Solar electricity via an Air Brayton cycle with an integrated two-step thermochemical cycle for heat storage based on $\text{Co}_3\text{O}_4/\text{CoO}$ redox reactions: Thermodynamic analysis

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Abstract

Solar electricity production is considered in an Air Brayton cycle with an integrated two-step thermochemical cycle for heat storage based on $\text{Co}_3\text{O}_4/\text{CoO}$ redox reactions. The two steps of the heat storage cycle are encompassed by 1) the high-temperature thermolysis of Co_3O_4 to CoO and O_2 under vacuum pressure utilizing concentrated solar irradiation for process heat; and 2) the highly exothermic re-oxidation of CoO with O_2 at elevated pressures, resulting in Co_3O_4 and providing the heat input to the Air Brayton cycle. The two steps may be decoupled, enabling long-term storage of heat (i.e., thermochemical storage of sunlight). A thermodynamic analysis is applied to determine cycle efficiencies over a range of operating parameters, and an exergy analysis is used to identify the major sources of irreversibilities. A maximum cycle efficiency of 44% was determined for re-oxidizing the CoO at 30 bar, with the maximum cycle efficiency reducing to 26% for a decrease in pressure to 5 bar.

Keywords: Concentrated Solar Energy; Thermochemical Energy Storage; Two – Step Thermochemical Cycle; Cobalt Oxide; Thermodynamic Analysis

1. Introduction

Sunlight is by far the most abundant energy resource available on earth. However, solar irradiation is relatively dilute and intermittent. Measures have been taken to overcome these obstacles in regions with abundant solar resources by concentrating solar irradiation and using the resulting heat to produce electricity [i.e., concentrated solar power (CSP)]. Solar concentrating facilities equipped with power towers with heliostat fields and parabolic dishes are capable of achieving solar concentrations in excess of 1000 suns (1 sun = 1 kW/m²). Major challenges to current CSP systems are effectively storing intermittent sunlight and operating at high temperatures, directly translating to higher efficiencies. Increasing CSP heat storage capabilities offers a renewable pathway forward towards significantly extending solar electricity production to periods when sunlight is unavailable. On-demand production greatly improves the value of CSP, and the economic competitiveness of CSP facilities is inherently tied to the capacity for energy storage (Pitz-Paal et al. 2012).

Three methods are currently employed to store solar heat: 1) sensible energy storage (SES), 2) latent energy storage (LES), and 3) thermochemical energy storage (TCES). SES systems store sensible energy using heat transfer fluids (e.g., oil, synthetic oil, molten salts, etc.). SES is commonly used for commercial CSP systems, but it affords numerous challenges due to high pressure components, cost of different heat transfer media, and temperature limitations that impede facility operations (Medrano et al. 2010). This is especially prevalent with molten salts (e.g., NaNO₃ and KNO₃ mixtures) that solidify below 200 °C and often degrade at temperatures greater than 600 °C (Medrano et al. 2010, Ho et al. 2014). Maintaining these temperatures is challenging, with the maximum temperature limiting the facility output work potential. An alternative SES system is a falling particle receiver, which utilizes a curtain of ceramic particles or proppants as a thermal storage medium. The particles are predicted to heat rapidly to temperatures greater than 600 °C and can be temporarily stored to retain sensible heat while remaining stable. The high temperature particles can be accessed on demand to supply process heat to the working fluid of a power cycle (Siegel and Kolb 2009, Ho et al. 2014).

CSP facilities with LES capability store heat in a phase change material (PCM) with a high heat of fusion. Heat is stored when a thermal gradient exists between the heat transfer fluid (HTF) and the PCM. A heat exchanger then transfers heat to the PCM, storing heat by driving the PCM

phase change. Heat extraction occurs when solar conditions fluctuate and the HTF becomes cooler than the PCM, removing the heat from the material. Challenges to LES include the selection of a PCM and the large thermal resistance between the PCM and HTF. A favorable PCM must have high thermal conductivity and a constant charge/discharge temperature during phase change that is tailored to the working conditions of the CSP facility (Sharma et al. 2009, Liu et al. 2012). The low thermal conductivities of most PCMs require specialized storage / heat exchange units with a series of highly conductive fins to promote heat transfer (Steinmann et al. 2009). One of the most extensively studied PCMs includes NaNO_3 . Previous works have assessed the eutectic mixture of NaNO_3 / KNO_3 in a 100 kW_{th} latent heat storage system. The system successfully stored and extracted heat from the PCM, providing process heat to a Steam – Rankine cycle despite low HTF temperatures (Bayón et al. 2010).

TCES systems utilize concentrated solar irradiation as process heat to drive reversible chemical reactions, enabling the storage of sunlight in a chemical form. Stored heat is extracted by running the reverse chemical reaction, releasing heat to drive power cycles. Previous work has resulted in an ammonia-based TCES able to deliver process heat at 475 °C to a power cycle (Lovegrove et al. 1999). Alternative TCES studies include two-step solar thermochemical cycles based on metal oxide redox reactions (Bilgen et al. 1977, Fletcher 2000, Kodama 2003, Steinfeld 2005, Meier and Sattler 2009, Perkins and Weimer 2009, Loutzenhiser et al. 2010, Neises et al. 2012), with a range of redox pairs having been evaluated for both energy storage and extraction potential (Abanades et al. 2006, Wong 2011). Evaluations have encompassed both thermogravimetry and economic analyses for different metal oxides with the most promising redox pairs, including BaO_2 / BaO , Mn_2O_3 / Mn_3O_4 , and Co_3O_4 / CoO (Wong 2011). Co_3O_4 / CoO redox reactions have been the focus of further TCES studies aimed at characterizing reaction parameters for complete and cyclic reduction and oxidation with particulate and monolithic structures (Agrafiotis et al. 2014, Pagkoura et al. 2014). Complete reduction and oxidation was demonstrated between 800-1000 °C. The cycle was additionally demonstrated in a rotary kiln with directly irradiated Co_3O_4 particles followed by off- sun re-oxidation of the reduced particles in air (Neises et al. 2012). Partnering the high energy density with encouraging experimental results, Co_3O_4 / CoO is an excellent redox pair for TCES.

