Green ammonia from air, water, and renewable electricity: energy costs using natural gas reforming, solid oxide electrolysis, liquid water electrolysis, chemical looping , or a Haber-Bosch loop

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Abstract

The purpose of this work is to quantitatively compare the energy cost of design alternatives for a process to produce ammonia (NH_3) from air, water, and renewable electricity. It is assumed that a Haber-Bosch (H.-B.) synthesis loop is available to produce 1000 metric tons (tonnes) of renewable NH_3 per day. The overall energy costs per tonne of NH_3 will then be estimated at U.S.$195, 197, 158, and 179 per tonne of NH_3 when H_2 is supplied by (i) natural gas reforming (reference), (ii) liquid phase electrolysis, (iii) solid oxide electrolysis (SOE) of water only, and (iv) simultaneous SOE of water and air. A renewable electricity price of U.S.$0.02 per $kWh_{electric}$, and U.S.$6 per 10^6 BTU for natural gas is assumed. SOE provides some energy cost advantage but incurs the inherent risk of an emerging process. The last consideration is replacement of the H.-B. loop with atmospheric pressure chemical looping for ammonia synthesis (CLAS)combined with SOE for water electrolysis, and separately oxygen removal from air to provide N_2, with energy costs of U.S.$153 per tonne of NH_3.

Overall, the most significant findings are (i) the energy costs are not substantially different for the alternatives investigated here (ii) direct SOE of a mixture of steam and air, followed by a H.-B. synthesis loop, or SOE to provide H_2 and N_2 separately, followed by CLAS) may be attractive for small scale production, modular systems, remote locations, or stranded electricity resources with the primary motivation being process simplification rather than significantly lower energy cost.

Keywords

Ammonia; Haber-Bosch; renewable; fossil-free; fertilizer; solid oxide, chemical looping

150 word significance statement

Synthetic ammonia for fertilizers enables almost half of all crops globally. The demand for synthetic ammonia will grow due to population increases and emerging applications for ammonia

as an energy vector. Synthetic ammonia is currently made from fossil fuels and is responsible for about 2% of all fossil CO_2 emissions world wide. One emerging technology (solid oxide electrolysis of steam to produce hydrogen) and one research stage technology (chemical looping for ammonia synthesis) are evaluated for the overall energy costs when using them with renewable electricity to produce green ammonia. The energy costs for green ammonia vs. fossil fuel based ammonia are competitive in all renewable energy scenarios without taking credit for CO_2 avoidance. Maturity may favor conventional electrolysis and the Haber-Bosch process at the 1000 tonne ammonia per day scale, while new technologies may come to the fore at small scale, in modular units, and for stranded resources.

Introduction

Process options investigated here

The goal of the work presented here is to quantitatively compare four technological approaches to synthesize NH_3 from renewable electricity, air, and water in regard to their energy demand and energy cost. Recent claims regarding solid oxide electrolysis (SOE) to produce hydrogen from water for NH_3 synthesis will be verified independently. Previous work (*1*) regarding the energy demand and cost of renewable NH_3 based on electrolysis of liquid water and a H.-B. synthesis loop will be updated with recent energy costs and compared to the approaches in Figure 1. The Approach 4 including chemical looping using manganese/manganese nitride (CLAS, only at the research stage, as opposed to all other technologies) is included since it operates at atmospheric pressure and 700ºC. These conditions are well matched to SOE conditions.

