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Efficient Cycles for Carbon Capture CLC Power Plants based on Thermally Balanced Redox Reactors

Chukwunwike Iloeje¹, Zhenlong Zhao, Ahmed F. Ghoniem

Department of Mechanical Engineering, Massachusetts Institute of Technology (MIT), 77 Massachusetts Avenue, Cambridge, Massachusetts 02139-4307, United States

Abstract

The rotary reactor differs from most alternative Chemical Looping Combustion (CLC) reactor designs because it maintains near-thermal equilibrium between the two stages of the redox process by thermally coupling channels undergoing oxidation and reduction. An earlier study showed that this thermal coupling between the oxidation and reduction reactors increases the efficiency by up to 2% points when implemented in a regenerative Brayton Cycle. The present study extends this analysis to alternative CLC cycles with the objective of identifying optimal configurations and design tradeoffs. Results show that the increased efficiency from reactor thermal coupling applies only to cycles that are capable of exploiting the increased availability in the reduction reactor exhaust. Thus, in addition to the regenerative cycle, the combined CLC cycle and the combined-regenerative CLC cycle are suitable for integration with the rotary reactor. Parametric studies are used to compare the sensitivity of the different cycle efficiencies to parameters like pressure ratio, turbine inlet temperature, carrier-gas fraction and purge steam generation. One of the key conclusions from this analysis is that while the optimal efficiency for regenerative CLC cycle was the highest of the three (56% at 3 bars, 1200C), the combined-regenerative cycle offers a trade-off that combines a reasonably high efficiency (about 54% at 12 bar, 1200C) with much lower gas volumetric flow rate and consequently, smaller reactor size. Unlike the other two cycles, the optimal compressor pressure ratio for the regenerative cycle is weakly dependent on the design turbine inlet temperature. For the regenerative and combined regenerative cycles, steam production in the regenerator below 2 x fuel flow rate improves exhaust recovery and consequently, the overall

¹ Corresponding Author. Email: nwike@mit.edu. Tel: +1-857-5000928. Fax: 615-253-5981
system efficiency. Also, given that the fuel side regenerator flow is unbalanced, it is more efficient to generate steam from the fuel side regenerator than from the air side regenerator.

Nomenclature

Symbols

\( c_p \): Specific heat capacity (at constant pressure)  
\( c_v \): Specific heat capacity (at constant volume)  
\( m_f \): Fuel side flow rate  
\( m_a \): Air side flow rate  
\( m_i c_{pi} \): Thermal Capacity of stream \( i \)  
\( Q \): Heat input (reaction heat release)  
\( P \): Pressure  
\( T \): Temperature  
\( W \): Work input

Greek Symbols

\( \alpha = \left( \frac{c_p}{c_v} \right) \right) - 1 \)  
\( \eta \): Efficiency  
\( \beta_a = \left( \frac{T_{ox}}{T_1} \right) \): oxidation reactor/ambient temperature ratio  
\( \beta_f = \left( \frac{T_{red}}{T_1} \right) \): reduction reactor/ambient temperature ratio  
\( \varepsilon \): ratio of HRSG steam exit to gas inlet temperature  
\( \pi = \frac{P_2}{P_1} = \frac{P_{max}}{P_{min}} \): Cycle pressure ratio

Subscripts

1: environment
1. Introduction

Chemical Looping Combustion (CLC) is an oxy-combustion technology with inherent CO₂ capture capability, which avoids the additional parasitic power demand typically associated with CO₂ separation. This feature makes CLC systems more efficient than most alternative capture technologies [1-8].

Typical CLC designs consist of two reactors, with an oxygen carrier particle stream circulating pneumatically and transferring oxygen from the oxidation reactor to the fuel stream in the reduction reactor. Thus, the exhaust of the reduction reactor will comprise
primarily of CO$_2$ and H$_2$O [9-12]. These circulating systems face a number of challenges, including non-trivial reactor pressure drop, possible defluidization, attrition, agglomeration and lower CO$_2$ separation efficiency [10, 12-14]. The temperature difference between the oxidation and reduction reactors also creates cyclic thermal stresses and heat transfer irreversibilities that penalizes cycle efficiency. Other reactor designs include the moving bed CLC reactor [9, 15], the fixed packed bed reactor [16, 17] and the rotating packed bed reactor [18, 19]. Although these designs avoid the problems associated with particle circulation, they still suffer temperature swings between the oxidation and the reduction cycles, particularly for oxygen carriers with endothermic reduction reactions.

The rotary reactor, proposed by Zhao et al. [20-23], has been designed to overcome this limitation. It consists of a solid wheel rotating between fuel and air streams, with steam purging sectors in-between, as shown in figure 1. The rotating wheel consists of a matrix of channels with the oxygen carrier coated or impregnated on the surface of the channel walls. A bulk layer that forms the walls of each channel supports the oxygen carrier coating. As the reactor rotates, oxygen is absorbed while the channels pass through the air sector, and subsequently used to oxidize the fuel in the fuel sector. Steam is used in the purge sectors to prevent gas carry-over between the air and fuel sectors. During the cyclic operation, the solid wheel also behaves as a thermal storage medium; it transfers heat to the gas streams and provides internal thermal coupling between all the sectors of the reactor, ensuring a thermally balanced reactor operation. This thermal coupling is facilitated by the bulk support layer, which forms a continuous heat conduction path, avoiding the solid-gas-solid and solid-solid contact resistances typical in many reactor designs. Consequently, the reactor temperature will essentially be the same at every radial
location, ensuring a nearly uniform temperature for the redox process and uniform exhaust temperatures.

In the previous paper [24], theoretical availability concepts, together with ideal and detailed regenerative CLC cycle models, were used to demonstrate that under practical operating conditions, the internal thermal coupling in the rotary reactor increases cycle efficiency. The analysis showed an increase of up to 2% points for the regenerative CLC cycle. This paper extends this analysis to alternative cycle configurations. Section 2 makes use of analytical thermodynamic models of the Brayton, Steam and Combined CLC cycles to study the impact of reactor thermal coupling on the system thermal efficiency. In section 3, the same analysis is carried out using higher fidelity Aspen Plus® models of the same cycles. Hybrid combined, steam and regenerative cycles are also included in the analysis and the results are used to validate the conclusions from section 2, as well as identify cycle configurations suitable for integration with the rotary reactor. Next, section 4 makes use of parametric studies to compare the sensitivity of the selected cycle configurations to design and operating parameters like pressure ratio, reactor outlet temperature (turbine inlet temperature), diluent (CO₂) fraction and purge steam generation. The results from this phase of the study are used to identify the key operating parameters, map out the optimal operating conditions for each configuration, and define criteria for selecting from among the different cycle options. Though focused on the rotary reactor, the results of this study will also be applicable to any other thermally coupled CLC reactor design.
2. Analytical Thermodynamic CLC Power Cycle Models

In the previous study [24], an ideal regenerative CLC cycle model was used to develop a functional relationship between cycle thermal efficiency and the reactor temperatures. This functional relationship was used to demonstrate a positive correlation between cycle thermal efficiency and reactor temperature ratio of the form

\[ \eta = 1 - \Psi_3 + \Psi_4 \left( \frac{T_{\text{red}}}{T_{\text{ox}}} \right) \]  

