

A Low-pressure Reactor Design for Solar Thermochemical Ammonia Production

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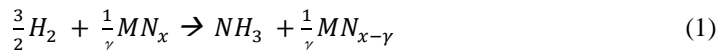
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1. Introduction

Ammonia (NH₃) is one of the most commonly produced industrial chemicals worldwide. Fertilizer for agriculture accounts for about 80% of NH₃ production. Many industrial and household applications such as refrigerant gas, water purification, and plastics manufacture use ammonia [1]. Furthermore, NH₃ is in consideration as a hydrogen carrier or as an energy vector in a deeply decarbonized energy system. Currently, synthesis of NH₃ uses the Haber-Bosch (H-B) process, an energy-demanding conversion from H₂ and N₂ at 150-250 bar and temperatures between 400-500 °C [2]. This is a highly carbon-intensive process, as the major source of H₂ is from steam reforming of methane and the source of N₂ is air after removing the oxygen via combustion of hydrocarbons, generally natural gas. Additionally, methane combustion provides the energy necessary for process heat and for pressurizing. As such, there is a strong incentive to develop a renewable NH₃ synthesis pathway, such as using concentrating solar irradiation for process heat and pursuing relative low-pressure operating conditions. A renewable NH₃ synthesis pathway will significantly help mitigate greenhouse gas emission and avoid the complex safety issues with high-pressure processes at elevated temperatures. There would also be advantages in alternative NH₃ synthesis technologies that can operate flexibly and at a smaller scale than H-B.

2. Ammonia synthesis reactor (ASR) design

Recent advances in concentrating solar power technologies have enabled renewable synthesis of N₂ and H₂ in carbon-free processes. Specifically, solar thermochemical cycles can produce high purity N₂ by removing oxygen from air with redox-active metal oxides, and advanced water splitting can produce renewable H₂ via a number of processes, such as a two-step thermochemical metal oxide cycle, PV-electrolysis, or photo-electrochemical pathways. In this context, renewable N₂ and H₂ can serve as feedstocks to a novel low-pressure NH₃ production process, characterized by the following chemical looping reactions:



In a mildly endothermic step (1), a stable metal nitride reacts with H₂ to produce NH₃ and a nitrogen deficient metal nitride. In step (2), the nitrogen-deficient nitride reacts with N₂ to form the initial nitride. Preliminary thermodynamic calculations suggest this chemical looping strategy to synthesize NH₃ could reduce the pressure demand considerably, likely by an order of magnitude compared to the H-B process. This significantly liberates the design constraints in a dedicated reactor, as most of the common materials such as 316 stainless steel can easily operate in this pressure range without further protective strengthening.

To demonstrate this novel concept, we designed an ammonia synthesis reactor (ASR) concept (Fig. 1). Reactions (1) and (2) alternate by switching between N₂ and H₂ inlet gas flows. Pressure regulators at the inlet and exit of the system maintain the pressure in the reactor. The design purposely maximizes the utilization of commercial off-the-shelf components, with well-specified performance characteristics, most importantly the

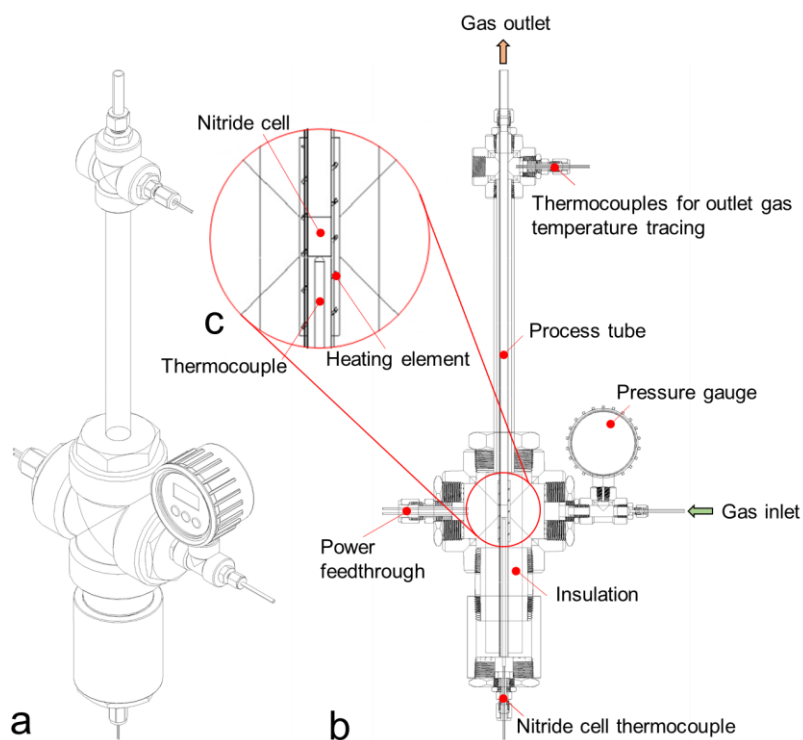


Figure 1: Illustration of the NH_3 synthesis reactor (ASR). (a) Isometric view. (b) Front cut-plane view with major components labeled. (c) Heated reaction zone. For reference, the reactor is ~24" tall.

handling of H_2 in the anticipated range of process pressures (up to 30 bar) and temperatures (below 600 °C). Additionally, to maximally capitalize on the existing experience of H-B operations, the ASR design fully addresses the compounding effect of high pressure and high temperature that may further amplify risks including hydrogen attack, hydrogen embrittlement, temper embrittlement, and nitriding effect on the reactor vessel and reaction zone. To achieve this, the design employed a philosophy of separating pressure differential (“cold-wall” pressure vessel) and temperature differential (“hot-wall” reaction zone). The enabler for this separation is cool inlet H_2/N_2 gases that fill an annulus between the process tube and the pressure vessel. The reactants then pass through the process tube, including the hot reaction zone containing the reactive metal nitride. To minimize the stored energy inside the system and enhance the flow profiles of the gas feedstocks, the design significantly minimizes unnecessary dead volumes in the pressurized zone.

The compact and flexible ASR design is a cost-effective and energy-efficient low-pressure reactor that will enable the evaluation of the reaction thermodynamics, kinetics, yield, mass transfer, heat transfer, cost, reliability, and operational complexity of a solar thermochemical NH_3 production system. Emulating key design features of H-B reactors limits the risk of scale-up and integration beyond concept demonstration.

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