Dynamic optimization of fixed bed chemical-looping combustion systems integrated in thermal power plants

Lu Han and George M. Bollas*

*Department of Chemical & Biomolecular Engineering, University of Connecticut, Storrs, 191 Auditorium Road, Unit 3222, CT 06269-3222, USA (e-mail: george.bollas@uconn.edu)

Abstract: Optimization methods can be used to improve the design and operation of batch processes. In this work, we illustrate the application of dynamic simulation and optimization for power generation in chemical-looping combustion systems, carried out in batch reactors. We present a framework for the optimization strategy, in which the objective is to maximize a measure of the energy efficiency, bounded by inequality constraints reflecting the industry standards. Several case studies are used to illustrate the applicability of the present problem formulation to enhance the process performance.

Keywords: dynamic modeling, batch models, optimization problems, power generation

1. INTRODUCTION

Batch processes are widely used to manufacture specialty chemicals, pharmaceutical products and polymers. Typically, batch processes are used when production volumes are low, isolation is required for sterility or safety, and the raw materials involved are difficult to handle. Scheduling of batch operations can be optimized to improve performance and quality. These problems can be computationally expensive due to the complexity of the production sequence (Méndez et al., 2006). The problem should take into account the sequence of products, equipment assignment and connectivity, variable batch sizes, and mixed intermediate storage policies.

This paper presents an application of dynamic optimization batch operations for power generation. We explore high-pressure fixed bed reactors for Chemical-Looping Combustion (CLC) as the application of the presented framework. CLC is a novel technology that combines power production with CO₂ capture. In CLC, an oxygen carrier is used to transfer the oxygen from the air to oxidize a hydrocarbon fuel. While most of the CLC studies focus on continuous processes using interconnected fluidized bed reactors, the use of fixed bed reactors enables the process to operate at high pressures. High-pressure operation is necessary for the seamless integration of CLC with a highly-efficient combined cycle power plant. Other advantages associated with the fixed bed reactor are better bed utilization, elimination of particle attrition, and simplicity in gas/solid separation (Hamers et al., 2013). The operation of a fixed bed CLC reactor is an inherent batch process. The oxygen carrier is static while the gaseous streams alternate between reduction and oxidation stages. During the reduction step, a gaseous hydrocarbon fuel is oxidized to produce CO₂ and steam. The bed is regenerated in the subsequent oxidation step with air. This step is exothermic and produces a high-temperature, high-pressure gas that can be converted into electricity in a downstream gas turbine of a combined cycle power plant. A short purging step is required between the oxidation and reduction cycles to avoid mixing of the combustible gases. The performance of the CLC reactor inside the power plant is highly constrained, because it needs to adhere to acceptable levels of CO₂ capture efficiency, while producing a suitable gas for the gas turbine, which is usually operated at steady-state conditions. Thus, an adequate cycle strategy is necessary for the process to achieve optimal operating conditions for the combined cycle power plant.

Simulation of power plants with CLC is complex due to the large number of units involved, interaction between CLC and power plant components, and presence of streams of diverse compositions and properties. Thus, investigators typically rely on thermodynamic models for calculating the mass and energy balances throughout the system (Iloeje et al., 2015). Kinetics is often ignored, in favor of assuming the conversion of the fuel and solid, on the basis of experimental measurements from bench-scale units (Erlach et al., 2011). Kolbitsch et al. (2009) showed that incorporation of the relevant kinetics and hydrodynamics is essential to accurately predict CLC performance. In their calculations they found incomplete conversion of solids in the air reactor, which was contrary to previous assumptions by Lyngfelt et al. (2001). Also, ideal assumptions of the mixing patterns inside the reactors can overpredict the conversion inside the fuel reactor, leading to an under-prediction of the solid inventory (Porrazzo et al., 2014). The accuracy of system models can be improved by including the process kinetics and hydrodynamics. Therefore, dynamic optimization should guide reactor design and operation of the CLC system and explore the theoretical limits of the efficiency of a combined cycle power plant with CLC.

The objective of this work is to present a mathematical formulation to optimally design and tune the cycle strategy of batch fixed bed reactors for power generation with in-situ CO₂ capture. We explore the optimality of batch CLC systems and investigate their batch operation with different
oxygen carriers and fuel types, to showcase the applicability of this generic approach. A reverse-flow reactor is proposed to increase the efficiency of batch CLC reactor systems. A model-based approach is used to compare the novel reverse-flow reactor with the conventional fixed bed and a fluidized bed processes. The novelty of this work is the formulation of dynamic optimization problems to enable a comparison between batch and continuous systems proposed for CLC. The most efficient process should be eventually nominated for scale-up.