(1)

\( \Psi_3 \) and \( \Psi_4 \) are positive constants, \( T_{\text{red}} \) is the reduction reactor temperature, \( T_{\text{ox}} \) is the oxidation reactor temperature and \( \eta \) is the cycle thermal efficiency. This was used to demonstrate the advantage of thermally balanced redox reactors \( (T_{\text{red}} = T_{\text{ox}}) \) over thermally imbalanced designs \( (T_{\text{red}} < T_{\text{ox}}) \) for the regenerative cycle. Given that each cycle configuration has unique features that could introduce specific constraints on the maximum cycle thermal efficiency, the same analysis is extended here to other cycles using analytical models of the Brayton, Steam and combined CLC cycles. For each of these ideal configurations, the expression for efficiency is determined by applying energy balance to subcomponents, then back-substituting all the known variables into the equation

\[ \eta = -\frac{W}{Q} \]  

(2)

2.1. Assumptions

Idealizing assumptions simplify analysis and make it possible to quantify and compare important trends without the need to precisely predict the performance of real life systems. To account for the effect of irreversibilities in the system, some 2nd law efficiencies are
included to partially relax these idealizations. The following are general assumptions used in the model formulation:

I. Air and fuel inlet temperatures are equal to ambient temperature

II. Thermal capacity \((mc_p)\) for air and fuel side streams are constant and independent of temperature

III. Fuel flow rate is fixed \((m_f = constant)\)

IV. Heat release (equal to net enthalpy of reaction) in the reactor is constant

V. Air side and fuel side pressure ratios are equal \((\pi_a = \pi_f = \pi)\)

VI. Air flow rate \((m_a)\) varies to control fuel exit temperature from the reactor

VII. Work \((W)\) and Heat \((Q)\) are defined as positive into the control volume

VIII. For the steam and combined cycles, exhaust gas leaves the Heat Recovery Steam Generator (HRSG) at ambient temperature

IX. Steam cycle low temperature reservoir is at ambient temperature \((T_1)\)

X. Steam engine 2\(^{nd}\) law efficiency is defined as a function of HRSG steam-exit to gas-inlet temperature ratio (see Appendices B and C)

XI. Compressors and turbines have specified isentropic efficiency

### 2.2. Simple (Brayton) CLC Cycle

A schematic representation of the simple Brayton CLC cycle is shown in figure 2. Applying the laws of thermodynamics to the air side components, fuel side components and the reactor, and substituting into equation 2 gives

\[
\eta = -\frac{W_{Ba} + W_{Bf}}{Q}
\]

\[
= \psi_1 - \psi_2 Q \left(1 - \frac{T_{red}}{T_{ox}}\right)
\]

(3)
where $\Psi_1 = \frac{\pi^{\alpha-1}}{\alpha} \left( \frac{\beta \eta \epsilon^{-\alpha} - \pi^{\alpha}}{\beta \eta \epsilon^{-\alpha+1-\epsilon}} \right)$; $\Psi_2 = \frac{\pi^{\alpha-1}}{Q \eta \epsilon^{\alpha}} \left( \frac{m_f c_p f T_1 \epsilon}{\beta \eta \epsilon^{-\alpha+1-\epsilon}} \right)$; $\Omega = (\eta_T \eta_c (1 - \eta_c) + \eta_c \pi^{\alpha} (1 - \eta_T))$; $W_{Ba}$ and $W_{Bf}$ are the work output of the air and fuel side Brayton cycles respectively, $\pi$ is the compressor pressure ratio, $\left( \frac{P_2}{P_1} \right)$, $m_f$ is the fuel mass flow rate, $c_{pf}$ is the fuel specific heat capacity at constant pressure, $c_{vf}$ is the fuel specific heat capacity at constant volume, $\eta_c$ is the compressor isentropic efficiency, $\eta_T$ is the turbine isentropic efficiency, $T_1$ is the ambient temperature, $T_{red}$ is the reduction reactor temperature, $T_{ox}$ is the oxidation reactor temperature, $\beta_a$ is the ratio of the oxidation reactor temperature to ambient temperature $\left( \frac{T_{ox}}{T_1} \right)$, $\alpha = \left( \frac{c_{pf}}{c_{vf}} \right)^{-1}$ and $Q$ is the net reaction heat release (see Appendix A for derivation). Equation 3 shows that efficiency is positively correlated with reduction/oxidation reactor temperature ratio. Discounting the compressor and turbine irreversibilities ($\eta_c = \eta_T = 1$) equation 3 reduces to the classical form, which is independent of the reactor temperature ratio

$$\eta = 1 - \pi^{-\alpha}$$

Equation 4 suggests that for an ideal Brayton CLC cycle with isentropic compressors and turbines, cycle efficiency is independent of reactor thermal balance. The dependence arises when irreversibilities are taken into account. This dependence is visualized in figure 3 by plotting the efficiency from equation 3 against the reduction/oxidation reactor temperature ratio. For this plot, $T_{ox} = 1473K$, $T_1 = 300K$, $m_f = 1kg/sec$, $c_{pf} = 2.22 \times 10^3 J/kg$, $\eta_T = \eta_c = 0.8$, $\pi = 8, 10$ and $12$, $\alpha = 0.2336$ and $LHV = 45 \times 10^6 J/kg$ and $Q = m_f * LHV$. The lower bound for each plot is defined such that $T_{red} > T_1 \pi^{\alpha}$. The plot area is divided into three sections covering the range of values of $T_{red}$ considered. The plot
shows a linear relationship with a constant positive slope. Now consider the following scenarios:

**Exothermic reduction reaction**: For an exothermic reduction reaction, assuming there are no material constraints on the temperature of the reduction reactor, the region to the right of B, where $T_{\text{red}} > T_{\text{ox}}$ defines the optimal cycle efficiency. However, as discussed in detail in [24], the maximum reduction reactor temperature is often limited by oxygen carrier material thermal properties or TIT such that it cannot be higher than the oxidation reactor temperature. In such a case, the oxidation and reduction reactor temperatures become equal and the optimal efficiency corresponds to the thermally balanced case defined by line B.

**Endothermic reduction reaction**: For an endothermic reduction reaction, the reduction reactor temperature cannot be greater than the oxidation reactor temperature without requiring an external heat source; so the feasible reduction reactor temperature lies in the region to the left of B in figure 3 and maximum efficiency also corresponds to the thermally balanced operating point at B.

