.15}$. The temperature of the exhaust gas during the heat removal phase should be at or very close to a desired reference value of the turbine inlet temperature, TIT . To ensure that the TIT fluctuations are not significant, we impose an inequality path constraint on $T_{HR,out}(t)$ to not exceed $\pm 50^\circ\text{C}$ of the TIT set-point. In this work, we consider two TIT set-points for the optimization study. While the state-of-the-art heavy-duty gas turbines can handle TIT values up to 1400°C ,^{17,50,51} the CLC reactor can realistically operate at $800\text{-}1200^\circ\text{C}$, to prevent thermal damage of the oxygen carrier.⁵²⁻⁵⁵ The temperature of the reactor always needs to be maintained below the melting or sintering points of the oxygen carrier, T^{max} . An inequality

constraint is, thus, incorporated, where the temperature inside the reactor at any time and point must be less than 50°C below the melting point of the oxygen carrier, $T(t, z) \leq T^{max} - 50^\circ\text{C}$. The CLC reactor during reduction also needs to achieve an acceptable level of performance in terms of emissions control. We impose inequality constraints during the reduction cycle to ensure that the process always behaves within commonly acceptable standards of fuel conversion ($X_{fuel}(t) \geq 98\%$) and CO₂ selectivity ($S_{CO_2}(t) \geq 90\%$).^{13,16,56} The pressure drop across the reactor must be below 8% of the inlet pressure,⁵⁷ to avoid excess pressure losses $\left(\frac{\Delta P(t)}{P(t, z=0)} \leq 8\% \right)$. These process constraints reflect the basic requirements of the CLC reactor according to the literature. The complete formulation for the discussed optimization problem is thus:

$$\begin{aligned}
& \max_{\varphi \in \Phi} \int_{t_0}^{t_f} \alpha T_{HR,out}(t) dt \\
& \text{subject to:} \\
& \mathbf{f}(\dot{\mathbf{x}}(t), \mathbf{x}(t), \mathbf{u}(t), \boldsymbol{\theta}, t) = 0, \\
& \mathbf{x}^{\min} \leq \mathbf{x}(t) \leq \mathbf{x}^{\max}, \\
& \mathbf{u}_i^{\min} \leq \mathbf{u}_i \leq \mathbf{u}_i^{\max}, \quad i = 1, \dots, N_u \\
& \tau_i^{\min} \leq \tau_i \leq \tau_i^{\max}, \quad i = 1, \dots, N_u \\
& \omega^{\min} \leq \omega \leq \omega^{\max} \\
& T_{HR,out}(t) = \mathbf{h}(\mathbf{x}(t)), \quad \forall t \in [t_0, t_f], \\
& TIT - 50^\circ\text{C} \leq T_{HR,out} \leq TIT + 50^\circ\text{C}, \quad \forall t \in [t_0, t_f], \\
& T(t, z) + 50^\circ\text{C} \leq T^{\max}, \quad \forall t \in [t_0, t_f], \forall z \in [0, L], \\
& S_{CO_2}(t) \geq 90\%, \quad \forall t \in [t_0, t_f], \\
& X_{fuel}(t) \geq 98\%, \quad \forall t \in [t_0, t_f], \\
& \Delta P(t) / P(t, z=0) \leq 8\%, \quad \forall t \in [t_0, t_f],
\end{aligned} \tag{2}$$

where $X_{fuel}(t)$ and $S_{CO_2}(t)$ are the time-integrated fuel conversion and CO₂ selectivity, respectively as:

$$S_{CO_2}(t) = \int_{t_0}^t F(t, z=L, CO_2) dt \bigg/ \int_{t_0}^t (F(t, z=0, i) + F(t, z=0, CO_2)) dt, \quad i = \text{CH}_4 \text{ or CO} \tag{3}$$

$$X_{fuel}(t) = 1 - \int_{t_0}^t F(t, z=L, i) dt \bigg/ \int_{t_0}^t F(t, z=0, i) dt, \quad i = \text{CH}_4, \text{H}_2, \text{or CO} \tag{4}$$

As shown in Eq.(2), the batch reactor is represented by a system of differential and algebraic equations, $\mathbf{f}$, where $\mathbf{x}(t)$ is the vector of state variables (*i.e.*, mass, temperature, and pressure), and $\boldsymbol{\theta}$ is the system parameters, including the kinetic constants, describing the reactivity of the oxygen carriers. The temperature measurement $T_{HR,out}(t)$ is a function $\mathbf{h}$ of the state variables, $\mathbf{x}(t)$.

The underlying physics of the fixed bed CLC reactor is described by a heterogeneous reactor model presented previously.^{58,59} The model incorporates the conservation equations of mass, energy, and momentum through the axial space of the fixed bed reactor. The dusty-gas diffusion model is used to capture the concentrated gas flows and internal diffusion limitations through oxygen carrier particles. External mass and heat transfer resistance is considered at the particle surface. In previous work, Zhou et al.^{60–62} proposed a set of reaction kinetics for Cu- and Ni-based oxygen carriers, capable of predicting atmospheric fixed bed experiments reported in the open literature. We utilized optimal experimental design methods to statistically verify the CLC kinetic models and in turn, maximize the fidelity of the kinetic model to predict data outside of its design space.^{63,64} We performed high-pressure fixed bed experiments with Cu- and Ni-based oxygen carriers and matched the data using an empirical pressure correlation⁶⁵ and the optimized kinetic models derived at atmospheric pressure.⁶⁶ Thus, we can conclude that the reactor and kinetic models used here are realistic and accurate enough for depiction of the large-scale fixed bed systems analyzed here. The mathematical model was developed and solved using the commercial software package gPROMS.⁶⁷ The complete mathematical model

including the mass, energy and momentum balances, as well as the reaction kinetics and constants used in this work, are provided in the **Supplementary Information**.

The partial differential equations of the dynamic model were solved by discretizing the spatial axial and radial coordinates using finite differences. The resulting set of differential and algebraic equations was solved with the non-linear solver, DASOLV.⁶⁸ The control vector parameterization technique with single-shooting algorithm (CVP_SS) was used to solve the nonlinear optimization program. The control variables were discretized as piecewise constant and/or linear functions of time over a finite set of time intervals. The control vector parameterization method is better suited for the problem presented in this paper (over collocation methods, for instance) because only the control trajectory is parameterized, which reduces the optimization problem of this large-scale system of equations to a manageable parameter space.⁴⁸

3. Dynamic simulation of a nominal design

In this section, we describe the performance of a reactor with a nominal design, in order to establish a basis of comparison with the optimal solution determined from Eq.(2). For simplicity, we utilize the reactor design and operating conditions proposed by Spallina et al.⁵⁷ for CLC of syngas with an ilmenite oxygen carrier. The goal of this section is not to optimize the reactor design, but to illustrate a baseline performance with process conditions proposed in the literature for a large-scale fixed bed process. It is possible that this reactor design is sub-optimal for CLC with CuO and NiO oxygen carriers, but the focus here is on the optimality of operation and not the reactor design.

The design variables that are consistent with Spallina et al.⁵⁷ are the following: reactor size, operating pressure, flow rate and composition of the syngas fuel, air, and purge streams, and oxygen carrier particle size and porosity. Spallina et al.⁵⁷ used different preheat temperatures for the air, purge, and fuel gases. For simplicity, all gases are preheated to one average temperature of 450°C. We expanded the scope of their study to consider CLC with CH₄, for which we used a higher air temperature (600°C) and decreased the fuel flow rate to 10% of the syngas flow rate. The higher air temperature was chosen in order for the reduction cycle to commence over a hotter bed, to favor complete conversion of the CH₄ to CO₂ and H₂O. The methane flow rate was chosen based on the work of Noorman et al.,⁶⁹ who investigated various reducing fuels over similar reactor configurations. The metal oxide loading for both oxygen carriers were set to 20 wt.% (**Table 2**) as a starting point for this analysis.