In the present work, an Air Brayton cycle is thermodynamically examined with an integrated two-step solar thermochemical cycle for heat storage based on $\text{Co}_3\text{O}_4/\text{CoO}$ redox reactions. The first step is the thermolysis of Co_3O_4 using concentrated solar irradiation as process heat, represented as:

The particles can then be stored in an inert environment and re-oxidized in the reversible second step that does not require solar energy and releases heat, represented as:

Co_3O_4 is then recycled to the first step, completing the cycle. The steps of the cycle may be decoupled, enabling the long-term chemical storage of sunlight to provide the necessary heat inputs to the power cycles to produce on-demand electricity. This work builds on previous analyses that examined thermodynamic constraints for CSP facility operation and two-step solar thermochemical cycles based on metal oxide redox reactions for fuel production (Lovegrove et al. 1999, Sturzenegger and Nüesch 1999, Loutzenhiser and Steinfeld 2011, Xu et al. 2011, Mahfuz et al. 2014).

Ranges for reactor temperature and O_2 partial pressure were determined thermodynamically to identify temperatures above which the $\text{Co}_3\text{O}_4 \rightarrow 3\text{CoO} + 1/2\text{O}_2$ reaction is spontaneous (i.e., $\Delta G \leq 0$). ΔG is given as a function of temperature and O_2 partial pressure in Figure 1. Three different O_2 partial pressures were plotted to show the impact of O_2 on the reaction. ΔG is positive at 800 K for $p_{\text{O}_2} = 0.001$ bar, indicative of a favorable back reaction, and decreases monotonically with increasing temperature until reaching $T = 1093.0$ K, where the reaction becomes spontaneous. The same trend for ΔG is shown for both $p_{\text{O}_2} = 1$ bar and 6 bar where the reaction is shifted further to the right according to Le Chatelier's principle, resulting in equilibrium temperatures of 1252.8 K and 1351.8 K respectively, where the back reaction is favored.

2. Thermodynamic analysis

The Air Brayton cycle integrated with the two-step solar thermochemical heat storage cycle is schematically depicted in Figure 2 with relevant energy flows. Concentrated solar irradiation

enters the solar thermochemical reactor through a quartz window and impinges directly upon $\text{Co}_3\text{O}_4/\text{CoO}$ particles entering from a cold storage bin. Particles are heated rapidly to T_{reactor} and undergo thermolyses to O_2 and CoO . The solar thermochemical reactor is maintained at a reduced pressure by a vacuum pump to ensure favorable thermodynamics and complete conversion for the Co_3O_4 thermolysis at lower temperatures. The O_2 evolves from the particles and is continuously extracted from the cavity, driving a non-equilibrium process, cooled to ambient temperature, and removed through the vacuum pump. CoO particles are fed into a hot storage bin and then introduced to a re-oxidizer. CoO particles flow in the opposite direction to a pressurized air flow, entering the re-oxidizer from an air compressor. The entering air comes into contact with particles that are cooled by the upstream flow and partially reacted. The lower temperatures further drive the re-oxidation of the CoO particles to Co_3O_4 due to a favorable $3\text{CoO} + \frac{1}{2}\text{O}_2$ reaction at lower temperature as shown in Figure 1. This enables the air stream to extract both the sensible and reaction heat. An O_2 -depleted, pressurized air flow exits the re-oxidizer at its maximum temperature and is expanded across a turbine to produce work. In actual practice, particle feeding to the re-oxidizer from the hot storage bin may be accomplished through a lock or screw-type feeder (Ermanoski et al. 2013) while a filter or similar component would prevent entrained particles from exiting the re-oxidizer and entering the turbine. CoO and/or Co_3O_4 particles exit the re-oxidizer depending on conversion and are stored in a cold bin until being re-introduced into the solar thermochemical reactor.

The thermodynamic analysis assumes a continuous, steady-state cycle to determine maximum theoretical efficiencies and identify major sources of irreversibility. In reality, the solar thermochemical reactor will be oversized compared to the re-oxidizer, enabling significant storage capacity of CoO during periods when sunlight is unavailable. The work required to transport the particles and overcome pressure losses throughout the system were neglected along with kinetic and potential energies. Thermophysical properties were extracted from HSC. The analysis was normalized to 3 mol/s of CoO exiting the solar thermochemical reactor. Steady flow rates of particles are assumed to pass between the solar thermochemical reactor and the re-oxidizer in the analysis. The environmental temperature and pressure (i.e., the dead state) were $T_0 = 298.15$ K and $p_0 = 1$ bar, respectively, and the molar fractions of N_2 and O_2 in air were assumed as $y_{\text{N}_2,0} = 0.79$ and $y_{\text{O}_2,0} = 0.21$, respectively (Moran and Shapiro 2000). Ideal gas and solution behaviors were assumed for gases and solids, respectively.

The CoO particles leaving the solar thermochemical reactor at T_{reactor} are deposited in a well-insulated and reversible hot storage bin. The particles enter the re-oxidizer and flow in the opposite direction of a stream of pressurized air introduced from an air compressor. Air from the environment composed of O_2 and N_2 is isentropically compressed to fixed pressure. The rate of work into the compressor is given as:

$$\dot{W}_{\text{comp}} = \dot{n}_{\text{air}} \Delta H \big|_{y_{\text{O}_2,0} \text{O}_2, y_{\text{N}_2,0} \text{N}_2 \text{ at } T_0 \rightarrow T_{\text{comp}}} \quad (3)$$

where ΔH is the total enthalpy change and $\dot{n}$ is the molar flow rates. Hot CoO particles are introduced at one end of the re-oxidizer at T_{reactor} and move in a counter flow to a pressurized air stream. Operation at increased O_2 partial pressures enables airflow temperatures greater than T_{reactor} to occur at the turbine due to favorable thermodynamics at higher temperatures according to Le Chatelier's principle as shown in Figure 1. The direct contact heat exchanger allows the O_2 to react with the CoO particles, recovering both sensible and reaction heat. The maximum turbine inlet temperature, $T_{\text{turbine,max}}$, was determined by calculating the temperature for $\Delta G = 0$ for $3\text{CoO} \rightarrow \text{Co}_3\text{O}_4 + \frac{1}{2}\text{O}_2$ using the partial pressure of O_2 of the air stream exiting the re-oxidizer. Air flow temperatures greater than $T_{\text{turbine,max}}$ are not thermodynamically favored as the reaction is no longer spontaneous. T_{turbine} is assumed equivalent to $T_{\text{turbine,max}}$ if supported by an energy balance across the re-oxidizer. The minimum temperature of the exiting particle stream, $T_{\text{recover,min}}$ was equal to T_{comp} . Chemical equilibrium between the incoming air stream and the exiting particle stream was employed in addition to an energy balance across the re-oxidizer to determine T_{recover} and the conversion extent of CoO to Co_3O_4 at the particle outlet. The re-oxidizer was assumed to be well-insulated and the particles and fluid were assumed to be in local thermal equilibrium at both the particle inlet and outlet. Air entering the re-oxidizer is assumed to heat rapidly to T_{recover} . T_{recover} and T_{turbine} were determined by applying the described thermodynamic constraints bounding the temperatures and applying an energy balance, given as:

$$0 = \dot{n}_{\text{Co}_3\text{O}_4,\text{recover}} \Delta H \big|_{3\text{CoO at } T_{\text{reactor}} + \frac{1}{2}\text{O}_2 \text{ at } T_{\text{comp}} \rightarrow \text{Co}_3\text{O}_4 \text{ at } T_{\text{recover}}} + \dot{n}_{\text{CoO},\text{recover}} \Delta H \big|_{\text{CoO at } T_{\text{reactor}} \rightarrow T_{\text{recover}}} + \left(\dot{n}_{\text{air}} - \frac{1}{2} \dot{n}_{\text{Co}_3\text{O}_4,\text{recover}} \right) \Delta H \big|_{y_{\text{O}_2,\text{turbine}} \text{O}_2, y_{\text{N}_2,\text{turbine}} \text{N}_2 \text{ at } T_{\text{comp}} \rightarrow T_{\text{turbine}}} \quad (4)$$

T_{recover} and T_{turbine} were solved iteratively with convergence criteria of < 0.1 K for both temperatures and the CoO and Co_3O_4 fractions at the outlet with a convergence criterion of $< 10^{-4}$. T_{turbine} was verified within a turbine operation range with temperatures (1000 – 1600 K) and

pressures (5-30 bars) as specified in (Hischier et al. 2012). The conversion extent of CoO to Co₃O₄ in the flow is given as:

$$X = \frac{3\dot{n}_{\text{Co}_3\text{O}_4, \text{recover}}}{\dot{n}_{\text{CoO}, \text{reactor}}} \quad (5)$$

The re-oxidizer was provided excess O₂ for all cases considered, thus X is dependent upon equilibrium conditions and the energy balance across the re-oxidizer. The rate of exergy destruction across the re-oxidizer was used to assess performance, given as:

$$\begin{aligned} \dot{\Xi}_{\text{D, re-oxidizer}} = & \dot{n}_{\text{Co}_3\text{O}_4, \text{recover}} \Delta \Xi_f \Big|_{3\text{CoO at } T_{\text{reactor}} + \frac{1}{2}\text{O}_2 \text{ at } T_{\text{comp}} \rightarrow \text{Co}_3\text{O}_4 \text{ at } T_{\text{recover}}} + \\ & \dot{n}_{\text{CoO}, \text{recover}} \Delta \Xi_f \Big|_{\text{CoO at } T_{\text{reactor}} \rightarrow T_{\text{recover}}} + \left(\dot{n}_{\text{air}} - \frac{1}{2} \dot{n}_{\text{Co}_3\text{O}_4, \text{recover}} \right) \Delta \Xi_f \Big|_{y_{\text{O}_2, \text{turbine}} \text{O}_2, y_{\text{N}_2, \text{turbine}} \text{N}_2 \text{ at } p_{\text{comp}}, T_{\text{comp}} \rightarrow p_{\text{comp}}, T_{\text{turbine}}} \end{aligned} \quad (6)$$

where $\Delta \Xi_f$ is the change in exergy flow (both mechanical and chemical). The particles exiting the re-oxidizer enter the well-insulated cold storage bin. The O₂ depleted air exiting the re-oxidizer is fed directly into the turbine. Expansion across the turbine to p_0 was assumed isentropic, and the rate of work across the turbine is given as:

$$\dot{W}_{\text{turbine}} = \left(\dot{n}_{\text{air}} - \frac{1}{2} \dot{n}_{\text{Co}_3\text{O}_4, \text{recover}} \right) \Delta H \Big|_{y_{\text{O}_2, \text{turbine}} \text{O}_2, y_{\text{N}_2, \text{turbine}} \text{N}_2 \text{ at } T_{\text{turbine}} \rightarrow T_{\text{exhaust}}} \quad (7)$$

CoO/Co₃O₄ particles are taken from the cold storage bin and fed directly to the solar thermochemical reactor. The solar thermochemical reactor was modeled as directly irradiated, requiring a quartz window that reflects a small portion of incoming solar irradiation to the environment, schematically shown in Figure 3. However, the spectral characteristics of the quartz window help to mitigate re-radiative losses as the window temperature is lower than the cavity temperature. A radiative exchange model was employed to determine the absorption efficiency of a solar thermochemical reactor composed of two surfaces: a quartz window (Surface 1) and a reactor cavity (Surface 2). The reactor cavity temperature was fixed to a specified temperature corresponding to typical CSP operation with a concentration ratio of $C=1000$ suns and direct normal irradiance of $I = 1 \text{ kW/m}^2$. The relevant parameter is the area ratio between the two surfaces, therefore, a detailed cavity geometry is not specified. A semi-gray, two-band approximation was used to account for spectral dependency of the quartz glass: Semi-transparent and opaque wavelength intervals over the ranges of (1) 0- λ_c and (2) λ_c - ∞ , respectively, where $\lambda_c = 4 \text{ } \mu\text{m}$ (Z'Graggen and Steinfeld 2004). Both surfaces were considered as

diffuse and isothermal. The radiative exchange equation over the semi-transparent band (i.e., radiative band 1) for N surfaces is given as (Loutzenhiser et al. 2010):

$$\frac{q_i^{(1)}}{1-\rho_i} - \sum_{j=1}^N \left(\frac{\rho_j}{1-\rho_j} \right) F_{i-j} q_j^{(1)} + H_{0,i}^{(1)} = \frac{\alpha_i}{1-\rho_i} \sigma T_i^4 f(T_i \lambda_c) - \sum_{j=1}^N \left(\frac{\alpha_j}{1-\rho_j} \right) F_{i-j} \sigma T_j^4 f(T_i \lambda_c) \quad (8)$$

where q is the net radiative heat flux, ρ is the slab reflectance, F is the view factor, α is the slab absorptance, H_0 is the external irradiation to a surface, σ is the Stefan-Boltzmann constant, T is the surface temperature, f is the radiative fractional function, and i and j are summing indices representing the emitting surface and incident surface(s) respectively. The incoming concentrated irradiation, assumed to be uniformly distributed and incident only on the cavity in the semi-transparent band, was represented as:

$$H_{0,2}^{(1)} = \frac{\tau_1 I C}{A_r} \quad (9)$$

where τ_1 is the slab transmittance for the quartz glass, I is the direct-normal solar irradiance, C is the solar concentration ratio, and A_r is the ratio of the areas of the cavity to the quartz window. The radiative exchange equation over the opaque bandwidth (i.e., radiative band 2) for N surfaces is given as:

$$\frac{q_i^{(2)}}{\varepsilon_i} - \sum_{j=1}^N \left(\frac{1}{\varepsilon_j} - 1 \right) F_{i-j} q_j^{(2)} = (1 - f(T_i \lambda_c)) \sigma T_i^4 - \sum_{j=1}^N F_{i-j} (1 - f(T_j \lambda_c)) \sigma T_j^4 \quad (10)$$

where ε is the surface emittance. The net radiative flux between the reactor cavity and the quartz window in both radiative bands was solved using equations 8-10 along with an energy balance considering external convection, transmitted radiative energy through the quartz window, and radiative exchange to and from the surroundings, given as:

$$q_1^{(1)} + q_1^{(2)} = \tau_1 \left(\frac{q_1^{(1)} - \alpha_1 f(T_1 \lambda_c) \sigma T_1^4}{1 - \rho_1} \right) - h_l (T_1 - T_0) - \alpha_1 f(T_1 \lambda_c) \sigma T_1^4 - \varepsilon_1 [1 - f(T_1 \lambda_c)] \sigma T_1^4 + \sigma T_0^4 \quad (11)$$

where h_l is the external convective heat transfer coefficient determined from free convection of a vertical surface (Maag et al. 2010), α_1 is the absorptance, τ_1 is the transmittance, ρ_1 is the

reflectance, ε_1 is the emittance of the quartz window, and T_1 refers to the window temperature.. The system of non-linear equations was solved iteratively until the window temperature converged to < 0.1 K. The results were used to determine reactor absorption efficiencies for a range of reactor cavity temperatures and surface emittances, given as:

$$\eta_{\text{abs}} = \frac{[q_2^{(1)} + q_2^{(2)}] A_r}{IC} \quad (12)$$

$q_2^{(1)} + q_2^{(2)}$ was assumed solely to heat incoming particles and drive the chemical reaction. The reaction absorption efficiency was compared to the theoretical absorption efficiency assuming a perfectly insulated, blackbody, cavity-receiver with no convective/conductive heat losses to the environment, given as:

$$\eta_{\text{abs,ideal}} = 1 - \frac{\sigma T_{\text{reactor}}^4}{IC} \quad (13)$$

The incoming particles to the solar thermochemical reactor were assumed to enter the reactor without a carrier gas and completely reduce to CoO in a non-equilibrium reaction with O_2 being continually removed. Spontaneous reaction occurs at $T_{\text{reactor}} \geq 1036.6$ K at $p_{\text{O}_2} = 0.001$ bar where $\Delta G \leq 0$ for $\text{Co}_3\text{O}_4 \rightarrow 3\text{CoO} + \frac{1}{2}\text{O}_2$. Therefore, $T_{\text{reactor}} > 1036.6$ K were considered to assess the impact of additional sensible heat storage coupled to higher re-radiative heat losses. $T_{\text{reactor}} = 1050$ K was chosen as it is just above the temperature where the Co_3O_4 thermolysis is spontaneous at 0.001 bar, ensuring conversion from Co_3O_4 to CoO and O_2 . The process heat required for complete reduction in the solar thermochemical reactor, the required concentrated solar irradiation (utilizing η_{abs} calculated from the radiation exchange model), and heat rejected to the surroundings are given, respectively, as:

$$\dot{Q}_{\text{reactor}} = \dot{n}_{\text{Co}_3\text{O}_4, \text{recovered}} \Delta H |_{\text{Co}_3\text{O}_4 \text{ at } T_{\text{recovered}} \rightarrow 3\text{CoO} + \frac{1}{2}\text{O}_2 \text{ at } T_{\text{reactor}}} + \dot{n}_{\text{CoO, recovered}} \Delta H |_{\text{CoO at } T_{\text{recovered}} \rightarrow T_{\text{reactor}}} \quad (14)$$

$$\dot{Q}_{\text{solar}} = \frac{\dot{Q}_{\text{reactor}}}{\eta_{\text{abs}}} \quad (15)$$

$$\dot{Q}_{\text{loss}} = (1 - \eta_{\text{abs}}) \dot{Q}_{\text{solar}} \quad (16)$$

The rate of exergy destruction in the solar thermochemical reactor to the surroundings is given as:

$$\begin{aligned} \dot{\Xi}_{D, \text{reactor}} = & \left(1 - \frac{T_0}{T_{\text{reactor}}}\right) \dot{Q}_{\text{solar}} - \left(1 - \frac{T_0}{T_0}\right) \dot{Q}_{\text{loss}} + \dot{n}_{\text{Co}_3\text{O}_4, \text{recovered}} \Delta \Xi_f \big|_{\text{Co}_3\text{O}_4 \text{ at } T_{\text{recovered}} \rightarrow 3\text{CoO} + \frac{1}{2}\text{O}_2 \text{ at } T_{\text{reactor}} \cdot P_{\text{reactor}}} \\ & + \dot{n}_{\text{CoO, recovered}} \Delta \Xi_f \big|_{\text{CoO at } T_{\text{recovered}} \rightarrow T_{\text{reactor}}} \end{aligned} \quad (17)$$

Exergy destruction due to the solar input was calculated using T_{reactor} according to previous literature (Steinfeld 2002, Loutzenhiser and Steinfeld 2011). An ideal cooling process to T_0 was assumed for the O_2 stream exiting the solar thermochemical reactor. The heat rejected to the surroundings during the cooling process and the associated exergy destruction rate are given, respectively, as:

$$\dot{Q}_{\text{cool}} = \dot{n}_{\text{O}_2, \text{vac}} \Delta H \big|_{\frac{1}{2}\text{O}_2 \text{ at } T_{\text{reactor}} \rightarrow T_0} \quad (18)$$

$$\dot{\Xi}_{D, \text{cool}} = \left(1 - \frac{T_0}{T_{b, \text{cool}}}\right) \dot{Q}_{\text{cool}} \quad (19)$$

where $T_{b, \text{cool}}$ is the effective temperature at the boundary of the cooling process, given as:

$$T_{b, \text{cool}} = \frac{\dot{Q}_{\text{cool}}}{\dot{n}_{\text{O}_2, \text{vac}} \Delta S \big|_{\frac{1}{2}\text{O}_2 \text{ at } T_{\text{reactor}} \rightarrow T_0}} \quad (20)$$