### 2.3. Simple Steam CLC Cycle

Figure 4a shows a schematic of a simple CLC steam cycle. The steam engine is modeled as an ideal engine extracting work from the exhaust gas stream as it cools to ambient conditions as shown in figure 4b. The actual work output is obtained by applying a 2nd law efficiency to the work output from this steam engine (see Appendix B). Applying the laws of
thermodynamics on the reactor, the air and the fuel side steam cycles gives the following expression for efficiency

\[
\eta = \frac{-W_{Sa} + W_{Sf}}{Q}
\]

\[
= \eta_{2sa} \left(1 - \frac{\ln(\beta_a)}{\ln(\beta_a - 1)} + \frac{m_{fc} c_{pf}) T_1}{Q} \left(\beta_a \frac{T_{red}}{T_{ox}} - 1\right) \right) \left(\eta_{2sf} \left(1 - \frac{\ln(\beta_a \frac{T_{red}}{T_{ox}})}{\ln(\beta_a \frac{T_{red}}{T_{ox}} - 1)}\right) - \eta_{2sa} \left(1 - \frac{\ln(\beta_a)}{\ln(\beta_a - 1)}\right)\right) \quad (5)
\]

\(W_{Sa}\) and \(W_{Sf}\) are the work output of the air and fuel side steam cycles respectively, \(\eta_{2sa}\) is the air side steam cycle second law efficiency, \(\eta_{2sf}\) is the fuel side steam cycle second law efficiency and all the other terms are as described in section 2.2. \(\eta_{2sa}\) and \(\eta_{2sf}\) are approximate 2\(^{nd}\) law efficiencies defined as

\[
\eta_{2sa} = \frac{\varepsilon(\beta_a - 1)}{\varepsilon(\beta_a - 1)} \quad (6)
\]

\[
\eta_{2sf} = \frac{\varepsilon(\beta_a \frac{T_{red}}{T_{ox}} - 1)}{\varepsilon(\beta_a \frac{T_{red}}{T_{ox}} - 1)} \quad (7)
\]

Where \(\varepsilon\) is the ratio of the HRSG steam exit to hot gas inlet temperature (see Appendix B for details). Assuming \(\eta_{2sa} = \eta_{2sf} = 1\), equation 5 reduces to

\[
\eta = 1 - \frac{\ln(\beta_a)}{\ln(\beta_a - 1)} + \left(m_{fc} c_{pf}) T_1\right) \left(\frac{\beta_a \ln(\beta_a)}{\beta_a - 1} \left(\frac{T_{red}}{T_{ox}} - 1\right) - 1\right) - \ln \left(\frac{T_{red}}{T_{ox}}\right) \quad (8)
\]

Figure 5 is obtained by plotting efficiency from equation 5 against the reduction/oxidation reactor temperature ratio. The parameter values used are the same as those for the Brayton cycle, \(\varepsilon\) is assumed to be 0.75 and the lower bound for \(\frac{T_{red}}{T_{ox}}\) is defined such that \(T_{red} > T_1\).
Exothermic reduction reaction: Assuming no material constraints on the temperature of the reduction reactor, efficiency is maximized in the region to the right of B in figure 5 where $T_{\text{red}} > T_{\text{ox}}$. However, in practical conditions where oxygen carrier or HRSG material thermal properties impose stricter bounds on the maximum temperature, the optimal efficiency will correspond to the thermally balanced case defined by line B.

Endothermic reduction reaction: Since an endothermic reduction reaction needs to be sustained by heat transfer from the oxidation reaction, its temperature is limited by that of the oxidation reactor. Therefore the feasible region is to the right of B in figure 5 and the maximum efficiency corresponds to the thermally balanced operating point defined by line B. Note, however, that the profile of the efficiency curve in figure 5 is a function of the value defined for $\varepsilon$. When $\varepsilon = 1$, the expression for efficiency will correspond to equation 8 and maximum efficiency values will occur both at B ($\frac{T_{\text{red}}}{T_{\text{ox}}} = 1$) and at the left end of the plot $\left(\frac{T_{\text{red}}}{T_{\text{ox}}}\right)_{\text{min}}$. The region to the left of A is characterized by low temperatures and consequently slower reactions. Closer to $\left(\frac{T_{\text{red}}}{T_{\text{ox}}}\right)_{\text{min}}$, the temperature may also fall below the feasible equilibrium limit for many common oxygen carriers. For example, for nickel, the equilibrium reduction temperature for reaction with methane corresponds to $\frac{T_{\text{red}}}{T_{\text{ox}}} \approx 0.3$ and the reaction rate at A is about 500 times slower than the rate at B. Therefore, it is preferable to operate in the region A-B, and the maximum efficiency point lies at the B-boundary where the oxidation and reduction reactor temperatures are equal.
2.4. Combined CLC Cycle

Here, the foregoing analysis is extended to a simplified model of a combined CLC cycle, sketched in figure 6. Details of the derivation are contained in Appendix C. The efficiency for the combined CLC cycle is given by

\[
\eta = 1 - \frac{(W_{Ba} + W_{Bf}) + (W'_{Sa} + W'_{sf})}{Q}
\]  

(\(W_{Ba} + W_{Bf}\)) represents the net work output from the Brayton cycles, equivalent to equation 5 (equation C2 in Appendix C) while (\(W'_{Sa} + W'_{sf}\)) represents the net work output from the bottoming steam (Rankine) cycles, equivalent to a modified form of equation 5 (equation C3 in Appendix C) and Q is the overall reaction heat release. Neglecting steam cycle, turbine and compressor irreversibilities, equation 9 simplifies to

\[
\eta = 1 - \frac{\ln\left(\frac{\beta_a}{\beta_a - \pi^a}\right) + m_r c_p T_1}{Q} \left(\frac{\beta_a \ln\left(\frac{\beta_a}{\beta_a - \pi^a}\right)}{\beta_a - \pi^a} \left(\frac{T_{red}}{T_{ox}}\right) - 1\right) - \ln\left(\frac{T_{red}}{T_{ox}}\right)
\]  

(10)

Where \(\pi\) is the compressor pressure ratio, \(\beta_a = \frac{Tox}{T_1}\) and \(\left(\frac{T_{red}}{T_{ox}}\right)\) is the reactor temperature ratio. Similar to the case for the steam cycle, the combined CLC cycle efficiency in equation 9 is plotted against the reduction/oxidation reactor temperature ratio in figure 7 for selected compressor pressure ratios, using the same parameter values as in the Brayton and Steam cycle plots. The range of \(\left(\frac{T_{red}}{T_{ox}}\right)\) for each plot is defined such that \(T_{red} > T_1\pi^a\).

Now consider the scenarios for exothermic and endothermic reduction reactions:

**Exothermic reduction reaction:** For each pressure ratio, the profile is similar to that described for the simple Rankine cycle in figure 9 (which corresponds to \(\pi = 1\)) and so, the
same arguments apply; material considerations typically preclude the region to the right of B, therefore maximum feasible efficiency occurs at the thermally balanced operating point (B) where $T_{\text{red}} = T_{\text{ox}}$.

**Endothermic reduction reaction:** Similar to the case for the simple steam cycle, the feasible operating region lies to the left of B and fast kinetics favors operation in the region A-B. Within this region, the Maximum efficiency occurs at the B where $T_{\text{red}} = T_{\text{ox}}$.

To summarize, simplified thermodynamic models for the Brayton CLC cycle, the simple Steam CLC cycle and the combined CLC cycles have been used to analyze the impact of thermally balanced reactor operation on cycle efficiency. The basic inference is that when oxygen carrier material properties, process material constraints and kinetic considerations are taken into account, the optimal performance is obtained when both reactors are in thermal equilibrium. These conclusions are summarized in table 1.