Table 2. Properties of the oxygen carriers simulated in this work.

Oxygen carrier		
Active metal	CuO	NiO
Support	SiO ₂	α-Al ₂ O ₃
Weight fraction of metal oxide (wt.%)	20	20
Solid porosity	0.40	0.40
Particle size (mm)	5	5
Melting point of reduced metal (°C)	1085	1455

Tables 2-3 summarize the nominal design parameters and operating variables used to establish a baseline performance of the fixed bed processes. The performance of the fixed bed reactor of **Table 3**, with the feedback control strategy discussed in **Section 2.1** is shown in **Figures 2-5**, presented in terms of the bed temperature *vs.* bed height, and exhaust gas temperature and composition *vs.* cycle time. The process decisions during the simulation sequence were to: (1)

feed fuel (syngas or CH₄) until $X_{fuel}(t) < 98\%$ or $S_{CO_2}(t) < 90\%$; (2) switch to inert gas and purge the system for 300s, (3) feed air to oxidize the solids and produce a suitable gas for power generation, and (4) switch to purging mode when the reactor exhaust reaches the temperature set-point ($T_{sp}=800^{\circ}\text{C}$ for syngas-fed and $T_{sp}=900^{\circ}\text{C}$ for methane-fed processes). These steps are repeated for multiple redox cycles to achieve a cyclic steady-state, where the temperature and conversion profiles of one cycle are identical to the next. The results of **Figures 2-5** are presented for this cyclic steady-state condition, usually reached within 2-3 cycles. The heat removal duration, feeding the gas turbine (HR-1), was selected over the time interval in which the exhaust temperature was within 50°C of the turbine inlet temperature (TIT). For simplicity, we set the TIT set-point to 1000°C for both oxygen carriers. In the later sections, we incorporate different TIT set-points in the constraint of the optimization problem. As shown in **Figures 2-5**, the maximum temperature reached in the fixed bed process is dependent on the oxygen carrier material and fuel type. In **Figure 3**, the system overshoots the set-point and in **Figures 2, 4**, and **5**, the system undershoots. The results shown here are used to illustrate the performance of a fixed bed process under a nominal design and operating conditions.

Table 3. Design and operating conditions of the studied fixed bed reactor configuration (adapted from Spallina et al,⁵⁷ suited for reduction by syngas-fuel and methane-fuel).

	Syngas-fuel	Methane-fuel
Reactor configuration		
Length (m)	11	11
Diameter (m)	5.5	5.5
Gas streams		
<i>Air (Oxidation + Heat Removal)</i>		
Mass flow (kg/s)	178	178
Pressure (bar)	17	17
Inlet Temperature ($^{\circ}\text{C}$)	450	600

Composition (%.vol)	0.92 Ar; 0.03 CO ₂ ; 1.03 H ₂ O; 77.28 N ₂ ; 20.73 O ₂	0.92 Ar; 0.03 CO ₂ ; 1.03 H ₂ O; 77.28 N ₂ ; 20.73 O ₂
<i>N₂ (Purge)</i>		
Mass flow (kg/s)	577.5	577.5
Pressure (bar)	17	17
Inlet Temperature (°C)	450	450
Composition (%.vol)	1.016 Ar; 0.04 CO ₂ ; 1.31 H ₂ O; 97.5 N ₂	1.016 Ar; 0.04 CO ₂ ; 1.31 H ₂ O; 97.5 N ₂
<i>Fuel (Reduction)</i>		
Mass flow (kg/s)	152	15
Pressure (bar)	17	17
Inlet Temperature (°C)	450	450
Composition (%.vol)	1 Ar; 33.6 CO; 34 CO ₂ ; 13.8 H ₂ ; 16.4 H ₂ O; 1.3 N ₂	100% CH ₄

Figure 2 presents the complete CLC sequence with the CuO oxygen carrier and syngas fuel. When oxidation is started, energy is released from the exothermic reactions and the bed temperature increases. As air is continually fed to the reactor, the heat front travels axially through the bed and the cycle switches to heat removal when the exhaust temperature is high enough to feed a downstream gas turbine (**Figures 2(a)** and **2(b)**). The progression of the heat front can be seen in **Figure 2(a)**, by the location of the high temperature zones at the end of oxidation and at the end of heat removal. The exhaust temperature during the heat removal phase is relatively constant and flat during HR-1 and then steadily decreases during HR-2 (**Figure 2(b)**), because of the temperature profile inside the bed produced from the oxidation phase (**Figure 2(a)**). The exit gas concentration during oxidation is predominantly composed of N₂ with some unreacted O₂ (**Figure 2(c)**). The bed is completely regenerated at the end of the oxidation cycle, as inlet feed concentrations of the air are detected at the reactor exit (**Figure 2(c)**). After a brief purge, the cycle switches to reduction. The reduction of CuO by syngas is exothermic and increases the internal bed temperature, which is shown in **Figure 2(a)** by comparing the temperature distribution at the end of heat removal (HR-2) with the distribution

at the end of reduction. The exhaust temperature during reduction first decreases (**Figure 2(b)**), because the residual low-temperature heat from the previous heat removal step (**Figure 2(a)**) is being pushed out of the reactor. When the heat front from the reduction reactions reaches the exit of the reactor, the exhaust temperature increases (**Figure 2(b)**). The gas composition of the reduction exhaust is mostly H_2O and CO_2 , with some minor slip of unconverted fuel occurring at the end of the reduction (**Figure 2(c)**).

Figure 2: Profiles of the (a) internal solid temperature, (b) exit gas temperature and (c) exit gas composition of the CLC reactor with the CuO oxygen carrier and syngas fuel. The reactor design is reported in **Table 3**.

The dynamic behavior of the fixed bed reactor with the NiO oxygen carrier and syngas fuel is presented in **Figure 3**. In this process, the reduction step is less exothermic than with the CuO oxygen carrier, indicated by the lower temperatures inside the reactor at the end of reduction (**Figure 3(a)**). The exhaust gas during reduction, thus, exhibits smaller temperature fluctuations (**Figure 3(b)**) as compared to **Figure 2(b)**. During the reduction phase, complete conversion of the fuel is achieved with minor release of H_2 and CO (**Figure 3(c)**). After oxidation, the bed

temperature is elevated (**Figure 3(a)**) and a high-temperature gas is produced for heat removal (**Figure 3(b)**). The main heat removal phase is relatively longer in this process (**Figure 3(b)**), as compared to **Figure 2(b)**). This can be explained by the greater uniformity in bed temperature at the end of oxidation (**Figure 3(a)**), allowing for the heat removal stage to the gas turbine (HR-1) to proceed for longer times (**Figure 3(b)**).

Figure 3: Profiles of the (a) internal solid temperature, (b) exit gas temperature and (c) exit gas composition of the CLC reactor with the NiO oxygen carrier and syngas fuel. The reactor design is reported in **Table 3**.