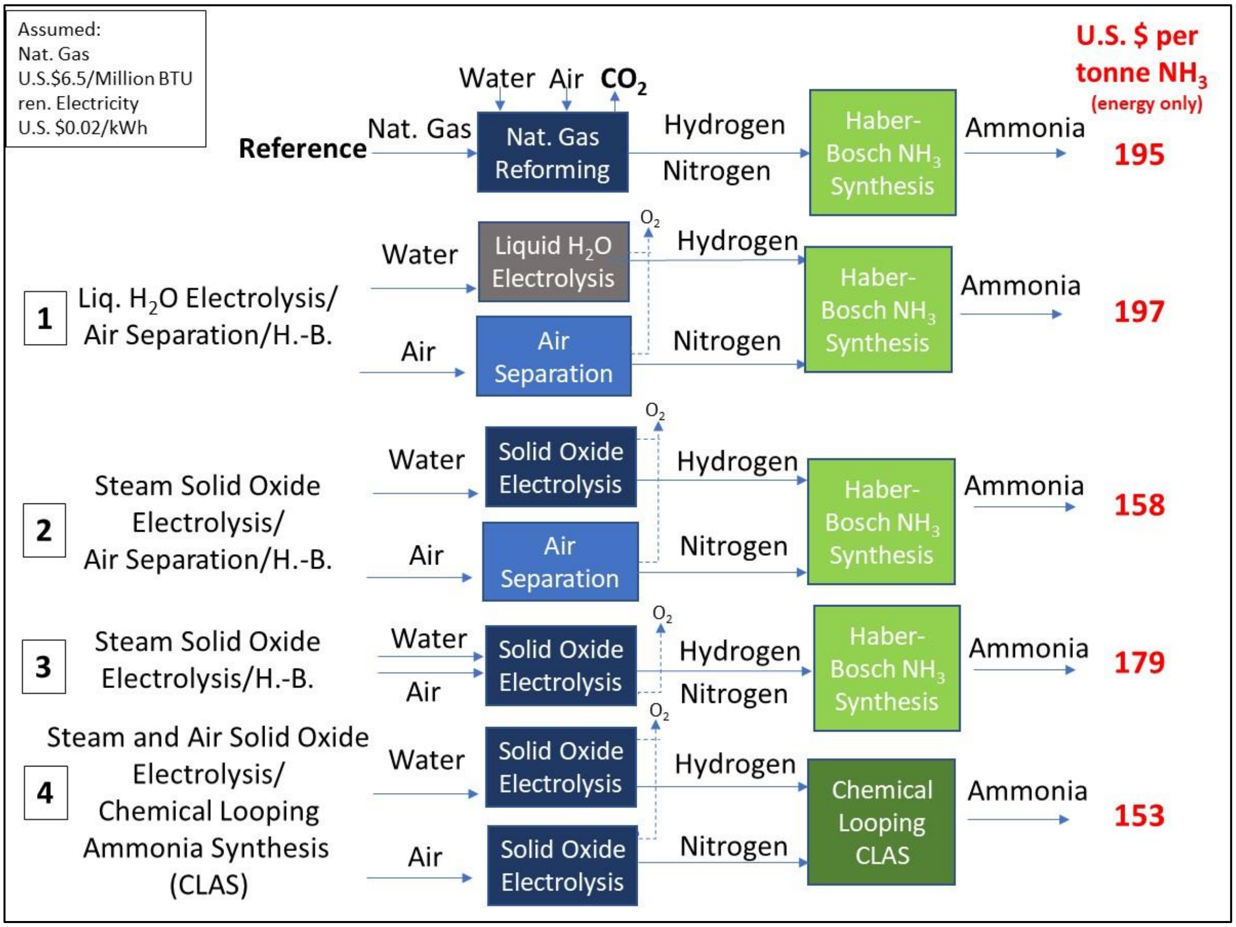

Figure 1: Four approaches to NH_3 synthesis based on renewable electricity (natural gas based as reference). Energy costs are previewed here, see below for details.

First, the less familiar processes of SOE and chemical looping ammonia synthesis (CLAS) will be introduced. Industrial claims regarding the energy efficiency of SOE will be independently verified. Mass- and energy balances for the Approaches 1-4 shown in Figure 1 will be shown resulting in the energy costs previewed in Figure 1. Capital expense estimates will be discussed.

In summary, none of the four approaches in Figure 1 has a decisive advantage regarding energy costs at this level of analysis. On the other hand, no approach should be discarded out of hand. The difficulty in predicting fossil energy prices and availability (*2*) may encourage investment in renewable electricity based NH_3 synthesis since renewable electricity has shown a remarkable and consistent decrease in levelized cost over many years and is often produced in-country. De-risking fertilizer cost is helpful to the required multi year planning of agricultural producers.

Scope of the work presented here

The focus in the work presented here is on the energy costs for a number of alternative processes, including SOE and CLAS.