**3. Detailed Aspen Flow Sheet Models**

The previous section examined the impact of reactor thermal coupling on the efficiency of the ideal Brayton, steam and combined CLC cycles. The results showed that when thermodynamic, kinetic and material constraints in practical CLC systems are factored in, thermally balanced reactor operation is preferred for optimizing system efficiency. Since the thermodynamic models used to arrive at this conclusion involved simplifying idealizations that may not capture some important constraints that exist in real systems, the current section uses the more detailed Aspen Plus® flow sheet models to assess the impact of thermal coupling on the different cycle configurations.
3.1. Cycle Description

A unique feature of CLC power generation systems is that there are two high temperature streams exiting the reactors, each of which can be used in different power generation arrangements. Therefore, there are up to $n^2$ possible configurational combinations for producing power compared to any $n$ for a conventional system, as shown in figure 8. The challenge then is to select an optimal combination of power generation strategies that would maximize performance. From the options listed in figure 8, there are 16 possible CLC cycle configurations that could be chosen. To avoid an intractable enumeration of all feasible cycle combinations, this study will select representative cycle arrangements for analysis. The configurations selected include the all the identical cycles – combined CLC cycle, regenerative CLC cycle, simple Brayton CLC cycle and simple steam CLC cycle – and some hybrid cycles – combined-regenerative CLC cycle, combined-steam CLC cycle and regenerative-steam CLC cycle. The naming convention omits the fuel side cycle name when the two are identical, and concatenates the air and the fuel side cycle names for the hybrid configurations. These configurations will be used to illustrate the main ideas from this study.

3.1.1. The Combined CLC Cycle

This configuration has received the most attention in CLC literature because of the high efficiencies associated with combined cycle systems. Cycle efficiencies reported in literature for single and multi-stage CLC reactors with methane fuel and complete CO$_2$ separation range from 47 – 53.5 % [1, 4, 6, 25-27]. The combined CLC cycle uses a combined cycle layout on both the air and fuel sides to produce work from each reactor exhaust stream, as shown in figure 9. On the air side, the inlet air stream is first
compressed, then sent to the rotary reactor, where it reacts exothermically with the oxygen carrier. Compression without intercooling is utilized to maximize the temperature of the reactor inlet stream. The air zone exhaust, which consists of a mixture of depleted air from the air sector and steam from the air purge sector, is first expanded in a turbine to produce power before flowing into the HRSG to generate steam for the bottoming steam cycle. Power is produced in the steam cycle from the high and low pressure steam turbines and the cool HRSG exhaust is released into the atmosphere. The fuel side follows an almost identical process up to the HRSG. Some of the CO$_2$ from the fuel side HRSG exhaust is recycled to the fuel inlet where it serves as a diluent gas for the fuel. The rest is dried and compressed in the CO$_2$ compression unit. Air and fuel sector purge steam are extracted from intermediate pressure turbines in the respective steam cycles, reheated in the HRSG and then sent to the rotary reactor.

### 3.1.2. Simple CLC cycles

The simple cycles refer to the Brayton and steam CLC cycles. The layouts are similar to that described for the combined cycle except that for the simple steam cycle, there are no gas turbines or compressors, and for the Brayton cycle, there are no bottoming steam cycles on either the fuel or air side.

### 3.1.3. Hybrid cycles

Hybrid configurations are motivated by the need to achieve some performance/complexity/cost tradeoff between cycle options. Hybrid cycles selected for this study include the combined-regenerative cycle (combined cycle on the air side, regenerative cycle on the fuel side), combined-steam cycle (combined cycle on the air side, steam cycle on the fuel side) and regenerative-steam cycle (regenerative cycle on the air side).
side, steam cycle on the fuel side). In the combined-steam and the regenerative-steam cycles, the CO\textsubscript{2}-rich reactor exhaust is used directly in a heat recovery steam generator without expansion in a gas turbine. This way, they reduce CO\textsubscript{2} compression energy penalty.

The schematic of the Aspen flow sheet for the combined-regenerative cycle is shown in figure 10. It adapts the combined CLC cycle design by replacing the fuel side combined cycle with a regenerative cycle instead. The regenerative cycle layout is has been described in detail in [24]. The regenerator in the combined-regenerative CLC cycle offers a less complex and probably more cost effective alternative to installing a bottoming steam turbine engine on the fuel side.

### 3.2. Rotary Reactor Model in Aspen

The rotary reactor, described in detail in [20-23], is essentially a solid wheel with a matrix of micro channels whose walls provide structural integrity and thermal management for the entire reactor. The Aspen Plus® setup for the reactor model is described in [24]. It accommodates the twofold objective of achieving quasi-thermally balanced operation and accounting for the air and fuel sector purge steam generation.

### 3.3. Model specifications

The modeling assumptions and specifications used in developing the Aspen Plus® system models are summarized in tables 2 and 3. For the reactor model, nickel is used as the oxygen carrier with boron nitride as the support material. The base case reactor temperature was set at 1200°C. A base case operating pressure of 10 bars is used and reactor pressure drop is neglected since the value is very small for the rotary reactor [23].
3.4. Results

3.4.1. The Brayton CLC cycle configuration

Figure 11 shows a slight negative correlation between the efficiency and the reduction/oxidation reactor temperature ratio \( \frac{T_{\text{red}}}{T_{\text{ox}}} \) at low operating pressures (10 and 14 bars). This contrasts with the results from the idealized cycle analysis, partially due to the effect of incorporating purge steam generation and CO\(_2\) recycle. Also, thermally balanced reactor operation results in a higher fuel side exhaust enthalpy which is lost to the environment as there is no exhaust heat recovery in the Brayton Cycle. However, at higher pressure ratios - when the turbine exhaust temperatures are closer to ambient and exhaust availability loss is low - the trend reverses and efficiency positively correlates with \( \frac{T_{\text{red}}}{T_{\text{ox}}} \) as shown in figure 11 for 40 and 50 bars.

3.4.2. The steam and the combined CLC cycle configurations

The efficiency of both the steam cycle and the combined cycle increase with increasing reactor temperature ratio, as shown in figures 12 and 13. This trend is consistent with the suggestion from the preceding theoretical analysis in section 2. Note from figure 13 that the relationship between efficiency and reactor temperature ratio for the combined CLC cycle is not linear; it levels off as reactor temperature ratio approaches unity. This is most likely a consequence of the externally constrained maximum steam temperature for the bottoming steam cycle. Thermally balanced reactor operation increases the reduction reactor temperature, creating a higher temperature gas turbine exhaust stream. Since the maximum permissible steam temperature remains at 560°C, HRSG entropy generation increases with increasing reduction reactor exhaust gas temperature. This creates an
increasingly inefficient bottoming steam cycle, partly eroding the advantage that derives from having a higher temperature fuel side exhaust stream.