A reversible vacuum pump was assumed to operate isothermally at T_0 to reduce the pressure in the solar thermochemical reactor. The rates of work and heat transfer to the environment are given, respectively, as:

$$\dot{W}_{\text{vac}} = -\dot{n}_{\text{O}_2, \text{vac}} T_0 \Delta S \big|_{\text{O}_2 \text{ at } T_0, P_{\text{reactor}} \rightarrow P_0} \quad (21)$$

$$\dot{Q}_{\text{vac}} = \dot{W}_{\text{vac}} \quad (22)$$

To assess the potential of the CSP facility, the overall cycle efficiency is given as:

$$\eta_{\text{cycle}} = \frac{\dot{W}_{\text{turbine}} - \dot{W}_{\text{comp}} - \dot{W}_{\text{vac}}}{\dot{Q}_{\text{solar}}} \quad (23)$$

3. Results and discussion

Parameters for the thermodynamic and exergy analyses are provided in Table 1.

T_{recover} and T_{turbine} as functions of $\dot{n}_{\text{air}}$ were determined using the energy balance across the re-oxidizer employing the thermodynamic constraints previously described and are given in Figure 4 at $T_{\text{reactor}} = 1050$ K and $p_{\text{comp}} = 30$ bar. At $\dot{n}_{\text{air}} < 13.7$ mol/s, $T_{\text{turbine}} \sim T_{\text{turbine,max}}$ and is greater than T_{reactor} as calculated from the thermodynamic limit where $\Delta G = 0$. T_{turbine} increases slightly with $\dot{n}_{\text{air}}$ as O_2 concentration increases at the airflow exit, favoring higher equilibrium temperatures and reaches a maximum of 1344.7 K at $\dot{n}_{\text{air}} = 13.7$ mol/s. T_{recover} decreases rapidly with $\dot{n}_{\text{air}}$, as more heat exits at the turbine to maintain $T_{\text{turbine}} = T_{\text{turbine,max}}$. T_{recover} achieves a minimum possible temperature at $\dot{n}_{\text{air}} = 13.7$ mol/s where $T_{\text{recover}} = T_{\text{comp}}$, corresponding to rapid decreases in T_{turbine} for increasing $\dot{n}_{\text{air}} > 13.7$ mol/s as greater airflows absorb greater sensible heat.

$\dot{\Xi}_{\text{D,re-oxidizer}}$ and X are given as functions of $\dot{n}_{\text{air}}$ in Figure 5 at $T_{\text{reactor}} = 1050$ K and $p_{\text{comp}} = 30$ bar. The $\dot{\Xi}_{\text{D,re-oxidizer}}$ initially increases until it reaches a maximum of 11.8 kW at $\dot{n}_{\text{air}} = 9.8$ mol/s, which corresponds the largest $\Delta\Xi_f$ between the particle and air streams. X increases as lower particle recovery temperatures favor complete conversion from CoO to Co_3O_4 . Once $T_{\text{recover}} = T_{\text{comp}}$, X remains constant at 0.985, which corresponds to a minimum $\dot{\Xi}_{\text{D,re-oxidizer}}$ at $\dot{n}_{\text{air}} = 13.7$ mol/s and the smallest $\Delta\Xi_f$ between the particle and air streams. The $\dot{\Xi}_{\text{D,re-oxidizer}}$ then begins a monotonic increase with larger $\dot{n}_{\text{air}}$ due to the introduction of additional irreversibilities related to a decreasing T_{turbine} .

A comparison of η_{abs} as a function of A_r is given in Figure 6. The η_{abs} as a function of A_r is given in Figure 6a at $T_{\text{reactor}} = 1050$ K for a range of ε_2 . The η_{abs} rapidly increases with an increasing $A_r \leq 3$ for $\varepsilon_2 \leq 0.8$, after which the curves begin to asymptotically approach η_{abs} for $\varepsilon_2 = 1$ (i.e., a blackbody cavity). At higher A_r , a large portion of the incoming solar irradiation is absorbed due to an increase in internal reflections and subsequent absorptions, resulting in near blackbody behavior. Blackbody behavior is also more closely approximated as ε_2 approaches 1 for all A_r .

The maximum η_{abs} never reaches the $\eta_{\text{abs,ideal}}$ as the quartz window reflects a portion of incoming solar radiation, subsequently reducing $H_{0,2}$ incident upon the cavity walls. The η_{abs} as a function of A_r for a range of T_{reactor} at $\varepsilon_2 = 0.8$ is provided in Figure 6b. The η_{abs} at all T_{reactor} increases initially and then begins to asymptotically approach the limit for a blackbody cavity. As T_{reactor} increases, η_{abs} decreases as result of increased internal cavity re-radiation, increasing both emissions and convective losses due to a higher T_1 which increases from 820 K to 1010 K. Active cooling is often required for solar thermochemical reactors to ensure window durability (Muller et al. 2005, Schunk et al. 2008, Villasmil et al. 2014), adding a small parasitic load not included in this analysis. A higher T_{reactor} results in a more efficient power cycle by increasing the Carnot efficiency of the cycle, but the efficiency is offset by increased re-radiative losses to the environment. A $T_{\text{reactor}} = 1106$ K is the optimal operating temperature for $C = 1000$ suns and $I = 1$ kW/m² (Steinfeld and Palumbo 2001), assuming an ideal blackbody solar receiver with an ideal heat engine (i.e., Carnot cycle) operating between hot and cold reservoirs with temperatures equal to T_{reactor} and T_0 , respectively.

$\dot{Q}_{\text{solar}}$, $\dot{Q}_{\text{loss}}$, and $\dot{Q}_{\text{cool}}$ as functions of $\dot{n}_{\text{air}}$ are given in Figure 7 at $T_{\text{reactor}} = 1050$ K and $p_{\text{comp}} = 30$ bar. $\dot{Q}_{\text{solar}}$ rapidly increases with $\dot{n}_{\text{air}}$ as additional process heat is required to both sensibly heat and fully reduce incoming CoO/Co₃O₄ particles. The recovered particles decrease in temperature and increase in concentration of Co₃O₄ with increasing $\dot{n}_{\text{air}}$, as more heat is transferred to the air stream. When $\dot{n}_{\text{air}} < 13.7$ mol/s, $\dot{Q}_{\text{solar}}$ and $\dot{Q}_{\text{loss}}$ increase with $\dot{n}_{\text{air}}$ as T_{recover} decreases and X increases, requiring more heat to drive the Co₃O₄ thermolysis. $\dot{Q}_{\text{quench}}$ increases with $\dot{n}_{\text{air}}$ as higher X results in more O₂ evolution in the solar thermochemical reactor. Maximum values of $\dot{Q}_{\text{solar}} = 306$ kW and $\dot{Q}_{\text{loss}} = 48$ kW correspond to $\dot{n}_{\text{air}} = 13.7$ mol/s, after which $T_{\text{recover}} = T_{\text{comp}}$ and X remain constant, resulting in constant $\dot{Q}_{\text{solar}}$ and $\dot{Q}_{\text{loss}}$ (i.e., the solar thermochemical reactor requires no additional heat). At $\dot{n}_{\text{air}} > 13.7$ mol/s, the equilibrium compositions of the incoming particles remain constant, resulting in a constant $\dot{Q}_{\text{cool}}$ as no additional O₂ is extracted by the vacuum pump from the solar thermochemical reactor.

