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Solar thermochemical production of ammonia from water, air and sunlight: Thermodynamic and economic analyses

Ronald Michalsky [a,b], Bryon J. Parman [a,c], Vincent Amanor-Boadu [c], Peter H. Pfromm [b,*]

[a] NSF IGERT, Kansas State University, Manhattan, KS 66506, USA
[b] Department of Chemical Engineering, Kansas State University, Manhattan, KS 66506, USA
[c] Department of Agricultural Economics, Kansas State University, Manhattan, KS 66506, USA

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ABSTRACT

Ammonia is an important input into agriculture and is used widely as base chemical for the chemical industry. It has recently been proposed as a sustainable transportation fuel and convenient one-way hydrogen carrier. Employing typical meteorological data for Palmdale, CA, solar energy is considered here as an inexpensive and renewable energy alternative in the synthesis of NH_3 at ambient pressure and without natural gas. Thermodynamic process analysis shows that a molybdenum-based solar thermochemical NH_3 production cycle, conducted at or below 1500 K, combined with solar thermochemical H_2 production from water may operate at a net-efficiency ranging from 23 to 30% (lower heating value of NH_3 relative to the total energy input). Net present value optimization indicates ecologically and economically sustainable NH_3 synthesis at above about 160 tons NH_3 per day, dependent primarily on heliostat costs (varied between 90 and 164 dollars/m^2), NH_3 yields (ranging from 13.9 mol% to stoichiometric conversion of fixed and reduced nitrogen to NH_3), and the NH_3 sales price. Economically feasible production at an optimum plant capacity near 900 tons NH_3 per day is shown at relative conservative technical assumptions and at a reasonable NH_3 sales price of about 534 ± 28 dollars per ton NH_3.

1. Introduction

The U.S. Census Bureau estimates that between 1900 and 2000, the world's population grew from 1.6 billion to 6.0 billion, and is projected to reach 9.0 billion by 2050 [1]. Global human population growth is projected to increase the strain on current natural resources, such as land, fossil hydrocarbons, and fresh water, if technological advances are not made in the production of products and services using these resources.

While technological advances in agriculture in the 20th century - chemical fertilizers, mechanization, breeding, genetic improvement, chemical pest control, processing and storage systems - have contributed to vastly increase the productivity of land globally, the interface between energy and fertilizer production, especially ammonia, promises to challenge the agricultural productivity in the future. At present, over 100 million metric tons of NH_3 [2] are produced annually, driven by increasing food demand and the need for higher crop yields [3]. NH_3 is the single-most important synthetic fertilizer, accounting for 58 wt% of all fertilizer consumed for example in the USA in 2007 [4]. Its role in the production of bioenergy feedstock and its potential use in solar-derived H_2 storage [5–7] or as a liquid fuel [8,9] augment its criticality and importance in the global economy.

NH_3 easily reaches the U.S. Department of Energy 2015 hydrogen storage target for H_2-based transportation fuels [8,10] or it can be blended into diesel for direct combustion in modified diesel engines releasing mainly H_2O and N_2 as combustion-products [11]. If these competitive uses and the duty of the agricultural industry to feed a growing global population at reasonable prices are to be realized new and innovative NH_3 synthesis technology will likely be required.

Industrially, the Haber–Bosch process synthesizes NH_3 by shifting the reaction equilibrium of a N_2/H_2 gas mixture at high pressure (about 30 MPa) towards formation of ideally 22.7 mol% NH_3 (relative to stoichiometric conversion) at 673–873 K and in presence of a catalyst [12]. The energy-intensive process [13], including natural gas/steam reforming for H_2 production (accounting for approximately 84% of the total energy required), consumes 28–40 GJ/t NH_3 in form of natural gas [12,14] (about

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* Corresponding author. 1036 Durland Hall, Kansas State University, Manhattan, KS 66506. Tel.: +1 785 532 4312; fax: +1 785 532 7372.
E-mail address: pfromm@ksu.edu (P.H. Pfromm).

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1–2% of the world's annual energy production [15]). Approximately 2.3 t of fossil-derived CO_2 are generated per t NH_3 synthesized [14]. Employing steam-reforming of coal increases the energy required for NH_3 production even further (about 47.6–165.9 GJ/t NH_3) and increases the associated generation of fossil CO_2 (16.7 t CO_2/t NH_3) [6,14]. Economies of scale have dictated current Haber–Bosch facilities producing above about 1500 t NH_3 per day, consuming significant quantities of natural gas and influencing that commodity's price trend. This in turn has a direct impact on NH_3 prices and their volatility.

Various alternatives proposed for nitrogen fixation from the atmosphere via synthesis of NH_3 including catalytic formation of NH_3 near ambient temperature and pressure in the liquid phase [16] and electrochemical NH_3 synthesis [17] have not yet reached maturity. Solar thermochemical NH_3 synthesis at ambient pressure is a proposed remedy to some of the difficulties associated with the Haber–Bosch process [5,18–21]. Reactive NH_3 synthesis via a two-step solar thermochemical cycle of metal oxide nitridation and metal nitride hydrolysis [19,22] has been demonstrated to form significant quantities of NH_3 from air and water at near 0.1 MPa [19]. The process neither requires a catalyst nor a fossil hydrogen source. The energy required for the generation of H_2 via H_2O splitting and for the reductive cleavage of N_2 is supplied in form of solar energy [18,20]. Concentrated solar radiation, absorbed at elevated temperature in an endothermic metal oxide reduction, creates a metal nitride in the presence of N_2. The fixed nitrogen is, thereafter, released from the solid metal nitride as NH_3 in an exothermic steam hydrolysis reaction. Given the abundance of solar radiation in many areas of the world, this approach has the potential to produce NH_3 sustainably and facilitates simultaneous storage of intermittently available solar energy [23,24].