3.4.3. The hybrid CLC configurations

The hybrid configurations show mixed results. The combined-regenerative cycle in figure 14 behaves consistently with the expectations from the theoretical analysis. On the other hand, the steam-based hybrid cycles exhibit a reverse trend as shown the same figure. The reason is because the 560°C steam temperature cap leads to larger entropy generation in the HRSG as the reduction reactor temperature increases. Thus, the larger enthalpy in the fuel side exhaust stream is much more inefficiently converted in the fuel side steam cycle. Therefore, the additional fuel side work output does not make up for the corresponding air side loss. This conclusion is also supported by the analysis carried out by Hammers et al for an IGCC plant integrated with a downstream combined-steam CLC cycle [28]. Therefore, in order to benefit from thermally balanced reactor operation, the fuel side cycle must be a high efficiency design capable of taking advantage of the resulting increase in the availability of the reduction reactor exhaust stream. Cycles like the combined CLC cycle, the regenerative CLC cycle or the combined-regenerative hybrid cycle can exploit this advantage and are therefore ideal for integration with the thermally coupled rotary reactor.

4. Parametric Studies

Section 3 identified the combined cycle and combined-regenerative cycles as suitable cycle configurations for integrating with the rotary reactor. The analysis of the regenerative CLC
cycle [24] also demonstrated its suitability for the rotary reactor. The objective of the parametric studies then is to characterize and compare how key design and operating parameters impact the efficiency of these rotary reactor-based power plant configurations. The design and operating parameters examined in this study are cycle pressure ratio, CO₂ fraction in the inlet fuel feed stream, purge steam generation strategy and purge steam demand. For the pressure sensitivity study, the system pressure ratio was varied from 2 to 20 for each cycle configuration while for the feed stream CO₂ fraction study, the CO₂ fraction was varied from around 0.3 to 0.9 by adjusting the exhaust CO₂ recycle ratio. All other design specifications are fixed at the base case values. The Pressure-TIT study is used to analyze how the efficiency/pressure profile varies with varying turbine inlet (or reactor) temperature. The steam generation study is used to compare the impact of steam requirement, as well as steam generation strategy, on system performance.

4.1. Pressure Ratio Sensitivity

The cycle pressure ratio has a significant impact on the efficiency of rotary reactor CLC-based systems. Figure 15 shows the variation of efficiency with pressure for the different cycle configurations. The profiles for combined cycle and the combined-regenerative CLC cycle configurations are similar because for both configurations, the air side combined cycle is the dominant contributor to net work output. The maximum efficiency for either cycle occurs between 11 and 13 pressure ratio range with values of 53.3% and 53.8% for the combined and the combined-regenerative CLC cycles respectively. The dip in efficiency beyond 15 bar is caused mainly by the drop in steam cycle power output as the
temperature of the turbine exhaust falls. There is also some penalty associated with the fact that the current cycle setup is not optimized for high pressure ratios. The regenerative cycle on the other hand peaks at the lower pressure ratio of around 3 with approximately 56% efficiency. Based solely on performance considerations, the regenerative configuration operating at low pressures appears to be the most attractive. However, lower pressures imply higher volumetric gas flow rates, which in turn may require larger regenerators and reactors, and probably, higher costs. The combined-regenerative cycle offers a tradeoff that is slightly more efficient than the combined cycle and avoids the large equipment sizes that the lower pressure regenerative cycle requires.

4.2. Pressure ratio – TIT Sensitivity

This study identifies and compares the optimal efficiency region in the space defined by pressure ratio and turbine inlet temperature (TIT) for the combined, regenerative and combined-regenerative cycles. The results are shown in figures 16-18.

From figure 16, the optimal pressure ratio for the combined CLC cycle is seen to be a strong function of TIT; it varies from 6 at 1000°C (48.6% efficiency) to 14 at 1250°C (54.3% efficiency). A similar trend is observed for the combined-regenerative CLC cycle (figure 17) which varies from 6 at 1000°C (48.5%) to 13 at 1250°C (55%). In contrast, the optimal pressure ratio for the regenerative CLC cycle is not a strong function of TIT, changing only from 3 to 4 as TIT varies from 1000°C (51%) to 1250 (57%), as illustrated in figure 18. Thus for the combined and combined-regenerative cycles, the optimal point lies in the high pressure, high TIT region while for the regenerative cycle, it lies in the low pressure, high TIT region.
4.3. CO₂ fraction sensitivity

Recycled CO₂ is used as the carrier or diluent gas for the fuel supply to the reactor. In fluid bed reactor designs, the amount of CO₂ recycle is determined by fluidization requirements. Since the rotary reactor does not require fluidization, the impact on efficiency provides an alternative criteria for determining the optimal CO₂ diluent fraction. The result for this study is shown in figure 19. The profiles for the regenerative and combined-regenerative configurations are very similar since they both have a regenerative engine on the fuel side and therefore show identical responses to CO₂ recycle. Moreover, at 10 bars, the efficiencies of the two designs are very similar. For both cases, higher CO₂ fraction increases cycle efficiency. On the other hand, increasing CO₂ recycle reduces efficiency for the combined CLC cycle and the reason for this trend is explained as follows: Since the fuel side turbine exhaust temperature is higher than that on the air side - though both have the same HRSG steam temperature constraint - the fuel side combined cycle engine experiences larger irreversibility in the HRSG and ends up the less efficient engine. Since increasing CO₂ recycle reduces air flow required for reactor temperature control, the net effect is moving more flue gas to the less efficient fuel side engine and thus, a resulting drop in efficiency. Therefore, the combined cycle performs better with lower fractions. The optimal CO₂ fraction will have to be determined from a tradeoff between cycle efficiency and the impact on reactor size and performance.

4.4. Purge Steam generation strategy

Purge steam is required in the rotary reactor to avoid gas leakage between the reduction (fuel) and the oxidation (air) zones of the rotary reactor. Nonetheless, providing purge
steam for the reactor purging could constitute a net parasitic power demand on the system. For this reason, care has to be taken in selecting the optimal amount of, as well as the least costly approach to, steam generation. Depending on the cycle configuration, there are a number of options for generating the required purge steam. These include direct steam generation from the air and fuel side regenerative heat exchangers, and steam extraction from the air and fuel side steam cycles. The strategy adopted affects the overall efficiency of the system. To illustrate this, each of the cycles are simulated with steam supplied entirely from the air side or fuel side cycle. Figure 20 presents the efficiency obtained for each case.

The efficiency for the regenerative and the combined-regenerative configurations drop when steam generation is switched from the fuel side to the air side cycle while that for the combined-CLC cycle does not change much. To understand why this happens, consider the fuel side regenerator temperature-duty profile in figures 21a and 21b. In figure 21a, the fuel side regenerator is used to generate steam and we see from the profile that the heat recovery process is efficient. Figure 21b shows the profile for the same exchanger when there is only fuel preheating and no steam generation. In this case, the thermal capacity of the hot exhaust stream is significantly higher than that of the cold fuel inlet stream. This creates an unbalanced heat exchanger with hot side pinch and substantial sensible enthalpy loss to the environment. Thus, there is a greater opportunity for exhaust enthalpy recovery on the fuel side, which can be exploited by generating all the purging steam from corresponding regenerative heat exchanger.