$\dot{W}_{\text{turbine}}$, $\dot{W}_{\text{comp}}$, and $\dot{W}_{\text{vac}}$ are given as functions of $\dot{n}_{\text{air}}$ in Figure 8 at $T_{\text{reactor}} = 1050$ K and $p_{\text{comp}} = 30$ bar. $\dot{W}_{\text{turbine}}$ monotonically increases with $\dot{n}_{\text{air}}$ until reaching $\dot{n}_{\text{air}} = 13.7$ mol/s. At $\dot{n}_{\text{air}} = 13.7$ mol/s, increases in airflow entering the turbine are offset by lower T_{turbine} , resulting in a continued, shallower increase in $\dot{W}_{\text{turbine}}$. $\dot{W}_{\text{comp}}$ increases steadily as $\dot{n}_{\text{air}}$ increases constantly and the temperature difference across the turbine remains the same. $\dot{W}_{\text{vac}}$ increases as a result of greater O_2 production in the reactor until $\dot{n}_{\text{air}} = 13.7$ mol/s and $\dot{W}_{\text{vac}} = 8.5$ kW at which the composition of the entering particle stream and the O_2 produced are constant. The $\dot{W}_{\text{vac}}$ is a minor parasitic load compared to $\dot{W}_{\text{comp}}$ and $\dot{W}_{\text{turbine}}$.

$\dot{\Xi}_{\text{D,reactor}}$ and $\dot{\Xi}_{\text{D,cool}}$ are compared to X as functions of $\dot{n}_{\text{air}}$ and given in Figure 9 at $T_{\text{reactor}} = 1050$ K and $p_{\text{comp}} = 30$ bar. The increase in X with $\dot{n}_{\text{air}}$ requires additional $\dot{Q}_{\text{solar}}$ to sensibly heat and fully-reduce the $\text{CoO/Co}_3\text{O}_4$ particle stream and overcome heat losses. Additional $\dot{Q}_{\text{solar}}$ greatly increases the incoming thermal exergy related to heat transfer across a boundary. However, once $\dot{Q}_{\text{solar}}$ and T_{recover} are constant for $\dot{n}_{\text{air}} \geq 13.7$ mol/s, both entering and exiting exergy flows become fixed and $\dot{\Xi}_{\text{D,cool}} = 37.5$ kW. Small $\dot{\Xi}_{\text{D,cool}}$ increases are correlated to increasing O_2 flowrates exiting the solar thermochemical reactor and the $\dot{\Xi}_{\text{D,cool}}$ plateaus at a maximum at 6.2 kW once X is constant.

Comparisons of η_{cycle} as a function of $\dot{n}_{\text{air}}$ are given in Figure 10 for a range of T_{reactor} and p_{comp} . For all of the analyses, η_{cycle} increases with larger $\dot{n}_{\text{air}}$ for different T_{reactor} and p_{comp} . η_{cycle} as a function of $\dot{n}_{\text{air}}$ is given in Figure 10a at $T_{\text{reactor}} = 1050$ K for a range of p_{comp} between 5-30 bar, a pressure range suitable for gas turbines. Increasing to $p_{\text{comp}} = 30$ bar results in η_{cycle} nearing 44% compared with η_{cycle} of 26% for a $p_{\text{comp}} = 5$ bar. The increased η_{cycle} is a result of higher T_{turbine} (Figure 1) and lower T_{exhaust} , directly translating to more $\dot{W}_{\text{turbine}}$. Increases in $\dot{W}_{\text{turbine}}$ more than offset the additional $\dot{W}_{\text{comp}}$ required. Operation at lower $\dot{n}_{\text{air}}$ resulted in some unreacted CoO , reducing $\dot{Q}_{\text{solar}}$ while decreasing the energy density of the redox material. In addition, $T_{\text{recover,min}}$

increases at higher p_{comp} , decreasing the required amount of $\dot{Q}_{\text{solar}}$. Increasing T_{reactor} results in decreases in η_{cycle} as T_{turbine} is thermodynamically limited by $3\text{CoO} + \frac{1}{2} \text{O}_2$ reaction. and remains relatively constant as shown in Figure 10b. Increases in T_{reactor} at $p_{\text{comp}} = 30$ bar result in larger $\dot{Q}_{\text{solar}}$ due to larger $\dot{Q}_{\text{loss}}$ that do not correspond to increases in $\dot{W}_{\text{turbine}}$. An additional analysis was performed assuming no reactions (i.e., SES) with 1 mol/s of Co_3O_4 flowing through the system. η_{cycle} was 51% for operation at $T_{\text{reactor}} = 1050$ K, $p_{\text{comp}} = 30$ bar, and $\dot{n}_{\text{air}} = 16$ mol/s compared to $\eta_{\text{cycle}} = 44\%$ under the same conditions with reactions. However, the improved efficiency of SES comes at the expense of lower energy densities, requiring more materials handling and larger infrastructure (e.g., storage bins, etc.) throughout the system to achieve the same amount of $\dot{W}_{\text{turbine}}$.

