

Solar-Thermal Ammonia Production: A Renewable, Carbon-Neutral Route to Ammonia via Concentrating Solar Thermochemistry

Andrea Ambrosini^{1*}, H. Evan Bush¹, Xiang Gao², Nhu "Ty" Nguyen, Alberto de la Calle, Ivan Ermanoski, Tyler Farr, Kevin Albrecht, Matthew W. Kury, Peter Loutzenhiser, and Ellen B. Stechel

¹ Concentrating Solar Technologies, Sandia National Laboratories, Albuquerque, NM USA 87185-1127

² ASU LightWorks®, Arizona State University, PO Box 875402, Tempe, AZ 85287-5402, USA

³George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0405, USA

* Corresponding author: aambros@sandia.gov, +1.505.284.1340

1. Introduction

Ammonia (NH₃) is an energy-dense chemical and a vital component of fertilizer. It is also a potential candidate for thermochemical energy storage for high-temperature concentrating solar power (CSP) and carbon-neutral liquid fuel. NH₃ is currently synthesized via the Haber-Bosch process, which requires pressures of 15- 25 MPa and temperatures of 400-500 °C. Burning hydrocarbons produces the heat and mechanical energy required to drive the NH₃ reaction. Hydrogen (H₂) and nitrogen (N₂) feedstocks are also sourced from methane. All three processes (sourcing the energy, producing H₂ and N₂) produce CO₂ emissions. As a result, NH₃ production accounts for almost 1.5% of global CO₂ emissions. The development of a renewable pathway to NH₃ synthesis that utilizes concentrated solar irradiation for the process heat instead of hydrocarbon combustion and operates under relatively low pressure, will result in both a decrease (or elimination) in greenhouse gas emissions and avoid the cost, complexity, and safety issues inherent in high-pressure processes.

2. Solar Thermal Ammonia Production

The aim of the Solar-Thermal Ammonia Production (STAP) project is to develop a solar thermochemical looping technology to produce and shuttle N₂ from air for the subsequent production of NH₃ in an advanced two-stage process. In the first cycle, the endothermic thermal reduction of redox-active metal oxide particles is driven by concentrated solar irradiation; subsequent exposure to air re-oxidizes the particles, removing O₂ and producing relatively pure N₂ gas. The N₂ serves as a feedstock for a renewable NH₃ production process in an advanced two-step, low pressure, looping cycle. In the first step, H₂ reacts with metal nitride particles to produce NH₃, resulting in a reduced (nitrogen deficient) metal nitride. In the second step, the nitride is regenerated utilizing the nitrogen produced in the air separation step. The net result is NH₃ produced from sunlight, air, and (green) H₂, while the metal oxide and nitride particles are recycled. As part of the project, a full systems model and techno-economic analysis were performed to optimize process conditions and determine the feasibility and costs of process scale up. The system concept will be summarized in this presentation.

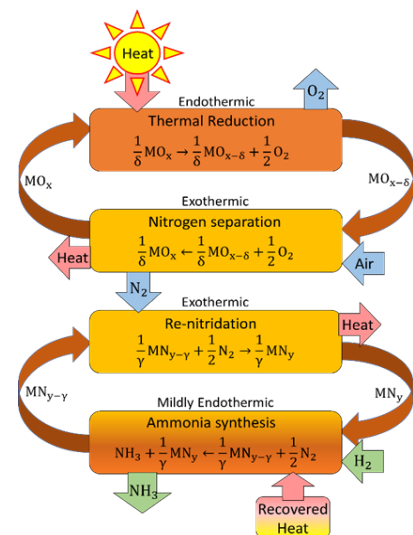


Fig. 1: The Solar Thermal Ammonia Production process.

3. Results and Discussion

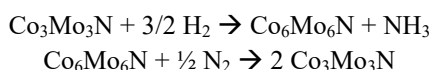
3.1. Nitrogen Separation

Metal oxides were synthesized from nitrate salts via a modified Pechini method described in previous work (1). An extensive screening based on redox capacity and chemical stability was performed for singly- and

doubly-substituted perovskite strontium ferrites, $A_xSr_{1-x}B_yFe_{1-y}O_{3-\delta}$, where A = La, Ba, Ca, B= Co, Cr, Cu, Mn. Based on the screening, $A_xSr_{1-x}FeO_{3-\delta}$ (A=Ba, La; x = 0.01-0.02) were chosen as candidate materials [1,2]. Informed by detailed thermodynamic and kinetics characterization and heat and mass transfer models [3], a lab-scale packed bed reduction reactor was designed and fabricated. ~35 g of $Ba_{0.15}Sr_{0.85}O_{3-\delta}$ were synthesized and tested for O_2 separation capacity, demonstrating >20 min of air separation at a reduction temperature of 800 °C under Ar and re-oxidation temperature of 500 °C in air. In addition to the bench-scale reactor, an on-sun thermal reduction reactor has been constructed for operation on a high-flux solar simulator.

3.2 Ammonia Synthesis

Metal nitrides were synthesized from their constituent oxides, using a modified literature preparation [4]. Metal oxides were first synthesized from metal nitrite hydrates and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ based on a modified Pechini method. The resulting oxide powders were then converted to nitrides by sintering at 785 °C under an atmosphere of 10 vol% H_2 in N_2 for up to 10 h. A series of mixed metal nitrides, A_xB_yN (A=Co, Ni, Fe; B=Mo, W) was synthesized and screened for reduction and re-nitridation. Co_3Mo_3N (CMN331) was chosen for further study based on its potential to lose up to 50 mol% of its nitrogen upon reduction in H_2 and re-uptake that nitrogen under N_2 while remaining isostructural [4]:



Under H_2/Ar mixtures at ambient conditions, the reduction with subsequent NH_3 production was observed. However, in the presence of N_2 , re-nitridation at 700 °C is sluggish and incomplete without the addition of significant amounts of H_2 (75% H_2/N_2). An ammonia synthesis reactor (ASR) was designed and constructed to investigate the reaction under non-ambient pressure. NH_3 production and re-nitridation were observed over multiple cycles under isothermal conditions (650 °C) and pressures an order of magnitude below that of Haber-Bosch. Preliminary results under both ambient and pressurized conditions imply a combined bulk and catalytic element to the NH_3 synthesis reaction.

3.3. Technoeconomic and Systems Analyses

An integrated systems model of the entire STAP process was generated to determine the optimal design and operating conditions for the process. The design envisions CSP-driven thermal oxide reduction in air and the N_2 separation step in a counter-current particle configuration. NH_3 synthesis and re-generation occur in two alternating fixed bed reactors. A technoeconomic analysis based on the system design, heat and mass transfer models, and empirical results reveals that the levelized cost of ammonia (LCOA) is most sensitive to the ammonia synthesis subsystem, which is also the process with the most performance uncertainty. The analysis will be continuously refined as data is collected from the empirical characterization. However, the results show that economical production of NH_3 via STAP is, in fact, feasible.

4. Acknowledgements

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