4.5. Purge Steam Generation Requirement

Figure 22 illustrates the sensitivity of cycle efficiency to the required amount of purge steam generation for the three cycle configurations. The net effect of steam addition is a
balance between the energetic cost of producing steam, the additional power output from increased exhaust flow and the resulting change in exhaust heat recovery. Steam generation always constitutes a net efficiency penalty for the combined cycle in the range considered because the steam is extracted from an intermediate pressure turbine in the steam cycle instead of being further expanded to produce more power. For the regenerative and the combined-regenerative cycles, the net effect is positive up to about twice the fuel flow rate because in this range, generating steam also improves exhaust heat recovery. Beyond this point, additional steam generation deteriorates exhaust heat recovery; the energetic cost of steam generation becomes dominant and the net impact on efficiency is negative. This impact is more dramatic for the regenerative cycle because the combined-regenerative cycle can extract additional steam from the steam cycle, which at this point has become less costly than additional steam production in the regenerator.

Purge steam demand depends primarily on the reactor temperature, pressure and oxygen carrier type. Highly reactive oxygen carriers like nickel need smaller purge steam flow while oxygen carriers with slower reduction reaction rate like iron have much higher purge steam demand. For example, using the rotary reactor model developed in [21], a particular design for a nickel based rotary reactor at 10 bar and 1180°C can achieve ~99% CO₂ separation efficiency steam demand at a little over twice the fuel flow rate while an iron-based reactor could require 6 x the fuel flow rate. Therefore, steam generation requirement should be an important oxygen carrier selection criteria, given the potential impact on cycle efficiency.
The optimal efficiency map in figure 23 presents a summary of the key results from the preceding parametric analysis.

5. Conclusion

In this study, the integration of the thermally coupled redox rotary reactor with energy conversion systems was examined in some detail. Conceptual and more detailed thermodynamic analyses demonstrate that the thermally balanced reactor operation creates the potential for higher cycle efficiencies. This potential, however, can only be actualized by high efficiency cycle configurations that are capable of exploiting the resulting increase in the reduction reactor exhaust enthalpy. Therefore, the regenerative, combined and hybrid combined-regenerative cycles are the recommended configurations for integration with the rotary reactor.

The key design and operating parameters that define system performance include allowable turbine inlet temperature, compressor pressure ratio and feed stream CO₂ fraction. An analysis of the sensitivity of cycle thermal efficiency to these parameters is used to map out the optimal performance region for each configuration. Of the three configurations compared, the regenerative cycle has the highest efficiency in the parameter space covered in this study. Another advantage of the regenerative cycle over the combined cycle is that the regenerators provide a means for sufficiently preheating the reactor inlet streams. Higher reactor inlet stream temperatures support faster reactions and minimize temperature gradients in the reactor; faster reactions mean smaller reactors while low
temperature gradients minimize thermal stresses and improve operational stability. The main drawback for the regenerative cycle is that its optimal operating point is at a low pressure ratio. This means larger regenerators, and other equipment to handle the large volumetric gas flows. The combined-regenerative cycle offers a useful tradeoff; like the regenerative cycle, the fuel side regenerator preheats the inlet fuel stream; since the oxidation reaction with nickel is highly exothermic, the inlet air stream is quickly heated up and does not significantly disrupt the thermal profile in the reactor; it operates optimally at elevated pressures and so, unlike the regenerative cycle, does not need to handle excessively large volumetric flows; finally, it can support larger purge steam demands with lower associated energy penalty than the other CLC cycles.

Another important factor to consider in rotary reactor-based system design is the purge steam generation strategy. The impact of the rotary reactor purge steam on efficiency depends on the amount of steam required, the steam generation strategy as well as the oxygen carrier type. Oxygen carriers with fast reduction reactions like nickel have lower purging steam requirements. Low purge steam requirement can increase efficiency in regenerative and combined-regenerative CLC cycles when it provides a means for improved exhaust heat recovery. It always constitutes an energetic penalty when the purge steam has to be extracted from a steam turbine, like in the case for a combined CLC cycle. This makes purge steam demand is a very important criteria for selecting oxygen carriers, specifying optimal reactor design parameters and choosing an appropriate cycle configuration.
6. Future Work

The thermodynamic models used in this study still incorporate simplifications that need to be relaxed in order to capture more accurately the performance of a real rotary reactor-based power plant. On the one hand, the current simplified reactor model does not match the fuel and air zone exhaust temperatures as demonstrated from the more detailed simulation results [20, 21]. The steam cycles used in the relevant cycle configurations are non-reheat systems; though this design has a lower capital cost, it is less efficient than a reheat system since it recovers less enthalpy from the hot exhaust stream. On the other hand, the reactor model does not predict the purge steam demand, which has been shown in this work to have a significant effect on the efficiency of the power plant. The analysis did not account for pressure drops in pipes and heat exchangers, and the low temperature/low pressure regenerators downstream of the HRSG in the combined cycle and the combined-regenerative cycle models increase efficiency by only about 0.5%, which may not justify the associated cost. To more accurately predict the performance of an actual system, future studies will integrate a higher fidelity rotary reactor model with a more detailed cycle model, which will account for all these factors. A detailed economic analysis will also be useful in identifying and eliminating superfluous components.
Acknowledgement

This study is financially supported by a grant from the MASDAR Institute of Science and Technology and the King Abdullah University of Science and Technology (KAUST) Investigator Award.

Appendices

The following ideal analytical models for CLC power cycle configurations are developed using classical thermodynamic cycle analysis and thermal engine concepts. More details on these fundamental concepts can be found in [29-31] or any other relevant thermodynamic text.

Appendix A: Simple Brayton CLC Cycle

Definitions

\[ T_{1f} = T_{1a} = T_1 \]  
\[ T_{ox} = T_{3a} \]  
\[ T_{red} = T_{3f} \]

A schematic representation of the simple Brayton CLC cycle is shown in figure 3. Applying energy balance to the air side components, fuel side components and the reactor gives

Air Side Balance

\[ W_{Ba} = W_{turb_{a}} + W_{compa} = m_a c_{pa} T_1 \left( \frac{\alpha^{\alpha-1}}{\eta_c} \right) \left( 1 - \frac{\beta a \eta_T \eta_c}{\eta_a} \right) \]  

(A1)

Fuel Side Balance
\[ W_{Bf} = W_{\text{turb}} + W_{\text{comp}} = m_f c_p f T_1 \left( \frac{\pi^a-1}{\eta_c} \right) \left( 1 - \frac{\beta a \eta_T \eta_c}{\pi^a \eta_{ox}} \right) \] (A2)

**Reactor Balance**

\[ m_a = \frac{Q \eta_c - m_f c_p f T_1 (\beta a \eta_c (\eta_{red} - \pi^a + 1 - \pi^a) - \pi^a - 1)}{c_p a T_1 \beta a \eta_c (\pi^a + 1 - \pi^a)} \] (A3)

Therefore, the efficiency of the system is given by

\[ \eta = - \frac{W_{Ba} + W_{Bf}}{Q} = \frac{\pi^a - 1}{\pi^a} \left( \frac{\beta a \eta_T \eta_c - \pi^a}{\beta a \eta_c - \pi^a + 1 - \pi^a} \right) \left( \eta_T \eta_c (1 - \eta_c) + \eta_c \pi^a (1 - \eta_T) \right) \left( 1 - \frac{\eta_{red}}{\eta_{ox}} \right) \] (A4)

For the ideal case where \( \eta_c = \eta_T = 1 \), equation A8 reduces to the classical expression for the ideal Brayton cycle efficiency

\[ \eta = \frac{\pi^a - 1}{\pi^a} \] (A5)