Studies based on the life cycle approach (often employing the GREET model curated by Argonne National Laboratory) are available for ammonia synthesis, although one has to carefully scrutinize assumptions such as the way heat is provided to SOE (*3*). It appears that the life cycle approach does confirm what may have been intuitively assumed: N_2 production is fairly inconsequential since the energy consumption is relatively small, while H_2 production consumes large amounts of fossil energy if cracking or steam methane reforming is used, while using renewable electricity to electrolyze water for H_2 lowers the fossil energy use and carbon emissions of ammonia synthesis very substantially.

Each of the unit operations that are assembled to produce ammonia has been exhaustively reported in the literature and practiced at the industrial scale over many decades, except SOE and CLAS. Unit operation comparisons regarding their impact are available (*4*) but the work presented here aims to use well-recognized performance parameters to arrive at the cost of energy. Capital cost is briefly discussed. In a process where energy cost dominates much of the economics it is most important to establish if a case can be made for competitive energy costs per unit of product since this can disqualify a processing option quickly and clearly.

It is acknowledged that improvements will generally occur over time, whether in capital cost (especially for emerging processes) or energy demand for a given process. Energy demand improvements, however, generally encounter a hard limit through thermodynamics. A future projection of improvements in capital cost is not the goal here, and energy demand is not likely to change significantly due to the thermodynamic limitations.

Natural gas reforming based NH_3 synthesis as the reference process

As an energy- and cost reference (Figure 1, top) the energy demand for state of the art natural gas based NH_3 via steam reforming and the H.-B. process has been estimated at 361 Megawatt (MW, as lower heating value of natural gas) for 1000 tonnes of NH_3 produced per day (1). With this energy demand, the energy cost per tonne of NH_3 can be approximated at the given scale as

$$\mathbf{C = 30 * (Price)} \qquad \textbf{Equation 1}$$

where Price is the price of natural gas in U.S.$ per million British thermal units (BTU), and C is the energy cost for NH_3 production from natural gas in U.S.$/tonne of NH_3. It is acknowledged that the natural gas price fluctuates, and sometimes in surprising ways due to economic or political boundary conditions. With recent energy costs of U.S.$6.5 per 10^6BTU for natural gas assumed, about U.S.$ 195 per tonne of natural gas based NH_3 is then used here as a reference. The above equation allows easy recalculation as natural gas prices fluctuate.

Importance and markets for renewable ammonia

The importance of synthetic NH_3 to produce food for our growing global population of more than 7 billion humans can not be overstated. Synthetic NH_3 and fertilizers derived from it enable 30-50% of all global agricultural crop output (*5*). Some may contemplate nitrogeneous fertilizers such as manure and feces instead of synthetic fertilizers. This is certainly useful locally or at a small scale, but these materials can not replace synthetic NH_3 at an impactful global scale (*6*). Renewable synthetic NH_3 opens a path to de-risk farming by decoupling fertilizer prices from volatile fossil fuel prices, largely decouple our food from fossil fuels, and significantly reduce global greenhouse gas emissions.

Renewable NH_3 shall here be defined as NH_3 produced using renewable electricity. The current global production of over 180 million tonnes of synthetic NH_3 per year will need to continue to rise due to population increases. Emerging applications for NH_3 as a renewable energy vector may raise global demand significantly. NH_3 from renewable electricity is at the center of numerous projects world wide ranging from pilot scale to the multiple 1000 tonnes per day since it may (in addition to serving as fertilizer), supply convenient storage and transport of renewable H_2 in form of NH_3, be used directly as an internal combustion engine fuel for marine engines (*7*,*8*) and turbines including aircraft engines, be used in industrial furnaces and powerplants (*9*), and be used as dispatchable storage of intermittent renewable electricity through fuel cells (*10*) and stationary turbines. The global market for NH_3 would for example double if only about 10% of global maritime shipping is converted from furl oil to NH_3 . The maritime shipping application is well under way at full scale with engines and ships under construction.