The performance of the fixed bed reactor under CuO reduction with methane is shown in **Figure 4**. When CH₄ is sent to the reactor, the entrance of the reactor is the first to be reduced. The reduced bed gets cooled down (**Figure 4(a)**) due to the endothermicity of the reduction reactions. The reduction of CuO by CH₄ produces partial combustion products (H₂ and CO),⁶² which travel through the bed and get oxidized by the fresh oxygen carrier, liberating heat. Thus, the interior and exit regions of the reactor at the end of the reduction are warmer than at the end of heat removal, shown in **Figure 4(a)**. The temperature of the exhaust gas first decreases and

then increases during reduction (**Figure 4(b)**). The temperature decrease (**Figure 4(b)**) is caused from the low-temperature heat front leaving the reactor and simultaneous cooling from the reduction reactions. Midway through reduction, temperature of the exhaust gas rises (**Figure 4(b)**) because the reactor gets warmed up from the oxidation of H_2 and CO inside the bed. At the exit of the reactor, only CO_2 and H_2O are observed during reduction (**Figure 4(c)**), indicating complete conversion of the fuel. The subsequent oxidation and heat removal stages follow similar patterns as described in **Figures 2-3**. At the end of oxidation, a high-temperature zone is formed inside the bed (**Figure 4(a)**), suitable for heat removal. The bed temperature near the reactor entrance slightly drops below the temperature of the inlet air at the end of oxidation (**Figure 4(a)**). The entrance was not fully reduced because of the slower reduction kinetics of CuO by CH_4 as opposed to syngas and the cooling effect of purge prior to reduction. Thus, less heat was liberated during oxidation and the feed of warm air slowly increases the temperature of the reactor entrance.

Figure 4: Profiles of the (a) internal solid temperature, (b) exit gas temperature and (c) exit gas composition of the CLC reactor with the CuO oxygen carrier and methane fuel. The reactor design is reported in **Table 3**.

Figure 5 presents the dynamic performance of the NiO oxygen carrier with methane fuel. Similar to **Figure 4(a)**, the reduction of the NiO by CH₄ is endothermic and decreases the temperature of the reactor (**Figure 5(a)**) as the conversion front moves through the bed. As a result, the temperature of the exhaust gas stream decreases over time during reduction and subsequent purge (**Figure 5(b)**). The effluents of the reduction step are mostly CO₂ and H₂O, with a small amount of fuel slip occurring at the end of reduction (**Figure 5(c)**). During the oxidation cycle, heat is liberated by the exothermic reactions and a high-temperature zone is formed inside the reactor bed (**Figure 5(a)**). At the end of oxidation, the oxygen carrier is regenerated, indicated by the unconverted air leaving the reactor (**Figure 5(c)**), and the temperature of the exhaust gas is within 50°C of the *TIT* set-point (**Figure 5(b)**). The exhaust gas during heat removal exhibits a high temperature drop, restricting energy extraction to the gas turbine to ~50% of the total heat removal time **Figure 5(b)**.

Figure 5: Profiles of the (a) internal solid temperature, (b) exit gas temperature, and (c) exit gas composition of the CLC reactor with the NiO oxygen carrier and methane fuel. The reactor design is reported in **Table 3**.

Figures 2-5 are representative of cycle strategies to conduct CLC in a large-scale fixed bed reactor. The issue with these nominal designs is the exit gas temperature and its fluctuations during the heat removal phase, which is not suitable for a downstream gas turbine. To find the optimal heat management strategy, we solve the optimization problem of **Section 2.2** for the reactor configurations of **Table 3**.

4. Results and discussion

4.1. Optimal fixed bed operation for CLC

The challenge in solving the optimization problem formulated in **Section 2.2** is that the conversion and temperature profiles from the previous cycle impact the performance of the next cycles and it typically takes 2-3 cycles for the system to reach a cyclic steady-state condition after modifying the cycle strategy. Thus, the optimization procedure needs to be carried out for several redox cycles and the optimal cycle strategy should be extracted from the last cycle. In this analysis, we first initialize all state variables at the end of the heat removal phase of the nominal design point (shown in **Figures 2-5**) and perform the optimization procedure for 3 redox cycles. For each oxygen carrier, we consider two set-points for the turbine inlet temperature (*TIT*), being: 1100°C and 1000°C for NiO and 1000°C and 900°C for CuO. These reference values are exemplary of the existing, commercial gas turbines offered by Siemens^{70,71} and GE.⁷²⁻⁷⁴ As mentioned, smaller *TIT*s are required in CLC to protect the oxygen carrier from

sintering or agglomeration. The results of this optimization are presented in **Figures 6-7** for the CuO oxygen carrier and in **Figures 8-9** for the NiO oxygen carrier. **Figures 6-9** showcase the optimal fixed bed performance with the low *TIT* set-point and in **Figures SI.1-4** of the **Supplementary Information** we present the performance with the high *TIT*-set-point. For brevity, we will focus our discussion on **Figures 6-9**. The optimal operating strategies are presented in **Table 4**.

Table 4: Summary of the optimal operating strategy for the fixed bed processes with the NiO and CuO oxygen carriers over the reactor design of **Table 3**.

	CuO with syngas	CuO with CH ₄	NiO with syngas	NiO with CH ₄
<i>TIT</i> set-point (°C)	1000, 900	1000, 900	1100, 1000	1100, 1000
<i>Reduction (RED)</i>				
Cycle time (sec)	1612, 1549	830, 758	929, 764	633, 540
<i>Oxidation (OX)</i>				
Mass flow (kg/s)	142, 142	160, 160	160, 164	162, 167
Temperature (°C)	443, 456	610, 610	516, 516	650, 610
Cycle time (sec)	1553, 1359	1210, 1129	940, 799	941, 836
<i>Heat removal 1 (HR-1)</i>				
Mass flow (kg/s)	142, 142	160, 160	160, 160	160, 151
Temperature (°C)	443, 456	610, 610	516, 516	650, 610
Cycle time (sec)	5451, 5340	4500, 5236	2722, 2820	2445, 2434
<i>Heat removal 2 (HR-2)</i>				
Mass flow (kg/s)	178, 178	178, 178	178, N/A	N/A, N/A
Temperature (°C)	443, 456	610, 610	516, N/A	N/A, N/A
Cycle time (sec)	1540, 663	900, 758	378, N/A	N/A, N/A
ω (wt.%)	20.7, 17.6	21.5, 17.7	21.7, 20	23.2, 21.2

Figure 6 presents the optimal fixed bed performance with the Cu-based oxygen carrier and syngas fuel. With the *TIT* set-point of 900°C, the optimal configuration achieves a lower temperature rise during oxidation (**Figure 6(a)**), compared to the nominal design (**Figure 2(a)**). This was accomplished by using a reduced CuO loading. Shown in **Figure 6(b)**, the temperature of the gas steam starts below the *TIT* set-point at the start of heat removal to the gas turbine

(HR-1), rises above the set-point, and then drops below the set-point at the end of HR-1. On average, the exhaust temperature with the optimal operating conditions is above the *TIT* set-point but within the 50°C variation allowed by Eq.(2). In the nominal design, the exhaust temperature during heat removal is always below the *TIT* set-point (**Figure 2(b)**). Another benefit with the optimal cycle strategy is the longer time interval to remove heat to the gas turbine (HR-1), from comparing **Figure 6(b)** with **Figure 2(b)**. At the same time, the duration of HR-2 is decreased and a higher bed temperature is available for reduction (indicated in **Figures 6(a)** and **2(a)**). The gas profiles during the entire CLC cycle (**Figure 6(c)**) follow the same trend as in **Figure 2(c)**, whereby high fuel conversion is achieved during the reduction and oxidation cycles and unconverted air leaves the reactor during the heat removal cycles.

Figure 6: Profiles of the (a) internal solid temperature, (b) exit gas temperature, and (c) exit gas composition of the optimal operating strategy with the CuO oxygen carrier and syngas fuel, for a turbine inlet temperature (*TIT*) set-point of 900°C.