2. OPTIMIZATION STRATEGY

2.1 Process Options

In this work, we explore three CLC reactor configurations: (1) fixed bed; (2) reverse-flow fixed bed; and (3) fluidized bed reactors. Due to the different modes of operation, the utilization of the energy produced from the combustion process is different. In the fixed bed processes, the oxygen carrier material is static and the inlet gas varies between fuel, air, and inert. The direction of the gas is switched intermittently during the reduction and/or oxidation cycles in the reverse-flow fixed bed reactor. A high-temperature gas stream is produced after the oxidation step, which can be used for power generation in a downstream gas turbine of the combined cycle. The gas stream produced from the reduction cycle leaves the reactor at lower temperatures and can be used for heat recovery within the power plant. In contrast, the fluidized bed process operates in continuous mode, by transferring the oxygen carrier material between the so-called fuel and air reactors. The depleted air stream downstream the air reactor can be sent to the combined cycle to generate power.

To operate at high efficiencies, the inlet to the gas turbine should be at the maximum allowable temperature and pressure permitted by the CLC reactor. The energy recovery components downstream the gas turbine should also be optimized, to balance the efficiency of the steam turbine with the preheating demands of the CLC reactor. The performance of the CLC reactor is also heavily constrained by the limits of CO₂ capture, melting points of the materials, and pressure drops. All of these considerations must be taken into account in the process design phase of an integrated power plant with CLC. Thus, there is potential to improve the efficiency of these systems and to explore the envelope of performance through process optimization.

2.2 Problem Formulation

A generic optimization problem for the CLC reactor system can be formulated as follows:

$$\text{max} \quad J$$

subject to

$$f(x(t), x(t), u(t), 0) = 0,$$

$$g(x(t), x(t), u(t), 0) \leq 0,$$

where $J$ is the scalar performance index to be maximized, $x$ is the vector of state variables, $u(t)$ is the vector of control variables, $f$ is the set of differential equations describing the dynamics of the system, $g$ is the vector of path constraints for the state variables, and $\phi$ is the vector of design variables to be optimized bounded by the design space $\Phi$.

2.3 Batch Process

The input to a batch CLC reactor is the feed gas, which dynamically alternates between fuel, air, and inert. This time-varying control vector is modeled with piecewise functions, $u(t)=u_i$, over the duration of the CLC step $t_i$, i.e., reduction, oxidation, heat removal, and purge. For a given reactor design and fuel flow, the optimizer manipulates the air flow rate and inlet temperature, time intervals for the CLC steps, and active metal content in the oxygen carrier, $\omega$. These variables are contained within the design vector, $\phi$:

$$\phi = [u_i, t_i, \omega]$$.

In the reverse-flow reactor, the direction of the gas flow is periodically reversed during the reduction and/or oxidation steps. The number of flow switches $n_{sw}$ and the time period for each flow switch $\tau_{n_{sw}}$ can be optimized. The design vector for the reverse-flow reactor is thus:

$$\phi = [u_i, t_i, \omega, n_{sw}, \omega]$$.

The power generation efficiency of the batch CLC process can be quantified in terms of the duration of the heat removal phase ($J'$) and the fraction of heat leaving the reactor during heat removal ($J''$):

$$J' = \int_{t_1}^{t_2} \alpha T_{out}(t) dt,$$

$$J'' = \frac{\int_{t_1}^{t_2} (\dot{m}_{out}(t) h_{out}(t)) dt}{\int_{t_1}^{t_2} (\dot{m}_{out}(t) h_{out}(t)) dt}.$$
avoid excess pressure losses and maximize plant efficiency. These path constraints reflect the basic requirements of the CLC reactor according to the literature.

2.4 Continuous Process

The operation of the interconnected fluidized bed reactor configuration is influenced by the solids inventory inside the fuel and air reactors, circulation rate of solids between the reactors, reactor temperatures, and particle size (Lyngfelt et al., 2001). In the continuous process, the control vector can be simply cast as \( u(t) = u \), which includes the aforementioned process variables.

We can define a performance index for the continuous process as:

\[
J^* = \frac{\left(\dot{m}_{\text{air}} h_{\text{air}}\right)_{\text{HR}} - \left(\dot{m}_{\text{air}} h_{\text{air}}\right)_{\text{FR}}}{\left(\dot{m}_{\text{air}} h_{\text{air}}\right)_{\text{HR}}} ,
\]

where \( J^* \) is the heat leaving the air reactor relative to the combined heat leaving the air and fuel reactors.