4. Verification

Thermodynamic analysis can be verified by performing an energy balance with a defined control volume that encompasses all components. This was done to compute the incoming concentrated solar irradiation, given as:

$$\begin{aligned} \dot{Q}_{\text{solar,ver}} = & \dot{Q}_{\text{loss}} + \dot{Q}_{\text{cool}} + \dot{Q}_{\text{pump}} + \dot{W}_{\text{turbine}} - \dot{W}_{\text{vac}} - \dot{W}_{\text{comp}} \\ & + \dot{n}_{\text{O}_2, \text{vac}} H|_{\text{O}_2 \text{ at } T_0} + \left(\dot{n}_{\text{air}} - \frac{1}{2} \dot{n}_{\text{Co}_3\text{O}_4, \text{recover}} \right) H|_{y_{\text{O}_2, \text{turbine}} \text{O}_2, y_{\text{N}_2, \text{turbine}} \text{N}_2 \text{ at } T_{\text{exhaust}}} - \dot{n}_{\text{air}} H|_{y_{\text{O}_2, 0} \text{O}_2, y_{\text{N}_2, 0} \text{N}_2 \text{ at } T_0} \end{aligned} \quad (24)$$

For operation at $T_{\text{reactor}} = 1050$ K, $p_{\text{comp}} = 30$ bar, and $\dot{n}_{\text{air}} = 16$ mol/s both $\dot{Q}_{\text{solar}}$ and $\dot{Q}_{\text{solar,ver}}$ are equal to 306kW.

The available work, the sum of all of the work flows, exergy destructions, and the exergy flow at the exit of the turbine, can be used to determine the maximum cycle efficiency. This efficiency is comparable to a Carnot cycle operating between hot and cold temperature reservoirs of $T_{\text{H}} = T_{\text{reactor}}$ and $T_{\text{C}} = T_0$, respectively. The maximum efficiency is given as:

$$\begin{aligned} \eta_{\text{max}} = & \frac{\dot{W}_{\text{turbine}} - \dot{W}_{\text{comp}} - \dot{W}_{\text{vac}} + \dot{\Xi}_{\text{d, reoxidizer}} + \dot{\Xi}_{\text{d, reactor}} + \left(\dot{n}_{\text{air}} - \frac{1}{2} \dot{n}_{\text{Co}_3\text{O}_4, \text{recover}} \right) \Xi_{\text{f}}|_{y_{\text{O}_2, \text{turbine}} \text{O}_2, y_{\text{N}_2, \text{turbine}} \text{N}_2 \text{ at } p_0, T_{\text{exhaust}}}}{\dot{Q}_{\text{solar}}} \quad (25) \\ = & 1 - \frac{T_0}{T_{\text{reactor}}} = \eta_{\text{Carnot}} \end{aligned}$$

For operation at $T_{\text{reactor}} = 1050$ K, $p_{\text{comp}} = 30$ bar, and $\dot{n}_{\text{air}} = 16$ mol/s both η_{max} and η_{Carnot} are equal to 0.716.

A control volume excluding the solar thermochemical reactor, storage bins, and vacuum pump was used to compute the Air Brayton cycle efficiency, represented as:

$$\eta_{\text{Brayton}} = \frac{\dot{W}_{\text{turbine}} - \dot{W}_{\text{comp}}}{\dot{n}_{\text{air}} \Delta H \Big|_{y_{\text{O}_2} \text{O}_2, y_{\text{N}_2} \text{N}_2 \text{ at } T_{\text{comp}} \rightarrow T_{\text{turbine}}} \quad (26)$$

Some O_2 was consumed during re-oxidation between the compressor and turbine. This was compared to the cycle efficiency of an ideal Air-Standard Brayton cycle, represented as:

$$\eta_{\text{Brayton,ideal}} = 1 - \frac{1}{\left(p_{\text{comp}} / p_0 \right)^{(k-1)/k}} \quad (27)$$

where k is the specific heat ratio for air. For operation at $T_{\text{reactor}} = 1050$ K, $p_{\text{comp}} = 30$ bar, $\dot{n}_{\text{air}} = 16$ mol/s, η_{Brayton} is 55 % while $\eta_{\text{Brayton,ideal}}$ is 62 %. Exergy destruction within the re-oxidizer due to the chemical reaction impacts the performance of the Air Brayton cycle.

5. Summary and conclusions

A thermodynamic analysis was performed for an Air- Brayton cycle coupled to a two-step thermochemical cycle for heat storage based on $\text{Co}_3\text{O}_4/\text{CoO}$ redox reactions through direct integration of direct counter-flow heat exchange between the high-temperature particles and the working fluid. Cycle performance was quantified and major sources of irreversibilities (i.e., exergy destruction) were identified using exergy destruction results. The analysis used a windowed cavity receiver for a solar thermochemical reactor to directly heat $\text{CoO}/\text{Co}_3\text{O}_4$ particles with concentrated solar irradiation. For a solar thermochemical reactor temperature of 1050 K and an outlet compressor pressure of 30 bar, the maximum cycle efficiency approached 44%. The cycle efficiency decreased to 26% for outlet compressor pressures of 5 bar. Operation at higher solar thermochemical reactor temperatures resulted in decreased cycle efficiencies, while increased airflow rates across the compressor increased cycle efficiencies for the range of solar thermochemical reactor temperature and outlet compressor pressures considered. The

dominant source of exergy destruction was in the solar thermochemical reactor, due to the incoming concentrated solar irradiation used to heat entering particles and thermolyze Co_3O_4 to CoO and O_2 . Smaller exergy destruction rates were determined for the re-oxidizer and the cooling process. The analysis shows the potential of directly integrating a two-step solar thermochemical cycle into an Air Brayton cycle as the cycle is capable of effectively utilizing the available exergy while incorporating heat storage, culminating in higher operating efficiencies.

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Nomenclature

A_r = area ratio between cavity and quartz window

C = solar concentration ratio

f = blackbody fraction

F = geometric view factor

G = Gibb's free energy function

H = total enthalpy

$H_{0,2}$ = transmitted solar irradiance incident on cavity

h_1 = external convective heat transfer coefficient

k = specific heat ratio for air

N = number of surfaces in solar thermochemical reactor

$\dot{n}_{\text{air}}$ = molar flow rate of air

$\dot{n}_{\text{CoO,reactor}}$ = molar flow rate for CoO produced in solar thermochemical reactor

$\dot{n}_{\text{CoO,recover}}$ = molar flow rate for CoO recovered from re-oxidizer

$\dot{n}_{\text{Co}_3\text{O}_4,\text{recover}}$ = molar flow rate for Co_3O_4 recovered from re-oxidizer

$\dot{n}_{\text{O}_2,\text{vac}}$ = molar flow rate for evolved O_2 stream in solar thermochemical reactor

p_0 = ambient air pressure

p_{comp} = compressed air pressure

p_{reactor} = solar thermochemical reactor pressure

q = net radiative flux at surface

q_{loss} = net radiative flux lost to atmosphere

q_{solar} = net radiative flux from concentrated solar

q_1 = net radiative flux at the inner window surface

q_2 = net radiative flux at the reactor cavity surface

$\dot{Q}_{\text{loss}}$ = external heat flow from re-radiative, emissive, transmissive, and convective losses from the window