The optimal performance of the fixed bed reactor with the CuO oxygen carrier and methane is shown in **Figure 7**. Similar to the syngas-fed process, the optimizer reduced the CuO loading to achieve the turbine inlet temperature (*TIT*) set-point of 900°C. The air preheat temperature was increased, to improve the fuel conversion in the subsequent reduction step. The heat removal

stage proceeds for longer times in the optimal design (**Figures 7(b)** and **7(c)**) as compared to the nominal design (**Figures 4(b)** and **4(c)**). Additionally, the temperature fluctuations of the reduction exhaust are suppressed in the optimal configuration (**Figure 7(b)**), which is the result of the better temperature uniformity inside the bed at the end of heat removal (**Figure 7(a)**). The gas selectivity profile (**Figure 7(c)**) shows that during the reduction step, the methane feed is completely converted to CO_2 and H_2O (**Figure 7(c)**). During the oxidation cycle, no significant carbon oxides are released (**Figure 7(c)**), indicating that carbon formation was minor during the reduction step. A low-temperature zone is exhibited near the reactor entrance at the end of oxidation (**Figure 7(a)**), due to the locally incomplete conversion of solids in the previous reduction step, whereas the reactor entrance reaches the inlet gas temperature.

Figure 7: Profiles of the (a) internal solid temperature, (b) exit gas temperature, and (c) exit gas composition of the optimal operating strategy with the CuO oxygen carrier and methane fuel, for a turbine inlet temperature (*TIT*) set-point of 900°C.

Figure 8: Profiles of the (a) internal solid temperature, (b) exit gas temperature, and (c) exit gas composition of the optimal operating strategy with the NiO oxygen carrier and syngas fuel, for a turbine inlet temperature (T/T) set-point of 1000°C.

Figure 8 shows the optimal performance for the NiO oxygen carrier with syngas fuel. The heat removal stage to the gas turbine was maximized to an extent that it was no longer necessary to consider a secondary heat removal step (HR-2). Instead only a purging step is shown in **Figure 8(b)-(c)**, in between the HR-1 and reduction phase. Shown in **Figure 8(b)**, the gas temperature during heat removal satisfies the requirements for the gas turbine. This can increase the energy efficiency of the combined cycle power plant by sending more heat to the gas turbine. The reason for the better heat removal efficiency is the more uniform temperature distribution inside the reactor at the end of the oxidation step (**Figure 8(a)**), providing a flat temperature profile for the exhaust stream (**Figure 8(b)**). After heat removal, the bed temperatures are higher in the optimal design (**Figure 8(a)**) compared to the nominal design (**Figure 3(a)**). This provides more heat for the reduction step and improves the conversion of the bed. The changes in the reduction cycle between the optimal and nominal designs can be seen by the higher temperature of the exhaust gas (**Figures 8(b)** and **3(b)**) and that of the solids at the end of the

reduction step (**Figures 8(a)** and **3(a)**). The gas selectivity during reduction (**Figure 8(c)**) follows the same behavior as the nominal design (**Figure 3(c)**), satisfying the constraints of Eq.(2).

Figure 9: Profiles of the (a) internal solid temperature, (b) exit gas temperature, and (c) exit gas composition of the optimal operating strategy with the NiO oxygen carrier and methane fuel, for a turbine inlet temperature (*TIT*) set-point of 1000°C.

For the reduction of NiO by methane, the optimal cycle configuration maximizes the heat removal step to the gas turbine and eliminates the HR-2 step entirely, as shown in **Figure 9**. The gas temperature during the heat removal step (**Figure 9(b)**) is on average higher than the turbine inlet temperature (*TIT*) set-point of 1000°C. This is mainly due to increasing the NiO loading, which favors a higher temperature rise inside the reactor after oxidation (**Figure 9(a)**). The reduction reaction for the NiO-CH₄ is highly endothermic and the kinetics is sensitive to the reaction temperature. Thus, the optimizer switches to reduction at a higher bed temperature (**Figure 9(a)**), compared to the nominal design (**Figure 5(a)**). More of the bed is able to be reduced and the gas selectivity (**Figure 9(c)**) indicates that the methane feed is fully oxidized. The reduction gas stream leaves the reactor at higher temperatures (**Figure 9(b)**) compared to the nominal design (**Figure 5(b)**).

4.2. Comparison of the cycle strategies

We define three metrics to calculate the heat removal efficiency achieved with the optimal and nominal cycle strategies. The energy efficiency of the heat removal step, η_{HR} , was expressed as a ratio of the enthalpy of the high temperature gas stream for the gas turbine to the total enthalpy of one complete cycle:

$$\eta_{HR} = \frac{\int_{t_0=0}^{\tau_{HR1}} (\dot{m} \cdot h)|_{t,z=L} - (\dot{m} \cdot h)|_{t,z=0} dt}{\int_{t_0=0}^{\tau_{cycle}} (\dot{m} \cdot h)|_{t,z=L} - (\dot{m} \cdot h)|_{t,z=0} dt}, \quad (5)$$

where $\dot{m}$ and h are the time- and space-dependent mass flow rates and enthalpy of the gas stream, τ_{HR1} is the time interval for the heat removal step to produce electricity in the gas turbine, and τ_{cycle} is the time interval for one complete redox cycle. The second metric used to evaluate the performance of CLC was the standard deviation of the exit gas temperature during the heat removal phase to the gas turbine, σ_{HR} . This performance evaluation quantifies the degree of temperature fluctuations experienced at the inlet of the gas turbine. The third metric was the fraction of time the process is in the main heat removal step (HR-1):

$$\chi_{HR} = \tau_{HR1} / \tau_{cycle}. \quad (6)$$

Table 5: Heat removal coefficients computed for the optimal cycle strategies of **Figures 6-9** and for the nominal operation of **Figures 2-5**.

Case study		η_{HR}	σ_{HR} (°C)	χ_{HR}
CuO with syngas	Optimal design ($TIT=1000^\circ\text{C}$)	6.30E-01	2.27E+01	5.07E-01
	Optimal design ($TIT=900^\circ\text{C}$)	6.28E-01	1.72E+01	5.61E-01
	Nominal design ($TIT=1000^\circ\text{C}$)	5.09E-01	1.15E+01	4.11E-01
NiO with syngas	Optimal design ($TIT=1100^\circ\text{C}$)	7.82E-01	1.88E+01	4.62E-01

	Optimal design ($TIT=1000^{\circ}\text{C}$)	8.36E-01	1.89E+01	5.66E-01
	Nominal design ($TIT=1000^{\circ}\text{C}$)	6.34E-01	2.05E+01	4.37E-01
CuO with CH₄	Optimal ($TIT=1000^{\circ}\text{C}$)	7.27E-01	1.86E+01	5.60E-01
	Optimal ($TIT=900^{\circ}\text{C}$)	7.12E-01	9.76E+00	5.46E-01
	Nominal design ($TIT=1000^{\circ}\text{C}$)	5.88E-01	1.02E+01	4.94E-01
NiO with CH₄	Optimal ($TIT=1100^{\circ}\text{C}$)	8.25E-01	2.46E+01	4.43E-01
	Optimal ($TIT=1000^{\circ}\text{C}$)	8.86E-01	2.02E+01	5.50E-01
	Nominal design ($TIT=1000^{\circ}\text{C}$)	4.82E-01	7.62E+00	2.85E-01

Table 5 summarizes the efficiencies calculated for the optimal case studies of **Figures 6-9** and **Figures SI.1-SI.4** of the **Supplementary Information**. For comparison, we also report η_{HR} , σ_{HR} , and χ_{HR} for the nominal design (**Figures 2-5**). The CLC reactors with the optimal cycle strategies have higher values of η_{HR} for all the studied oxygen carriers, fuel types, and turbine inlet temperatures, indicating that more of the heat from the CLC reactions can be efficiently converted into electricity. The actual efficiency of the process can be higher because the remaining heat will be recovered in the steam cycle, but this was not considered in the present study. The standard deviation of the heat removal gas, σ_{HR} , is higher in the optimal designs. This can be interpreted as consequence of removing more heat to the gas turbine. Nonetheless, the maximum temperature change of the exhaust gas during the heat removal phase is within the constraints of the problem. For a process to have smaller temperature fluctuations, the corresponding constraint can be adjusted to be tighter in the optimization problem. To maximize the energy efficiency of the gas turbine, the duration of the heat removal phase of the reactor was increased. Shown in **Table 5**, higher values of χ_{HR} were obtained for the optimized cases. Overall, dynamic optimization of the cyclic fixed bed operation increased the energy efficiency of the reactor while satisfying operating constraints.