The path constraints are formulated to keep the same bounds on performance as the batch process. The fuel reactor is constrained by \( X_{\text{fuel}} \geq 98\% \) and \( S_{\text{CO}_2} \geq 90\% \) and the air reactor is constrained by \( T_{\text{HR}}(z) \leq T_{\text{max}} - 50 \, ^\circ\text{C} \) and \( T_{\text{HR}}(z=L) \leq T_{\text{IT}} \pm 50 \, ^\circ\text{C} \).

The optimization problem presented in (1) with the objective of maximizing process efficiency can be used to design optimal CLC reactor processes. The power generation potential of the CLC reactor can be quantified by either \( J' \) or \( J'' \) for batch processes and by \( J^* \) for continuous processes. By solving these dynamic optimization problems, we can compare the optimal efficiency of batch systems with that of an optimally operated continuous system.

3. PROCESS MODELS

The process models utilized were developed and validated in previous work. CLC with CuO and NiO oxygen carriers was simulated, using detailed reaction kinetics (Han et al., 2016a; Han et al., 2016b; Nordness et al., 2015; Zhou et al., 2015b), derived from fixed bed experiments at various operating pressures, flow regimes, and temperatures. These kinetic models accurately predicted CLC reduction data of the open literature (Han et al., 2014, 2013; Zhou et al., 2014a, 2013).

The underlying physics of the fixed bed reactor was described by the heterogeneous reactor model of Han and Bollas (2016a), which incorporates the mass, energy, and momentum conservation equations. The fluidized bed reactor was modeled by the three-phase hydrodynamic model of Zhou et al. (2015a). The models developed in previous work are accurate for representing the CLC behavior and are suitable for design analysis of large-scale systems. The optimization problem of (1) was implemented in gPROMS, using the control vector parameterization (CVP) with single-shooting algorithm.

4. CASE STUDIES

Three case studies are presented to demonstrate the feasibility of the approach to increase the efficiency of CLC. In the first example, we optimized the cycle strategy of a fixed bed reactor and compared the optimal performance against a nominal design. The results of this case study show the impact of the cycle strategy on the operability and efficiency of batch CLC. The second case study explored the effect of reverse-flow operation on the batch CLC performance. Flow reversal was introduced to the nominal fixed bed reactor design presented in Han and Bollas (2016a). The comparison between the reverse-flow and nominal fixed bed reactor was executed over their respective optimal operating strategies. In the third case study, we compared the CLC efficiency in batch and continuous processes. The CLC fluidized bed unit of Chandel et al. (2009) was chosen as the reactor prototype for the continuous process. This fluidized bed reactor was compared to equivalent fixed bed and reverse-flow reactors, at the same operating conditions. The reactor with the highest fuel conversion and CO\(_2\) capture efficiency is recommended as the most suitable reactor configuration for CLC.

5. RESULTS & DISCUSSION

A practical approach to controlling the dynamic switching scheme is with the feedback control strategy depicted in Fig. 1. In this scheme, the reduction step is stopped when either low CO\(_2\) selectivity or fuel conversion are detected in the exhaust stream. After a brief purge, air is fed to the reactor to commence the oxidation step. When the temperature of the gas exhaust is within 50°C of the \( T_{\text{IT}} \) set-point (selected here at 1000°C), the cycle switches to heat removal (HR-1), to discharge the exhaust to a downstream gas turbine. A secondary heat removal step (HR-2) sends lower-quality gas stream to the steam turbine for energy recovery, but at lower energy efficiency. After the heat removal steps, the reactor is briefly purged and the process returns to the reduction step.

![Fig. 1. Cycling strategy of fixed bed CLC reactor.](image)
temperature and composition vs. cycle time. Heat was liberated during the oxidation cycle and led to an increase in the exhaust gas temperature shown in Figure 2a. The O₂ in the air was consumed until all the metal oxide in the bed was regenerated (Fig. 2b). Temperature fluctuations were observed in the exhaust gas (Fig. 2a), due to the non-uniformities in temperature and solid conversion at the start of oxidation. The gas stream exiting the reactor was suitable to feed a downstream gas turbine for half of the total heat removal time (Fig. 2a). The remaining heat was utilized less efficiently in the power plant. The energy efficiency of the nominal fixed bed reactor design was, thus, limited by the process dynamics of the reactor. After heat removal and a brief purge, methane was fed to the reactor and got oxidized into CO₂ and H₂O in the reduction step (Fig. 2b). The heterogeneous reduction reactions between NiO and CH₄ are generally endothermic, causing the decrease in exit gas temperature (Fig. 2a).

