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

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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 (MOx) cycle. The first step is thermal reduction of a redox active MOx at high temperature, releasing gaseous oxygen from the material. In the second step, the reduced MOx 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 MOx, 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 MOx, reactant flows in both steps are countercurrent by design. To avoid second law violations, we ensure mass conservation and the Gibbs criterion (ΔG ≤ 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 MOx. The reactor is directly irradiated, gravity-driven, with a granular flow. The air sweep is countercurrent. The reduced MOx 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 MOx leaves the re-oxidation reactor and returns to the reduction reactor.

3. Thermodynamic analysis

To guarantee ΔG ≤ 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 MOx and p′ is the dimensionless pressure variable defined as p′ = PO2/(Psys - PO2). 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 (ΔG = 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.
This methodology enables an optimization of the operating conditions of the N\textsubscript{2} separation system. Figure 3 shows a performance analysis when the MO\textsubscript{x} is SrFeO\textsubscript{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\textsubscript{O\textsubscript{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\textsubscript{O\textsubscript{2,OUT}} requires higher Δδ and higher ΔT. Figure 3c shows an estimate of the heat required per mol of N\textsubscript{2} separated where the content of sensible heat associated with the MO\textsubscript{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\textsubscript{O\textsubscript{2,OUT}} = 10\textsuperscript{2}, 10\textsuperscript{1}, 10\textsuperscript{0}, and 10\textsuperscript{-1} Pa, the optimal operating temperatures in the reduction reactor are 822, 977, 1164 and 1417 °C respectively. Lower P\textsubscript{O\textsubscript{2,OUT}} than 10\textsuperscript{-1} Pa is not achievable using atmospheric air as the oxidant in the temperature range studied.

Figure 3: System operation analysis of the N\textsubscript{2} separation process for P\textsubscript{O\textsubscript{2,IN}} = 0.21 kPa (re-oxidation): a) Δδ, b) temperature, c) heat required per mol of N\textsubscript{2}. See main text for the distinction between solid and dotted regions.

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References