**Appendix B: Simple Steam CLC Cycle**

**Definitions**

\[ T_{1f} = T_{1a} = T_1 \] (i)

\[ T_{ox} = T_{2a} \] (ii)

\[ T_{red} = T_{2f} \] (iii)

A schematic representation of the simple Steam CLC cycle is shown in figure 4 and the thermodynamic representation of the Rankine engine is shown in figure 5. Applying the laws of thermodynamics to the air side components, fuel side components and the reactor gives

**Air Side Balance**
\[-W_{Sa} = m_a c_p a T_1 \eta_{sa} (\beta_a - 1 - \ln(\beta_a)) \quad (B1)\]

Fuel Side Balance

\[-W_{Sf} = m_f c_p f T_1 \eta_{sf} \left(\beta_a \left(\frac{T_{\text{red}}}{T_{\text{ox}}}\right) - 1 - \ln \left(\frac{T_{\text{red}}}{T_{\text{ox}}}\right)\right) \quad (B2)\]

Reactor Balance

\[m_a = \frac{Q - m_f c_p f T_1 (\beta_a \frac{T_{\text{red}}}{T_{\text{ox}}} - 1)}{c_p a T_1 (\beta_a - 1)} \quad (B3)\]

Therefore, the efficiency of the system is given by

\[\eta = - \frac{W_{Sa} + W_{Sf}}{Q} = \eta_{2sa} \left(1 - \frac{\ln(\beta_a)}{\beta_a - 1}\right) + \frac{m_f c_p f T_1}{Q} \left(\beta_a \frac{T_{\text{red}}}{T_{\text{ox}}} - 1\right) \left(\eta_{2sf} \left(1 - \frac{\ln(\beta_a \frac{T_{\text{red}}}{T_{\text{ox}}})}{\beta_a \frac{T_{\text{red}}}{T_{\text{ox}}}}\right) - \eta_{2sa} \left(1 - \frac{\ln(\beta_a)}{\beta_a - 1}\right)\right) \quad (B4)\]

The approximate steam cycle 2nd law efficiencies can be defined such that

\[\eta_{2sa} \left(1 - \frac{T_1}{T_{sa}}\right) = 1 - \frac{T_1}{T_{sa}} \quad (B5)\]

\[\eta_{2sf} \left(1 - \frac{T_1}{T_{\text{red}}}\right) = 1 - \frac{T_1}{T_{\text{red}}} \quad (B6)\]

Assuming that \(T_{sa} = \varepsilon T_{ox}\) and \(T_{sf} = \varepsilon T_{ox}\) for \(0 < \varepsilon \leq 1\) and \(\beta_a \geq 1\), then

\[\eta_{2sa} = \frac{\varepsilon \beta_a - 1}{\varepsilon (\beta_a - 1)} \quad (B7)\]

\[\eta_{2sf} = \frac{\varepsilon \beta_a \frac{T_{\text{red}}}{T_{\text{ox}}} - 1}{\varepsilon (\beta_a \frac{T_{\text{red}}}{T_{\text{ox}}} - 1)} \quad (B8)\]

Assuming ideal process (\(\eta_{sa} = \eta_{sf} = 1\)), equation B4 reduces to

\[\eta = 1 - \frac{\ln(\beta_a)}{\beta_a - 1} + \left(\frac{m_f c_p f T_1}{Q}\right) \left(\frac{\beta_a \ln(\beta_a)}{\beta_a - 1} \left(\frac{T_{\text{red}}}{T_{\text{ox}}} - 1\right) - \ln \left(\frac{T_{\text{red}}}{T_{\text{ox}}}\right)\right) \quad (B9)\]
For a thermally balanced reactor \( \frac{T_{\text{red}}}{T_{\text{ox}}} = 1 \), equation B9 simplifies to the classical expression for an ideal steam cycle power plant efficiency

\[
\eta = 1 - \frac{\ln \beta_a}{\beta_a - 1}
\]  

(B10)

Appendix C: Combined CLC Cycle

Definitions

\[
T_{1f} = T_{1a} = T_1
\]  

(i)

\[
T_{ox} = T_{3a}
\]  

(ii)

\[
T_{\text{red}} = T_{3f}
\]  

(iii)

A schematic representation of the combined CLC cycle is shown in figure 6. It can be seen that the efficiency of the combined cycle is the sum of components from the Brayton cycle and the bottoming steam (Rankine) cycle. Therefore,

\[
\eta = -\frac{(W_{Ba} + W_{Bf}) + (W'_{Sa} + W'_{Sf})}{Q}
\]  

(C1)

Similar to equation A8

\[
\frac{(W_{Ba} + W_{Bf})}{Q} = \frac{\pi^{a-1}}{\pi^a} \left( \frac{\beta_a \eta_T \eta_c - \pi^a}{\beta_c \eta_c - \pi^{a+1} - \eta_c} \right) - \frac{\pi^{a-1}}{Q \eta^a} \left( \frac{m_{fc} \eta_{T1} \beta_a}{\beta_a \eta_c - \pi^{a+1} - \eta_c} \right) \left( \eta_T \eta_c (1 - \eta_c) + \eta_c \pi^a (1 - \eta_T) \right) \left( 1 - \frac{T_{\text{red}}}{T_{ox}} \right)
\]  

(C2)

Similar to equation B4,

\[
\frac{(W'_{Sa} + W'_{Sf})}{Q} = \eta'_{sa} \left( 1 - \frac{\ln (\beta'_a)}{\beta'_a - 1} \right) + \frac{m_{fc} \eta_{T1}}{Q} \left( \beta'_a \frac{T_{\text{red}}}{T_{ox}} - 1 \right) \left( \eta_{sf} \left( 1 - \frac{\ln (\beta'_{T \text{red}})}{\beta'_{a T_{\text{red}}} - 1} \right) - \eta'_{sa} \left( 1 - \frac{\ln (\beta'_a)}{\beta'_a - 1} \right) \right)
\]  

(C3)

Where

\[
\beta'_a = \beta_a (1 - \eta_T + \eta_T \pi^{-\alpha})
\]  

(C4)
Equation C4 captures the fact that the hot gas inlet temperature to the steam cycle HRSG is the turbine exhaust temperature and not the reactor exhaust, as in the case for the simple steam cycle. Thus,

\[
\eta'_2sa = \frac{e^{\beta_{ra} - 1}}{e^{(\beta_{ra} - 1)}} \tag{C5}
\]

\[
\eta'_2sf = \frac{e^{\beta_{ra} (T_{red}/T_{ox}) - 1}}{e^{(\beta_{ra} (T_{red}/T_{ox}) - 1)}} \tag{C6}
\]

For an ideal process (\(\eta'_2sa = \eta'_2sf = \eta_c = \eta_T = 1\)), equation C1 simplifies to

\[
\eta = 1 - \frac{\ln(\beta_a/\beta_a - \pi a)}{\beta_a - \pi a} + \frac{m_f c_p f T_1}{Q} \left[ \frac{\beta_a \ln(\beta_a)}{\beta_a - \pi a} \left( \frac{T_{red}}{T_{ox}} - 1 \right) - \ln \left( \frac{T_{red}}{T_{ox}} \right) \right] \tag{C7}
\]

For a thermally balanced reactor (\(T_{red}/T_{ox} = 1\)), equation C7 simplifies to the following expression for an ideal combined cycle power plant efficiency

\[
\eta = 1 - \left( \frac{\ln (T_{ox}/T_1 \pi a)}{T_{ox}/T_1 - \pi a} \right) \tag{C8}
\]

References


[22] Zhao, Z., Rotary bed reactor for chemical-looping combustion with carbon capture, Massachusetts Institute of Technology, Massachusetts, 2012.