Fig. 2. Profiles of the (a) exit gas temperature and (b) exit gas composition of the CLC reactor with NiO and methane fuel under a nominal cycle strategy (TIT=1000°C).

Fig. 3 presents the results of optimal operation of the fixed bed process by solving the dynamic problem of (1) with the objective function of (4). In simple words, the cycle strategy for the batch process, φ', was optimized to maximize the time interval that the reactor can discharge a hot gas to a downstream gas turbine. The optimizer increased the metal oxide content of the oxygen carrier in order to increase the temperature rise during oxidation. As a result, a higher temperature gas was produced during the subsequent heat removal step, as shown in Fig. 3a, which could feed the gas turbine for the entire duration of heat removal. Consequently, the optimizer eliminated the secondary heat removal step to the steam turbine. The reduction cycle was initiated over a warmer bed in the optimal case (Fig. 3a) than in the nominal case (Fig. 2a). This promoted the endothermic reduction reactions to convert more of the NiO in the bed, while maintaining high selectivity to CO₂ and H₂O (Fig. 3b). Based on the higher outlet temperatures, the steam cycle efficiency can be potentially increased. In summary, the fixed bed reactor with the optimal cycle strategy achieved better process efficiency than the nominal design, by maximizing the heat stream to the gas turbine, eliminating the need for a secondary, less efficient heat removal step, and increasing the gas temperature of the reduction exhaust.

In the next analysis, we investigated whether reverse-flow operation can be used to increase the efficiency of the fixed bed CLC reactor. The concept is to periodically change the flow direction of the fuel during the reduction step. With the reverse-flow operation, we can enhance the contact between the fuel and the fresh oxygen carrier, which could lead to a more uniform bed conversion and temperature distribution. Optimal cycle strategies were calculated for the fixed bed and reverse-flow reactors, by solving (1) with the objective function of J" for both. For the reverse-flow reactor, the number of flow reversals, nᵣₒ, of φ" was fixed to 2 prior to optimization.

Fig. 3. Profiles of the (a) exit gas temperature and (b) exit gas composition of the optimal fixed bed reactor with NiO and methane fuel (TIT=1000°C). The design variables were optimized using (1) with the objective function of (4).

Fig. 4. Performance of the one-directional (1D) and reverse-flow (RF) reactors with the optimal cycle strategies for the CLC of NiO with syngas fuel (TIT=1100°C). Figs. 4a and 4c show the internal bed conversion (J=fully converted). Fig. 4b and 4d show the internal bed temperature.

Fig. 4 shows the internal bed profiles of oxygen carrier conversion and temperature during reduction in the optimized fixed bed and reverse-flow processes. As shown in Fig. 4a, the reactor entrance was first reduced followed by the interior and outer regions of the bed, due to the progression of the reaction front. The exit of the reactor was not fully reduced, to maintain a high CO₂ capture efficiency of the process. The reverse-flow reactor exhibited a bilateral conversion profile (Fig. 4b), in which reactions occurred at both sides of the reactor due to the periodic switching of the fuel direction. The reactor bed was most reduced at the inlet and exit regions and the least in the middle (Fig. 4b). The temperature inside the reactor varied following the progression of the conversion front. The reduction reactions examined in Fig. 4 are overall slightly exothermic, so the bed temperature increased with
reaction extent (Fig. 4c and 4d). Smaller temperature fluctuations were observed in the reverse-flow process (Fig. 4d) compared to the one-directional process (Fig. 4c), because of the more uniform bed conversion profile.

The temperature and concentration profiles over one cycle at cyclic steady state operation are shown in Fig. 5 for the reverse-flow reactor with the optimal cycle strategy. For brevity, the results for the equivalent one-directional process are not presented, but we will mention the differences in the comparison. There are sharp changes in the outlet gas temperature (Fig. 5a) and selectivity profiles (Fig. 5b) of the reverse-flow reactor. This was the result of the instantaneous change in boundary conditions to accomplish flow reversal. After the first flow reversal, the outlet temperature immediately dropped (Fig. 5a) because the entrance of the reactor was originally colder than the exit (Fig. 4d). After the second flow reversal, the exhaust temperature increased (Fig. 5a), because the reactor exit was heated by the exothermic CuO reduction reactions. In a laboratory setting, the fluctuations in the exit gas temperature and composition would be less pronounced because of mixing of gases downstream the reactor and heat losses through the system. Flow reversal was also accompanied by an instantaneous slip of unconverted fuel at the reactor outlet (Fig. 5b), however this effect was marginal compared to the overall CO₂ selectivity. After reduction, the oxidation step proceeded over a more uniformly converted bed in the reverse-flow process. Thus, the heat removal step can operate at higher flow rates and longer times compared to the one-directional process, which increased the energy efficiency of the batch process.