A critical design variable that dictates the temperature rise during oxidation is metal loading in the oxygen carrier.³⁶ High metal loadings are desired for better bed utilization and process capacity. However, the process is also heavily constrained by the maximum temperature that can occur inside the reactor at any point and time. Oxygen carriers that have high carrying capacity and high oxidation enthalpy, such as NiO and CuO, are limited in the amount of active metal that they can use without undesirable hot spots.³⁴ The use of large particles can actually lower the extrema of the temperature fluctuations, by decreasing the reaction rates due to the intraparticle diffusion resistance.^{58,59} In this analysis, we found that as the *TIT* set-point increases, the maximum allowed metal oxide content increases (**Table 4**). To reach the same *TIT* set-point, a higher loading of CuO was needed as compared to NiO because of the higher heat of reaction of Ni (**Table 4**). There was also an effect of the fuel type on the optimal metal loading, for the same *TIT* values and materials. We found that CLC with methane can operate at higher loadings of CuO and NiO than CLC with syngas (**Table 4**), which can be the result of a higher diffusion resistance associated with CH₄ oxidation reactions and their slower kinetics.

In addition to optimizing the *TIT* value, the impact of the heat removal phase on the overall process efficiency is also a function of cycle duration of each CLC step. During heat removal, the total enthalpy of gas sent to the gas turbine can be increased by converting more of the oxygen carrier in the preceding reduction cycle. Hence, the exothermic reaction rate is higher and more heat is transferred to the heat removal gas. As discussed previously, the reduction cycle is highly constrained by the requirements in CO₂ capture efficiency and fuel conversion. If the reduction period continues for too long, solid carbon accumulates over the oxygen carrier,

as shown in the work of Zhou et al.⁷⁵ and Nordness et al.⁷⁶ Combustion of the solid carbon in the subsequent oxidation step produces temperature gradients inside the bed (for example, **Figure 2(a)**), resulting in unfavorable temperature fluctuations in the exhaust stream. The optimal cycle configuration shortens the secondary heat removal phase (HR-2) and manipulates the air temperature, so that reduction step occurs over a slightly hotter bed and a higher conversion can be obtained. It strikes a balance between the endothermicity and exothermicity of the CLC reactions to maximize the heat removal. By solving the dynamic optimization problem for the fixed bed CLC operation, we can find the optimal flow conditions and cycle times that maximize temperature uniformity, while maintaining high fuel combustion efficiency. The results show that despite the inherent reactor dynamics, the fixed bed system is a promising option for power generation in gas turbine-based power cycles.

4.3. Dynamics of the CLC reactor network

The next step of the analysis is to illustrate the scale-up of the CLC reactors for integration with a power plant operating in continuous mode. We are interested in exploring how the dynamics of the each reactor will affect the downstream power plant components. We followed the procedure by Spallina et al.⁵⁷ to devise an operation strategy for a series of fixed bed reactors operated in parallel. According to Spallina et al.,⁵⁷ the sequence is based on running the reactors with a phase displacement, ζ , equaling 1/3 of the time to complete the reduction step. The total number of reactors for the system is calculated from τ_{cycle} / ζ , to provide a constant input of fuel to the CLC reactor network. The performance of each reactor is based on the numerical results described in the preceding sections. The gas streams are mixed downstream of the reactors,

assuming ideal gas behavior, into combined streams of $\text{CO}_2/\text{H}_2\text{O}$ from reduction, N_2/O_2 from oxidation, and air from heat removal. These streams define the inputs to the power plant components, downstream of the CLC block.

Figure 10: Gas temperature of the mixed gas streams leaving the system of fixed bed reactors for the (a) CuO process with syngas fuel and (b) NiO process with methane fuel.

We calculated a sequence of operation for the reactor systems with CuO and NiO oxygen carriers and syngas and methane reducing fuels and evaluated the behavior of the mixed streams leaving the reactor system. For brevity, we present the results for two dissimilar process operations: the CuO reactor with syngas fuel at the *TIT* set-point of 900°C (**Figure 10(a)**) and the NiO reactor with methane fuel at the *TIT* set-point of 1000°C (**Figure 10(b)**). The performance of the reactors of **Figure 10** is evaluated over their optimal cycle strategies. As shown, the system generates a time-varying temperature profile for the mixed gas streams, as a result of the

dynamic operation of each fixed bed reactor. The gas turbine receives a high-temperature gas that has practically no temperature fluctuations (**Figures 10(a)** and **10(b)**). The temperature fluctuations of the other gas streams are $\sim 50^{\circ}\text{C}$ or less. This illustrates that even though the temperature change experienced in each reactor is severe (around 500°C), running multiple reactors in parallel helps to equalize the temperature fluctuations so the power plant sees a more stable stream input. The extent of gas temperature fluctuations to the steam turbine can be reduced by use of an accumulator tank downstream the reactors to further mix the gases for a more uniform temperature profile.

To assess the feasibility of the fixed bed system, we discuss possible heat recovery opportunities for the lower-quality heat streams downstream the CLC reactors. As mentioned by Hamers et al.,³⁸ preheating the syngas fuel before feeding the CLC reactors can be performed by cooling the $\text{CO}_2/\text{H}_2\text{O}$ stream, which leaves the reactor at higher temperatures and mass flow rates compared to the inlet syngas. The depleted air stream produced from oxidation can be used to supplement the air stream used for heat removal to the gas turbine.²⁰ The temperature of the gas turbine exhaust is approximately $500\text{--}600^{\circ}\text{C}$,⁷⁴ which provides the temperature differential to preheat the air stream, leaving the compressor at 450°C ,²⁰ before feeding the CLC reactors. To meet higher preheat temperature for the air, such as that shown in **Figure 10(b)**, the process can utilize the higher temperature gas streams, such as the reduction exhaust and a portion of the heat removal gas, noting that this would reduce the process efficiency. Preheating the inert gas for the purging steps is not expected to be a problematic, because the N_2 is recycled through the system and can be used to preheat itself. From a qualitative point of view, the fixed bed reactor

system optimized in this work shows promise for integrating into a combined cycle power plant. In a subsequent work we demonstrate the application of this optimization-based approach to advanced fixed bed reactor concepts of CLC systems,⁷⁷ as well as integrated chemical-looping combined plant optimization.⁷⁸

5. Conclusions

This work explored the optimality in integration of high-pressure fixed bed CLC reactors with combined cycle systems for power generation. One of most challenging aspects of the fixed bed process is the dynamic cycling between redox reactions and the resulting temperature fluctuations. This work formulated and solved a dynamic optimization problem to find operation strategies that enable the integration of the batch and transient operating profiles of fixed bed CLC reactors with the requirements for constancy and disturbance rejection of gas turbines. The results of this approach showed that fixed bed CLC reactors can provide a stable, high-temperature and high-pressure gas that is suitable for a downstream gas turbine, while accomplishing performance constraints in the reduction and oxidation cycles. The study focused on two synthetic oxygen carriers, two different gaseous fuels, and two set-points for the turbine inlet temperature. At the optimal conditions, the fixed bed reactor operates in its heat removal stage with a relatively flat exhaust gas temperature profile consistent with the requirements of the gas turbine of a combined cycle power plant. The oxygen carrier conversion during the reduction cycle was maximized, in order to generate a high-temperature gas stream to feed the gas turbine for longer periods. Optimization of the cycle strategy allowed for the fixed bed process to reach higher energy efficiencies than a baseline design. We extended the analysis to consider a system of reactors for an integrated large-scale power plant. The combination of multiple reactors decreased the temperature fluctuations of the gas streams sent to the power plant units. The drawbacks of this process are the high temperature variations inside the CLC bed between the redox cycles, the dynamic switching of reactors to achieve

continuous operation for the power plant, and the corresponding need for high-temperature valves.

