

Solar-driven nitrogen separation process from air based on two-step thermochemical cycle: thermodynamic analysis

Alberto de la Calle^{1*}, H. Evan Bush², Ivan Ermanoski¹, Xiang Gao¹, Andrea Ambrosini², Ellen B. Stechel¹

¹ ASU LightWorks®, Arizona State University, PO Box 875402, Tempe, AZ 85287-5402, USA

² Sandia National Laboratories, PO Box 5800, MS 0734, Albuquerque, NM 87185, USA

*Corresponding author: alberto.delacalle@asu.edu

1. Introduction

Ammonia is the second most produced industrial chemical, responsible for over 1.4% of global CO₂ emissions [1]. Ammonia is produced via the Haber–Bosch process, which includes the production of H₂ and N₂ from CH₄, air, and water via steam reforming and CH₄ combustion in air [2]. N₂ separation from air is typically an energy-demanding process. Furthermore, synthesis of CO₂-neutral ammonia requires acquiring N₂ using renewable energy.

The present work focuses on a solar-driven N₂ separation process from air, based on a two-step thermochemical metal oxide (MO_x) cycle. The first step is thermal reduction of a redox active MO_x at high temperature, releasing gaseous oxygen from the material. In the second step, the reduced MO_x re-oxidizes in air at lower temperature to remove most of the oxygen. The reduction reaction requires a heat input, in this case provided using solar concentration. The re-oxidation reaction is exothermic and does not require an energy input.

To avoid unwanted re-oxidation during the reduction reaction, it is necessary to remove the oxygen released from the MO_x, typically achieved by vacuum pumping or inert gas sweeping. However, the pumping energy consumption is significant for high volumetric oxygen flows, such as considered here. Inert gas sweeping is entirely counterproductive, as it requires more inert gas than produced by the process. Here, we analyze an air sweep, which cannot provide a low oxygen partial pressure but is relatively low cost.

To maximize the chemical potential utilization of the MO_x, reactant flows in both steps are countercurrent by design. To avoid second law violations, we ensure mass conservation and the Gibbs criterion ($\Delta G \leq 0$) along the reaction path. The thermodynamic analysis of the system enables an evaluation of the energy feasibility of the process, to assess different plant configurations, and to determine optimal operating conditions.

2. System description

Figure 1 shows the system diagram of the analyzed process. A heliostat field concentrates the solar irradiance onto the aperture of the reduction reactor, heating the flowing MO_x. The reactor is directly irradiated, gravity-driven, with a granular flow. The air sweep is countercurrent. The reduced MO_x then flows through a heat exchanger where it heats a heat transfer fluid (HTF) for reuse elsewhere in the process. The cooled oxide proceeds to the re-oxidation reactor, where it removes oxygen from air to yield low oxygen impurity nitrogen. The MO_x leaves the re-oxidation reactor and returns to the reduction reactor.

3. Thermodynamic analysis

To guarantee $\Delta G \leq 0$ during the countercurrent reactors, we ensure mass conservation and the Gibbs criterion at each infinitesimal point along the flow path. Figure 2 shows the behavior of the reduction and re-oxidation reactions in δ - p^* coordinates for fixed operating conditions (reduction and re-oxidation temperatures, and sweeping molar flow), where δ is the extent of reduction of the reacting MO_x and p^* is the dimensionless pressure variable defined as $p^* = p_{O_2} / (p_{sys} - p_{O_2})$. In this conditions, mass conservation is defined by straight lines [3]. To ensure the Gibbs criterion is guaranteed, the mass conservation lines must not cross the chemical equilibrium lines ($\Delta G = 0$). In the reduction reactor, chemical equilibrium is only reached at a single point, namely at the particle outlet, while in the re-oxidation reactor this equilibrium can be reached at both ends.