$\dot{Q}_{\text{cool}}$ = heat flow output from cooled O_2

$\dot{Q}_{\text{reactor}}$ = heat flow input required for sensible heating and complete thermolysis of particle flow

$\dot{Q}_{\text{solar}}$ = concentrated solar heat input

S = total entropy

T_0 = ambient temperature

$T_{b,cool}$ = effective temperature for cooled O_2

T_{comp} = compressor outlet airflow temperature

$T_{exhaust}$ = temperature of depleted- O_2 airflow from turbine outlet

$T_{reactor}$ = solar thermochemical reactor temperature

$T_{recover}$ = temperature of particle flow recovered from re-oxidizer

$T_{recover,min}$ = minimum possible temperature of particle flow recovered from re-oxidizer

T_{solar} = assumed blackbody temperature of sun

$T_{turbine}$ = temperature of depleted- O_2 airflow from turbine inlet

$T_{turbine,max}$ = maximum possible temperature of depleted- O_2 airflow from turbine inlet

T_1 = quartz window temperature

$\dot{W}_{vac}$ = work input rate for evacuating O_2

$\dot{W}_{comp}$ = work input rate for compressing airflow

$\dot{W}_{turbine}$ = work output rate from turbine

X = conversion extent

$y_{O_2,0}$ = atmospheric mole fraction of O_2

$y_{O_2,turbine}$ = mole fraction of O_2 in turbine

$y_{N_2,0}$ = atmospheric mole fraction of N_2

$y_{N_2,turbine}$ = mole fraction of N_2 in turbine

Greek letters

α_2 = cavity absorptance

α_1 = surface absorptance at window

ϵ_1 = surface emittance at window

ϵ_2 = cavity emittance

η_{abs} = solar thermochemical reactor absorption efficiency

$\eta_{abs,ideal}$ = ideal solar thermochemical reactor absorption efficiency

$\eta_{Brayton}$ = Air Brayton cycle efficiency

$\eta_{\text{Brayton,ideal}}$ = ideal Air-Standard Brayton cycle efficiency

η_{Carnot} = CSP facility Carnot efficiency

η_{cycle} = CSP facility efficiency

η_{max} = maximum possible CSP facility efficiency

λ_c = transparent to opaque transition wavelength for quartz window

ρ_2 = surface reflectance at window

ρ_1 = surface reflectance at window

σ = Stefan-Boltzmann constant

τ_1 = surface transmittance at window

$\dot{\Xi}_{\text{D,reactor}}$ = exergy destruction rate for solar thermochemical reactor

$\dot{\Xi}_{\text{D,re-oxidizer}}$ = exergy destruction rate for re-oxidizer

$\dot{\Xi}_{\text{D,quench}}$ = exergy destruction rate for cooling O₂

Ξ_f = total exergy flow

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Tables

Table 1. Properties and values for the thermodynamic analysis of the Air Brayton cycle integrated with thermochemical heat storage.

Property	Value(s)
I	1 kW·m ⁻²
C	1000 suns
T_{solar}	5780 K
T_0	298.15 K
p_0	1 bar
T_{reactor}	1050-1250 K
p_{reactor}	0.001bar
p_{comp}	5 – 30 bar
A_r	5
$\dot{n}_{\text{CoO,reactor}}$	3 mol/s
$\dot{n}_{\text{air}}$	8 – 16 mol/s
α_1	0 (0-4 μm) and 0.9 (4 μm - ∞)
ρ_1	0.06 (0-4 μm) and 0.1(4 μm - ∞)
τ_1	0.94 (0-4 μm) and (4 μm - ∞)
ε_1	0.9
ε_2, α_2	0.8
ρ_2	0.2

Figure 1. Gibb's free energy function difference for the $\text{Co}_3\text{O}_4 \rightarrow 3\text{CoO} + \frac{1}{2} \text{O}_2$ reaction as a function of temperature at partial O_2 pressures of 0.001 bar, 1 bar, and 6 bar.

Figure 2. A flow diagram of the Air-Standard Brayton cycle with an integrated two-step solar thermochemical heat storage cycle based on $\text{Co}_3\text{O}_4/\text{CoO}$ redox reactions is depicted with relevant heat and work flows into and out of the system.

Figure 3. A schematic depiction of a simplified solar thermochemical reactor geometry for radiative exchange analysis between a quartz window (Surface 1) and reactor cavity (Surface 2) with incident concentrated solar irradiation passing through the window and directly impinging on the reactor cavity.

Figure 4. Particle temperature exiting re-oxidizer to the cold storage bin (solid) and air temperature entering turbine from the re-oxidizer (dashed) as functions of molar flow of air exiting the compressor at 30 bar for a solar thermochemical reactor temperature of 1050 K.

Figure 5. Exergy destruction rate (dashed) and conversion of CoO to Co₃O₄ (solid) across the re-oxidizer as functions of molar flow of air exiting the compressor at 30 bar and solar thermochemical reactor temperature of 1050 K.

Figure 6. Absorption efficiency versus area ratio between the cavity and the quartz window for a solar thermochemical reactor for (a) a range of cavity emittances (solid) compared to a theoretical blackbody cavity (dashed) at a cavity temperature equal to 1050 K; and (b) a range of cavity temperatures for the cavity emittance equal to 0.8.

Figure 7. Concentrated solar power input (solid) and heat loss rate to the surrounding (dashed) for the solar thermochemical reactor and the rate of heat rejected to the surroundings from O_2 cooling (dash-dot) as functions of the molar flow of air exiting the compressor at 30 bar and a thermochemical reactor temperature of 1050 K.

Figure 8. Rates of work for the turbine (solid), compressor (dashed), and vacuum pump (dash-dot) as functions of molar flow of air exiting the compressor at 30 bar and a thermochemical reactor temperature of 1050 K.

Figure 9. Exergy destruction rates in the solar thermochemical reactor (solid) and quench (dashed) and conversion of CoO to Co_3O_4 in the re-oxidizer (dashed-dotted) as functions of molar flow of air exiting the compressor at 30 bar and a thermochemical reactor temperature of 1050 K.

Figure 10. Overall cycle efficiency as a function of molar flow of air exiting the compressor for (a) a range of pressures exiting the compressor between 5-30 bar for solar thermochemical reactor temperature of 1050 K; and (b) a range of solar thermochemical reactor temperatures between 1050-1225 K for a pressure exiting the compressor of 30 bar.