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7. Nomenclature

Acronyms

<i>CCPP</i>	Combined cycle power plant
<i>CCS</i>	Carbon capture and sequestration
<i>CLC</i>	Chemical-looping combustion
<i>GT</i>	Gas turbine
<i>HR-1</i>	Heat removal to the gas turbine
<i>HR-2</i>	Heat removal to the steam turbine
<i>IGCC</i>	Integrated gasification combined cycle
<i>OX</i>	Oxidation
<i>PU</i>	Purge
<i>RED</i>	Reduction
<i>ST</i>	Steam turbine
<i>TIT</i>	Turbine inlet temperature

General symbols

F	Molar flow of gas, mol/s
h	Enthalpy of gas, J/kg
L	Bed height, m
$\dot{m}$	Mass flow rate of gas, kg/s
N_u	Number of time-varying controls
P	Total pressure, bar
S_{CO_2}	CO ₂ capture efficiency
T	Temperature, °C
T^{max}	Maximum temperature, °C
$T_{HR,out}$	Temperature of exhaust gas during heat removal (HR-1)
T_{sp}	Temperature set-point, °C
t	Time, sec
$\mathbf{u}_i$	Vector of time-varying controls
$\mathbf{u}_i^{max}$	Upper bound for the control variables
$\mathbf{u}_i^{min}$	Lower bound for the control variables
X_{fuel}	Fuel conversion
$\mathbf{x}$	Vector of state variables
$\mathbf{x}^{max}$	Upper bound for the state variables
$\mathbf{x}^{min}$	Lower bound for the state variables
$\dot{\mathbf{x}}$	Vector of derivatives of state variables
z	Axial position, m

Greek letters

α	Temperature normalization factor
ζ	Phase displacement
θ	System parameters

σ_{HR}	Standard deviation of the exit gas temperature during HR-1
τ_{cycle}	Time interval for one complete redox cycle
τ_{HR1}	Time interval for the HR-1 cycle
τ_i	Time intervals for the i -th CLC step
τ_i^{max}	Upper bound for the time intervals for the i -th CLC step
τ_i^{min}	Lower bound for the time intervals for the i -th CLC step
Φ	Design space
ϕ	Design vector
χ_{HR}	Fraction of time the process is in HR-1
ω	Weight fraction of metal oxide content
ω^{max}	Upper bound for the metal oxide content
ω^{min}	Lower bound for the metal oxide content

8. References

- (1) Carbon Dioxide Capture and Storage, A Special Report of Working Group III of the Intergovernmental Panel on Climate Change. *IPCC Spec. Rep.* **2005**.
- (2) Mondal, M. K.; Balsora, H. K.; Varshney, P. Progress and Trends in CO₂ Capture/separation Technologies: A Review. *Energy* **2012**, *46* (1), 431.
- (3) Boot-Handford, M. E.; Abanades, J. C.; Anthony, E. J.; Blunt, M. J.; Brandani, S.; Mac Dowell, N.; Fernández, J. R.; Ferrari, M.-C.; Gross, R.; Hallett, J. P.; et al. Carbon Capture and Storage Update. *Energy Environ. Sci.* **2014**, *7* (1), 130.
- (4) Jenni, K. E.; Baker, E. D.; Nemet, G. F. Expert Elicitations of Energy Penalties for Carbon Capture Technologies. *Int. J. Greenh. Gas Control* **2013**, *12*, 136.
- (5) Ishida, M.; Zheng, D.; Akehata, T. Evaluation of a Chemical-Looping-Combustion Power-Generation System by Graphic Exergy Analysis. *Energy* **1987**, *12* (2), 147.
- (6) IPCC. *IPCC Special Report on Carbon Dioxide Capture and Storage*; Cambridge University Press: Cambridge, UK, 2005.
- (7) Kerr, H. R. Capture and Separation Technologies Gaps and Priority Research Needs. *Carbon Dioxide Capture for Storage in Deep Geologic Formations - Results from the CO₂ Capture Project*, 2005, *1*, 655–660.
- (8) Adanez, J.; Abad, A.; Garcia-Labiano, F.; Gayan, P.; De Diego, L. F. Progress in Chemical-Looping Combustion and Reforming Technologies. *Prog. Energy Combust. Sci.* **2012**, *38* (2), 215.
- (9) Brandvoll, O.; Bolland, O. Inherent CO₂ Capture Using Chemical Looping Combustion in a Natural Gas Fired Power Cycle. *J. Eng. Gas Turbines Power* **2004**, *126* (2), 316.
- (10) Franco, A.; Franco, A.; Casarosa, C.; Casarosa, C. On Some Perspectives for Increasing the Efficiency of Combined Cycle Power Plants. *Appl. Therm. Eng.* **2002**, *22*, 1501.
- (11) Heppenstall, T. Advanced Gas Turbine Cycles for Power Generation: A Critical Review. *Appl. Therm. Eng.* **1998**, *18*, 837.
- (12) Sargent & Lundy. *New Coal-Fired Power Plant Performance and Cost Estimates*; 2009.
- (13) Woods, M. C.; Capicotto, P. J.; Haslbeck, J. L.; Kuehn, N. J.; Matuszewski, M.; Pinkerton, L. L.; Rutkowski, M. D.; Schoff, R. L.; Vaysman, V.; DOE/NETL; et al. *Cost and Performance Baseline for Fossil Energy Plants. Volume 1: Bituminous Coal and Natural Gas to Electricity*; DOE/NETL, 2013; Vol. 1.
- (14) Adams II, T. A.; Barton, P. I. High-Efficiency Power Production from Natural Gas with Carbon Capture. *J. Power Sources* **2010**, *195* (7), 1971.
- (15) Chiesa, P.; Consonni, S. Natural Gas Fired Combined Cycles With Low CO₂ Emissions. *J. Eng. Gas Turbines Power* **2000**, *122*, 429.
- (16) Erlach, B.; Schmidt, M.; Tsatsaronis, G. Comparison of Carbon Capture IGCC with Pre-Combustion Decarbonisation and with Chemical-Looping Combustion. *Energy* **2011**, *36* (6), 3804.
- (17) Kim, Y. S.; Lee, J. J.; Kim, T. S.; Sohn, J. L.; Joo, Y. J. Performance Analysis of a Syngas-Fed Gas Turbine Considering the Operating Limitations of Its Components. *Appl. Energy* **2010**, *87* (5), 1602.
- (18) Descamps, C.; Bouallou, C.; Kanniche, M. Efficiency of an Integrated Gasification Combined Cycle (IGCC) Power Plant Including CO₂ Removal. *Energy* **2008**, *33* (6), 874.
- (19) Rolf Bachmann; Nielsen, H.; Warner, J.; Kehlofer, R. *Combined-Cycle Gas & Steam Turbine Power Plants*, 3rd ed.; PennWell: Tulsa, Oklahoma, 2009.
- (20) Spallina, V.; Romano, M. C. C.; Chiesa, P.; Gallucci, F.; van Sint Annaland, M.; Lozza, G. Integration of Coal Gasification and Packed Bed CLC for High Efficiency and near-Zero Emission Power Generation. *Int. J. Greenh. Gas Control* **2014**, *27*, 28.
- (21) Hossain, M. M.; de Lasa, H. I. Chemical-Looping Combustion (CLC) for Inherent Separations—a Review. *Chem. Eng. Sci.* **2008**, *63* (18), 4433.