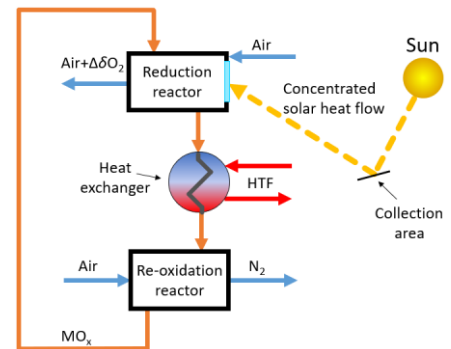


Figure 1: System diagram of the nitrogen separation process

This methodology enables an optimization of the operating conditions of the N_2 separation system. Figure 3 shows a performance analysis when the MO_x is $SrFeO_3$ and the oxidant is atmospheric air. The lines depict the optimal operation points for different target partial pressures of oxygen at the outlet of the re-oxidation reactor ($p_{O_2,out}$). Due to anticipated kinetic limitations, the minimum operating temperature is set to 600 °C (solid lines). Nevertheless, Figure 3 shows values down to 500 °C (dotted lines). As expected, lower $p_{O_2,out}$ requires higher $\Delta\delta$ and higher ΔT . Figure 3c shows an estimate of the heat required per mol of N_2 separated where the content of sensible heat associated with the MO_x is high (around 65-85%) suggesting an opportunity for heat integration to maximize system efficiency. This heat required increases with the reduction temperature, suggesting the lowest possible reduction temperature as the optimal one. For $p_{O_2,out} = 10^2, 10^1, 10^0,$ and 10^{-1} Pa, the optimal operating temperatures in the reduction reactor are 822, 977, 1164 and 1417 °C respectively. Lower $p_{O_2,out}$ than 10^{-1} Pa is not achievable using atmospheric air as the oxidant in the temperature range studied.

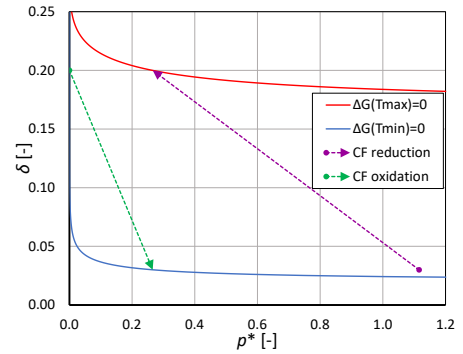


Figure 2: Reduction and oxidation reactor in δ - p^* coordinates

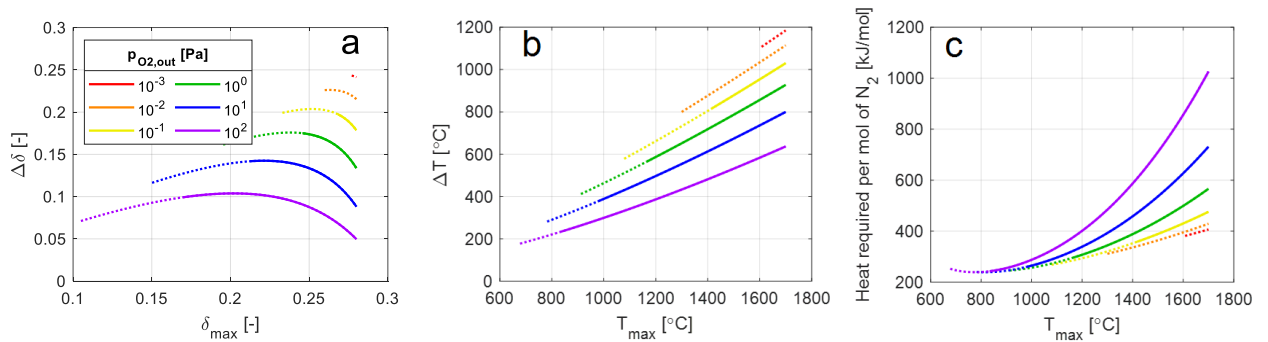


Figure 3: System operation analysis of the N_2 separation process for $p_{O_2,in} = 0.21$ kPa (re-oxidation): a) $\Delta\delta$, b) temperature, c) heat required per mol of N_2 . See main text for the distinction between solid and dotted regions.

Acknowledgements

This material is based on work supported by the U.S. Department of Energy Solar Energy Technologies Office under Award No. DE-EE0001529. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

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