![Profiles of gas temperature and composition of the optimal reverse-flow reactor with CuO and syngas fuel (TIT=900°C).](image)

The operation of CLC in the batch mode is compared to a continuous process. For this investigation, we focused on the fuel conversion efficiency and bed utilization of the fuel fluidized bed reactor, in comparison with that of the fixed bed and reverse-flow reactors. To establish a basis for comparison, we designed a fixed bed reactor that matched the capacity of an existing fluidized bed reactor in the literature (Chandel et al., 2009). The fixed bed and fluidized reactors are comparable because they use the same solids inventory, fuel flow rate, operating temperatures and pressures, and oxygen carrier type (Zhou et al., 2014b). We also explored reverse-flow operation in this fixed bed design, wherein the flow direction was reversed at evenly spaced time intervals during reduction.

Fig. 6 shows the reduction performance achieved in the batch (fixed bed and reverse-flow) and continuous (fluidized bed) processes. The fluidized bed model was run for a range of bed conversions, to generate the plots of gas and solid selectivities vs. bed-averaged solid conversion. The results shown for the batch reactors were derived from a single dynamic simulation. As can be seen, the fluidized bed process can operate at most 50% solid conversion to deliver ~100% fuel conversion to CO₂. The conventional fixed bed process achieved higher CO₂ selectivities and fuel conversion than the fluidized bed reactor over the same bed conversions. The solid carbon selectivity (Fig. 6c) was higher in the fixed bed but still very low for the reverse-flow fixed bed reactor, even at considerably high oxygen carrier conversions. These results indicate that the bed utilization is better in the fixed bed reactor. The reverse-flow process, as depicted in Fig. 6, enabled the high transient CO₂ selectivity and fuel conversion to be maintained over longer solid conversions. Thus, implementation of CLC as a batch process with flow reversal enables the enhancement of oxygen carrier reactivity and fuel conversion, without necessitating larger inventories of material or increasing the reactor size.

![Results of the cycle-averaged (a) CO₂ selectivity, (b) CH₄ conversion and (c) solid carbon deposition in the reverse-flow fixed bed with switch time intervals of 30s, fixed bed reactor, and fluidized bed reactor with NiO and CH₄ fuel.](image)
6. CONCLUSIONS

A dynamic optimization problem was formulated for the design and operation of reactors for chemical-looping combustion (CLC) systems. A framework was presented and applied to optimize the dynamic operation of the fixed bed batch process in order to maximize the energy efficiency of CLC integrated with a combined cycle power plant. This methodology was shown to increase the heat removal efficiency of the batch process, while satisfying strict operating constraints. We compared two reactor configurations of the batch process against an “equivalent” continuous design, implemented in a fluidized bed reactor. From the model-based analysis, we showed that better utilization of the oxygen carrier material can be achieved with the batch fixed bed reactor with flow reversal and an optimized cycle strategy. Future work will focus on incorporating the process dynamics of the CLC system into a dynamic power plant model, to explore the feasibility of real-time plant optimization. The proposed formulation has potential applications to other CLC reactor systems and plant configurations.

7. ACKNOWLEDGEMENTS

This material is based upon work supported by the National Science Foundation under Grant No. 1054718.

APPENDIX A.

Table A.1. Calculated $J^*$ for the optimal batch reverse-flow (RF) and one-directional (1D) reactors for two TIT set-points.

<table>
<thead>
<tr>
<th></th>
<th>NiO with CH$_4$</th>
<th>NiO with syngas</th>
</tr>
</thead>
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<tr>
<td></td>
<td>(1100°C)</td>
<td>(1000°C)</td>
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<tr>
<td>RF</td>
<td>0.782</td>
<td>0.774</td>
</tr>
<tr>
<td>1D</td>
<td>0.729</td>
<td>0.703</td>
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<tr>
<td>CuO with CH$_4$</td>
<td>CuO with syngas</td>
<td></td>
</tr>
<tr>
<td>(1000°C)</td>
<td>(900°C)</td>
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</tr>
<tr>
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<td>0.780</td>
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REFERENCES