- (22) Lyngfelt, A.; Leckner, B.; Mattisson, T. A Fluidized-Bed Combustion Process with Inherent CO₂ Separation; Application of Chemical-Looping Combustion. *Chem. Eng. Sci.* **2001**, *56* (10), 3101.
- (23) Ryu, H.; Jin, G.; Yi, C. Demonstration of Inherent CO₂ Separation and No NO_x Emission in a 50kW Chemical-Looping Combustor: Continuous Reduction and Oxidation Experiment. In *Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies*; Vancouver, 2004.
- (24) Lyngfelt, A.; Thunman, H. Chemical-Looping Combustion: Design Construction and 100 H of Operational Experience of a 10 kW Prototype. In *Carbon Dioxide Capture for Storage in Deep Geologic Formations-results from the CO₂ Capture Project: Vol. 1-Capture and Separation of Carbon Dioxide from Combustion*; Thomas, D., Ed.; Elsevier: London, UK, 2004.
- (25) Linderholm, C.; Abad, A.; Mattisson, T.; Lyngfelt, A. 160 H of Chemical-Looping Combustion in a 10 kW Reactor System with a NiO-Based Oxygen Carrier. *Int. J. Greenh. Gas Control* **2008**, *2* (4), 520.
- (26) Adánez, J.; Gayán, P.; Celaya, J.; De Diego, L. F.; García-Labiano, F.; Abad, A. Chemical Looping Combustion in a 10 kW_{th} Prototype Using a CuO/Al₂O₃ Oxygen Carrier: Effect of Operating Conditions on Methane Combustion. *Ind. Eng. Chem. Res.* **2006**, *45* (17), 6075.
- (27) Johansson, E.; Mattisson, T.; Lyngfelt, A.; Thunman, H. Combustion of Syngas and Natural Gas in a 300 W Chemical-Looping Combustor. *Chem. Eng. Res. Des.* **2006**, *84* (A9), 819.
- (28) Johansson, E.; Mattisson, T.; Lyngfelt, A.; Thunman, H. A 300W Laboratory Reactor System for Chemical-Looping Combustion with Particle Circulation. *Fuel* **2006**, *85* (10-11), 1428.
- (29) Abad, A.; Mattisson, T.; Lyngfelt, A.; Rydén, M. Chemical-Looping Combustion in a 300 W Continuously Operating Reactor System Using a Manganese-Based Oxygen Carrier. *Fuel* **2006**, *85* (9), 1174.
- (30) Abad, A.; Mattisson, T.; Lyngfelt, A.; Johansson, M. The Use of Iron Oxide as Oxygen Carrier in a Chemical-Looping Reactor. *Fuel* **2007**, *86* (7-8), 1021.
- (31) Xiao, R.; Song, Q.; Song, M.; Lu, Z.; Zhang, S.; Shen, L. Pressurized Chemical-Looping Combustion of Coal with an Iron Ore-Based Oxygen Carrier. *Combust. Flame* **2010**, *157* (6), 1140.
- (32) Xiao, R.; Song, Q.; Zhang, S.; Zheng, W.; Yang, Y. Pressurized Chemical-Looping Combustion of Chinese Bituminous Coal: Cyclic Performance and Characterization of Iron Ore-Based Oxygen Carrier. *Energy & Fuels* **2010**, *24* (2), 1449.
- (33) Bischi, A.; Langørgen, Ø.; Saanum, I.; Bakken, J.; Seljeskog, M.; Bysveen, M.; Morin, J.-X.; Bolland, O.; Langørgen, T. Design Study of a 150kW_{th} Double Loop Circulating Fluidized Bed Reactor System for Chemical Looping Combustion with Focus on Industrial Applicability and Pressurization. *Int. J. Greenh. Gas Control* **2010**, *5* (3), 467.
- (34) Fernández, J. R.; Abanades, J. C. Conceptual Design of a Ni-Based Chemical Looping Combustion Process Using Fixed-Beds. *Appl. Energy* **2014**, *135*, 309.
- (35) Clarke, D. R.; Oechsner, M.; Padture, N. P. Thermal-Barrier Coatings for More Efficient Gas-Turbine Engines. *MRS Bull.* **2012**, *37* (10), 891.
- (36) Noorman, S.; van Sint Annaland, M. Packed Bed Reactor Technology for Chemical-Looping Combustion. *Ind. Eng. Chem. Res.* **2007**, *46* (12), 4212.
- (37) Hamers, H. P.; Gallucci, F.; Cobden, P. D.; Kimball, E.; Van Sint Annaland, M. A Novel Reactor Configuration for Packed Bed Chemical-Looping Combustion of Syngas. *Int. J. Greenh. Gas Control* **2013**, *16*, 1.
- (38) Hamers, H. P.; Romano, M. C.; Spallina, V.; Chiesa, P.; Gallucci, F.; Annaland, M. V. S. Comparison on Process Efficiency for CLC of Syngas Operated in Packed Bed and Fluidized Bed Reactors. *Int. J. Greenh. Gas Control* **2014**, *28*, 65.
- (39) Noorman, S.; Gallucci, F.; van Sint Annaland, M. M.; Kuipers, J. a. M. A. M. A Theoretical Investigation of CLC in Packed Beds. Part 2: Reactor Model. *Chem. Eng. J.* **2011**, *167* (1), 369.
- (40) Spallina, V.; Gallucci, F.; Romano, M. C. C.; Chiesa, P.; Lozza, G.; Van Sint Annaland, M.