Solid carbon (biomass or charcoal) has been suggested as reducing agent of the metal oxide in the process discussed above [18,20]. However, carbon may not be available in the right quantities and proximity to the manufacturing plant, requiring transportation or production, using up arable land, and requiring expensive and energy-intensive processing [25,26]. On the other hand, reactants forming metal oxides which can be reduced with H_2 unfortunately tend to not fix 0.1 MPa N_2 in form of metal nitrides and show low NH_3 yields when reacting their nitrides with steam [21]. Molybdenum considered here represents a trade-off [21]: The oxide (MoO_2) that is formed during nitride (Mo_2N) hydrolysis at above 800 K can be reduced [27] and nitridated with moderate yields in H_2/N_2 gas mixtures in the range of 800–1500 K [28,29]. Given the relative high ionicity of the nitride [30,31], significant quantities of NH_3 are liberated during the hydrolysis of Mo_2N at atmospheric pressure.

The work presented here conceptually assesses the technical and economic attractiveness of Mo-based solar thermochemical NH_3 synthesis in the absence of any carbonaceous material or natural gas as feedstock or for energy (Fig. 1). Experimentation towards the technical feasibility of the reaction cycle is described elsewhere [20].

A thermodynamic analysis for synthesizing NH_3 in a two-step solar thermochemical reaction cycle from H_2 and N_2 with a Mo-based reactant at 0.1 MPa (Fig. 1) is presented in Section 2.1. Section 2.2 determines plant capacity and energy efficiency and CO_2 emissions of the Haber–Bosch process implemented with natural gas as a benchmark for a process analysis of the proposed reaction cycle (Fig. 2) in Section 2.3. The analysis simulates an implementation of the reaction cycle with H_2 generated via a well-studied solar thermochemical H_2O splitting cycle using zinc [24,32,33]. In practice, the proposed NH_3 synthesis may be implemented with other solar-to-hydrogen technologies [33]. Section 3.1 estimates investment costs for unit operations and chemical commodities used in Section 3.2 that develops an economical optimization model for scalable solar thermochemical NH_3 synthesis. The model is evaluated and discussed employing net present value calculations in Section 3.3. Section 3.4 shows that the proposed concept is economically attractive under fairly conservative assumptions.

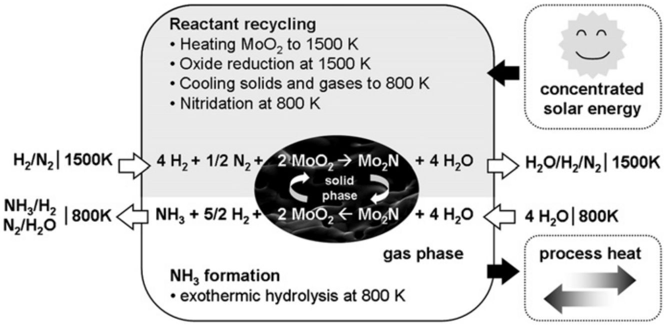

Fig. 1. Concept for solar thermochemical NH_3 synthesis near atmospheric pressure using a molybdenum reactant.

2. Thermochemical NH_3 synthesis cycle

The Gibbs free energy of formation for a metal nitride is relatively small compared to the corresponding oxide. Thus, only a few metals such as Mo allow simultaneously for oxide reduction with H_2 and reductive cleavage of dinitrogen at 0.1 MPa [21,28,29]. Mo is shown here to be a promising reactant for solar thermochemical NH_3 synthesis.

To estimate the equilibrium reaction yield achievable in a system closed to mass transfer, the free energy of reaction, $\Delta_{rxn}g$, was computed based on the literature [27]. The absolute error of energy of formation data was estimated previously with ±3 kJ [34] and was taken as 2% of the value in kJ/mol. The computed formation of Mo_2N was extrapolated at >800 K using a linear fit ($R^2 > 0.999$). With the free energy computations in hand, the equilibrium constants, K_{eq}, were determined at atmospheric pressure taking the total number of chemical species in the system for simplicity as the arithmetic mean of the number of reactants and the number of products at complete conversion [35]. This allows solving the elemental mol balances of the given reaction system symbolically ("live" Symbolics, Mathcad 13) as a function of K_{eq}, that is yielding the equilibrium composition of the reaction system as a function of temperature, T, at 0.1 MPa.

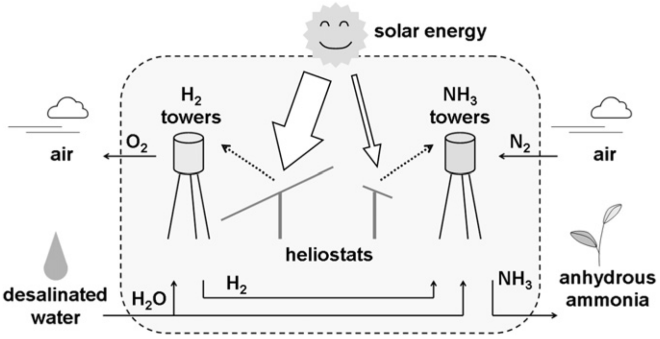

Fig. 2. Conceptual implementation of solar thermochemical NH_3 synthesis coupled with solar thermochemical H_2 synthesis.