Figures

Figure 1: Isometric projection of the Rotary Reactor wireframe. The inlet side is divided into four fixed-size sectors; air, air purge, fuel and fuel purge. The exit side is divided into two zones: the fuel zone, which combines the fuel and fuel purge sector exhaust streams; and the air zone, comprising of depleted air and air purge steam streams [21,23]
Figure 2: Simple (Brayton) CLC Cycle

![Diagram of the Simple (Brayton) CLC Cycle]

- $W_{Ta}$
- $W_{Tf}$
- $W_{ca}$
- $W_{cf}$
- $Q = |\Delta H|$
Figure 3: Analyzing impact of reactor thermal balance on efficiency for a Simple Brayton CLC Cycle

![Diagram of CLC Cycle](image1)

Figure 4a: Schematic for idealized Simple CLC Steam cycle

![Diagram of Rankine Cycle and CLC Reactor](image2)

Figure 4b: Ideal Steam (Rankine) engine model

![Diagram of Ideal Steam Engine](image3)
Figure 5: Analyzing impact of reactor thermal balance on efficiency for a Simple Steam CLC Cycle

Figure 6: Schematic for idealized combined CLC cycle
Figure 7: Analyzing impact of reactor thermal balance on efficiency for a combined CLC Cycle

Figure 8: Possible energy conversion systems configurations for CLC
Figure 9: Aspen Plus® Flowsheet Schematic for the Combined CLC Cycle

Figure 10: Aspen Plus® Flowsheet Schematic for the Combined-Regenerative CLC Cycle
Figure 11: Fuel/Air reactor temperature ratio \(\frac{T_{\text{red}}}{T_{\text{ox}}}\) sensitivity for Brayton CLC Cycle. At low operating pressures, thermally balanced reactor operation results in increased fuel side exhaust enthalpy loss to the environment, hence, the drop in efficiency. At higher operating pressures, exhaust enthalpy loss is minimized, resulting in increased efficiency.

Figure 12: Fuel/Air reactor temperature ratio \(\frac{T_{\text{red}}}{T_{\text{ox}}}\) sensitivity for simple CLC steam cycle. Efficiency appears to be positively correlated to reactor thermal balance.
Figure 13: Fuel/Air reactor temperature ratio ($\frac{T_{\text{red}}}{T_{\text{ox}}}$) sensitivity for combined CLC cycle. Efficiency is generally positively correlated to degree of reactor thermal balance.

Figure 14: Fuel/Air reactor temperature ratio ($\frac{T_{\text{red}}}{T_{\text{ox}}}$) sensitivity for the hybrid CLC cycles. Thermally balanced reactor operation increases efficiency for combined-regenerative (CR) cycle but decreases in the case of the combined-steam (CS) and regenerative-steam (RS) cycles because the maximum temperature constraint on the bottoming steam cycle increases availability loss as $T_{\text{red}}$ increases.
Figure 15: Pressure sensitivity

Figure 16: Pressure/TIT multivariable analysis result for the combined CLC cycle: optimal conditions in the high pressure and high TIT region
Figure 17: Pressure/TIT multivariable analysis result for the regenerative CLC cycle: optimal conditions in the low pressure and high TIT region

Figure 18: Pressure/TIT multivariable analysis result for the combined-regenerative CLC cycle: optimal conditions in the high pressure and high TIT region
Figure 19: Feed stream CO$_2$ fraction sensitivity

Figure 20: Choice of Steam Generation Strategy could impact efficiency by as much as 2% points for the regenerative cycles. The combined cycle is much less sensitive. Results obtained 10bar and 1.5 kmol/sec steam demand.
Figure 21a: Fuel side regenerator temperature profile (with steam generation) for the Combined-Regenerative CLC cycle configuration – shows substantial exhaust heat recovery

Figure 21b: Fuel side regenerator temperature profile (without steam generation) for Combined-Regenerative CLC cycle configuration – shows significant sensible heat still in the exhaust stream, lost to the environment
Figure 22: The effect of purge steam generation on efficiency is mostly a balance between steam generation energy penalty, additional work output from larger exhaust flow and change in exhaust enthalpy recovery. This balance is also a function of the required steam flow rate. Results obtained at 10 bar; fuel flow is 1kmol/sec.

Figure 23: Optimal efficiency map summarizing the results from the parametric analysis.
Tables

Table 1: Summary table for non-ideal Brayton, steam cycle and combined cycle analysis in section 2

<table>
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<tr>
<th>Reduction Reaction</th>
<th>Condition for Maximum Efficiency</th>
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<tr>
<td></td>
<td>Thermodynamic Constraints only</td>
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<td>Endothermic</td>
<td>$T_{\text{red}} = T_{\text{ox}}$</td>
</tr>
<tr>
<td>Exothermic</td>
<td>$T_{\text{red}} &gt; T_{\text{ox}}$</td>
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Table 2: Simulation Specifications for base case models

<table>
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<th>Item</th>
<th>Units</th>
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<td>Ambient Temperature</td>
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<td>Pressure Ratio$^1$</td>
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<td>Gas Compressor Isentropic Efficiency</td>
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<tr>
<td>Gas Turbine Isentropic Efficiency</td>
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<td>90%</td>
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<td>Oxygen Carrier (MeO / Me)</td>
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<td>NiO / Ni</td>
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<td>Regenerative Heat Exchanger Minimum</td>
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<td>Internal Temperature Approach</td>
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<td><strong>Steam Cycle</strong></td>
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<td>Pump Efficiency</td>
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<td>Inlet Air N$_2$ Composition</td>
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</tr>
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</table>
Inlet Air \(O_2\) Composition | Fraction | 0.21
---|---|---
Recycled CO\(_2\) / CH\(_4\) Composition in inlet Stream | Ratio | 3 : 1
Oxidation Reactor Purge Steam Rate | Kmol/sec | 1
Reduction Reactor Purge Steam Rate | Kmol/sec | 0.5

**Variable Design/Operating Parameters**

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<tr>
<th>Inlet air flow rate</th>
<th>Varied to control the oxidation reactor temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron nitride (bulk support material) circulation rate</td>
<td>Varied to control reduction reactor temperature</td>
</tr>
</tbody>
</table>

1. Does not apply to the ambient pressure simple steam cycle
2. For sensitivity studies, when exhaust gas inlet temperatures are lower (e.g. high pressure ratio cases), the value is freed and allowed to vary subject to the specified pinch value.

### Table 3: Base case configuration-specific design strategy

<table>
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<tbody>
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<td>Air side regenerator</td>
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