- Investigation of Heat Management for CLC of Syngas in Packed Bed Reactors. *Chem. Eng. J.* **2013**, 225, 174.
- (41) Martínez, I.; Romano, M. C.; Fernández, J. R.; Chiesa, P.; Murillo, R.; Abanades, J. C. Process Design of a Hydrogen Production Plant from Natural Gas with CO₂ Capture Based on a Novel Ca/Cu Chemical Loop. *Appl. Energy* **2014**, 114, 192.
 - (42) Fernández, J. R.; Alarcón, J. M. Chemical Looping Combustion Process in Fixed-Bed Reactors Using Ilmenite as Oxygen Carrier: Conceptual Design and Operation Strategy. *Chem. Eng. J.* **2015**, 264, 797.
 - (43) Amrollahi, Z.; Andreas, P.; Ystad, M.; Ertesvåg, I. S.; Bolland, O. Optimized Process Configurations of Post-Combustion CO₂ Capture for Natural-Gas-Fired Power Plant – Power Plant Efficiency Analysis. *Int. J. Greenh. Gas Control* **2012**, 8, 1.
 - (44) Jordal, K.; Andreas, P.; Ystad, M.; Anantharaman, R.; Chikukwa, A.; Bolland, O. Design-Point and Part-Load Considerations for Natural Gas Combined Cycle Plants with Post Combustion Capture. *Int. J. Greenh. Gas Control* **2012**, 11, 271.
 - (45) Variny, M.; Mierka, O. Improvement of Part Load Efficiency of a Combined Cycle Power Plant Provisioning Ancillary Services. *Appl. Energy* **2009**, 86 (6), 888.
 - (46) Casella, F.; Farina, M.; Righetti, F.; Scattolini, R.; Milano, P. An Optimization Procedure of the Start-up of Combined Cycle Power Plants. In *Proceedings of the 18th IFAC World Congress*; Milano, Italy, 2011; pp 7043–7048.
 - (47) Larsson, P.-O.; Casella, F.; Magnusson, F.; Andersson, J.; Diehl, M.; Akesson, J. A Framework for Nonlinear Model-Predictive Control Using Object-Oriented Modeling with a Case Study in Power Plant Start-Up. *2013 IEEE Conf. Comput. Aided Control Syst. Des.* **2013**, 346.
 - (48) Bausa, J.; Tsatsaronis, G. Dynamic Optimization of Startup and Load-Increasing Processes in Power Plants — Part I : Method. *J. Eng. Gas Turbines Power* **1999**, 123 (1), 246.
 - (49) Tică, A.; Guéguen, H.; Dumur, D.; Faille, D.; Davelaar, F. Design of a Combined Cycle Power Plant Model for Optimization. *Appl. Energy* **2012**, 98, 256.
 - (50) He, F.; Li, Z.; Liu, P.; Ma, L.; Pistikopoulos, E. N. Operation Window and Part-Load Performance Study of a Syngas Fired Gas Turbine. *Appl. Energy* **2012**, 89 (1), 133.
 - (51) Kim, Y. S.; Park, S. K.; Lee, J. J.; Kang, D. W.; Kim, T. S. Analysis of the Impact of Gas Turbine Modifications in Integrated Gasification Combined Cycle Power Plants. *Energy* **2013**, 55, 977.
 - (52) Fernandez, J. R.; Abanades, J. C.; Murillo, R. Modeling of Cu Oxidation in an Adiabatic Fixed-Bed Reactor with N₂ Recycling. *Appl. Energy* **2014**, 113, 1945.
 - (53) Jerndal, E.; Mattisson, T.; Lyngfelt, A. Thermal Analysis of Chemical-Looping Combustion. *Chem. Eng. Res. Des.* **2006**, 84 (9), 795.
 - (54) Sathyaseelan, B.; Baskaran, I.; Sivakumar, K. Phase Transition Behavior of Nanocrystalline Al₂O₃ Powders. *Soft Nanosci. Lett.* **2013**, 3, 69.
 - (55) Iloeje, C.; Zhao, Z.; Ghoniem, A. F. Analysis of Thermally Coupled Chemical Looping Combustion-Based Power Plants with Carbon Capture. *Int. J. Greenh. Gas Control* **2015**, 35, 56.
 - (56) Lawal, A.; Wang, M.; Stephenson, P.; Obi, O. Demonstrating Full-Scale Post-Combustion CO₂ Capture for Coal-Fired Power Plants through Dynamic Modelling and Simulation. *Fuel* **2012**, 101, 115.
 - (57) Spallina, V.; Chiesa, P.; Martelli, E.; Gallucci, F.; Romano, M. C.; Lozza, G.; van Sint Annaland, M. Reactor Design and Operation Strategies for a Large-Scale Packed-Bed CLC Power Plant with Coal Syngas. *Int. J. Greenh. Gas Control* **2015**, 36, 34.
 - (58) Han, L.; Zhou, Z.; Bollas, G. M. Heterogeneous Modeling of Chemical-Looping Combustion. Part 1: Reactor Model. *Chem. Eng. Sci.* **2013**, 104, 233.
 - (59) Han, L.; Zhou, Z.; Bollas, G. M. Heterogeneous Modeling of Chemical-Looping Combustion. Part 2: Particle Model. *Chem. Eng. Sci.* **2014**, 113, 116.

- (60) Zhou, Z.; Han, L.; Bollas, G. M. Model-Based Analysis of Bench-Scale Fixed-Bed Units for Chemical-Looping Combustion. *Chem. Eng. J.* **2013**, *233*, 331.
- (61) Zhou, Z.; Han, L.; Bollas, G. M. Kinetics of NiO Reduction by H₂ and Ni Oxidation at Conditions Relevant to Chemical-Looping Combustion and Reforming. *Int. J. Hydrogen Energy* **2014**, *39*, 8535.
- (62) Zhou, Z.; Han, L.; Nordness, O.; Bollas, G. M. Continuous Regime of Chemical Looping Combustion (CLC) and Chemical-Looping with Oxygen Uncoupling (CLOU) Reactivity of CuO Oxygen Carriers. *Appl. Catal. B Environ.* **2015**, *166-167*, 132.
- (63) Han, L.; Zhou, Z.; Bollas, G. M. Model-Based Analysis of Chemical-Looping Combustion Experiments. Part I: Structural Identifiability of Kinetic Models for NiO Reduction. *AIChE J.* **2016**, *in press* (DOI:10.1002/aic.15225).
- (64) Han, L.; Zhou, Z.; Bollas, G. M. Model-Based Analysis of Chemical-Looping Combustion Experiments. Part II: Optimal Design of CH₄ -NiO Reduction Experiments. *AIChE J.* **2016**, *in press* (DOI:10.1002/aic.15242).
- (65) García-Labiano, F.; Adánez, J.; de Diego, L. F.; Gayán, P.; Abad, A. Effect of Pressure on the Behavior of Copper-, Iron-, and Nickel-Based Oxygen Carriers for Chemical-Looping Combustion. *Energy & Fuels* **2006**, *20* (1), 26.
- (66) Nordness, O.; Han, L.; Zhou, Z.; Bollas, G. M. M. High-Pressure Chemical-Looping of Methane and Synthesis Gas with Ni and Cu Oxygen Carriers. *Energy & Fuels* **2016**, *30* (1), 504.
- (67) Process Systems Enterprise Limited, gPROMS, 2015.
- (68) Jarvis, R. B.; Pantelides, C. C. *DASOLV: A Differential-Algebraic Equation Solver*; 1992.
- (69) Noorman, S.; Gallucci, F.; van Sint Annaland, M. M.; Kuipers, J. a M. A Theoretical Investigation of CLC in Packed Beds. Part 2: Reactor Model. *Chem. Eng. J.* **2011**, *167* (1), 369.
- (70) Fischer, W. J.; Nag, P. H-Class High Performance Siemens Gas Turbine SGT-8000H Series. In *Power-Gen International*; Las Vegas, NV, 2011.
- (71) Foust, A. Siemens SGT6-5000F Gas Turbine - An Evolutionary Approach. In *Electric Power Conference and Exhibition*; New Orleans, LA, 2014.
- (72) Brooks, F. J. *GE Gas Turbine Performance Characteristics*; Schenectady, NY, 2000.
- (73) Johnston, J. R. *Performance and Reliability Improvements for Heavy-Duty Gas Turbines*; Schenectady, NY, 2000.
- (74) Consonni, S.; Lozza, G.; Pelliccia, G.; Rossini, S.; Saviano, F. Chemical-Looping Combustion for Combined Cycles With CO₂ Capture. *J. Eng. Gas Turbines Power* **2006**, *128* (3), 525.
- (75) Zhou, Z.; Han, L.; Bollas, G. M. Overview of Chemical-Looping Reduction in Fixed Bed and Fluidized Bed Reactors Focused on Oxygen Carrier Utilization and Reactor Efficiency. *Aerosol Air Qual. Res.* **2014**, *14*, 559.
- (76) Nordness, O.; Han, L.; Zhou, Z.; Bollas, G. M. High-Pressure Chemical-Looping of Methane and Synthesis Gas with Ni and Cu Oxygen Carriers. *Energy & Fuels* **2016**, *30* (1), 504.
- (77) Han, L. and Bollas, G. M. Chemical-looping combustion in a reverse-flow fixed bed reactor, *Energy*. **2016**, *102*, 669.
- (78) Chen, C.; Han, L.; Bollas, G. M. Dynamic simulation of fixed bed chemical looping combustion reactors integrated in combined cycle power plants. *Energy Technol.* **2016**, *in press*.