Importance of hydrogen production in NH_3 synthesis

The energy demand of NH_3 synthesis (and thereby a large part of the operating cost) resides mainly in H_2 production. H_2 production consumes over 90% of the energy expended to produce NH_3. Currently essentially all NH_3 is synthesized using coal or natural gas, leading to about 2% of global fossil CO_2 emissions (*11*). This illuminates the fact that catalysts for the H.-B. process beyond commercially available catalysts are only of academic interest. Developing H.-B. catalysts that operate at lower temperatures than the existing industrial catalysts is, for example, actually detrimental from an energy perspective since the large amount of energy from the H.-B. reactors due to the exothermal synthesis reaction would then be devalued compared to higher quality thermal energy available through high temperature catalysis.

Down-scaling research and experience forNH$_3$ synthesis

Cussler and co-workers have for some years advanced pilot-scale developments for a modification of the NH_3 recovery from a Haber-Bosch loop by replacing condensation of the NH_3 from the loop with adsorption of NH_3 on a solid (*12*). The target of this work is renewable energy-driven NH_3 synthesis that is efficient and simple at a scale far below the typical world-scale 1000 tonnes per day NH_3 produced.

An on-farm installation using liquid water electrolysis and H.-B. synthesis to produce NH_3 and H_2 from air, water, and mainly solar photovoltaic electricity has been implemented on an Iowa farm (*13*). It is perhaps most notable that this demonstration (covering about 10% of the needed energy for tractoring and fertilization for the farm) was realized with essentially off the shelf conventional technology in a farm environment. This confirms that economics and practicality, rather than technological barriers are most significant.

Down-scaling renewable NH_3 synthesis to the tonne-per-day scale has recently become an active area for research and development. Issues are exacerbated if an intermittent (on the scale of minutes to days) electricity supply is also considered (14). An energy supply will be needed to maintain reactors at temperature for minute-scale startup, and a blanket nitrogen supply is needed to preserve H.-B. catalysts. This continuing energy demand in the face of intermittency of electrical energy, say, from a wind turbine could be addressed perhaps by using an internal combustion generator set to supply electricity and some heat operated directly with easily stored NH_3, with H_2 from cracked NH_3, or even with an auxiliary supply of fossil fuel.

Simplification

All gas streams routed to a H.-B. reactor must be scrupulously purified to remove oxygen. This process step is neglected. Energy for recycling (SOE: steam, H.-B.: unreacted syngas, CLAS: unreacted H_2 if present) is neglected since little compression is required. Energy losses to the environment are neglected.

Principle of SOE

The principle of SOE (Figure 2) is enticing in its simplicity due to the membrane material possessing perfect selectivity for oxygen transport, and a low electrical energy demand (albeit supplemented by thermal energy) compared to state of the art electrolysis of liquid water.

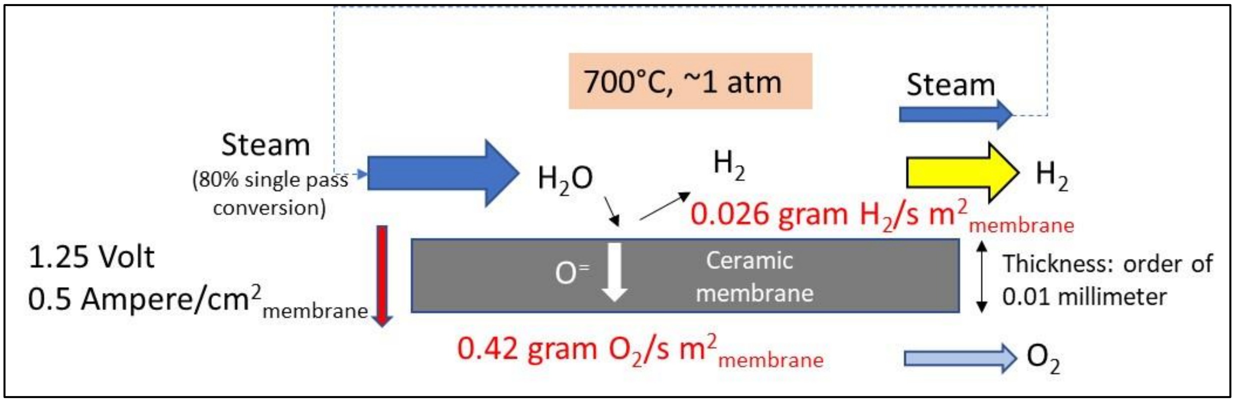

Figure 2: The principle of solid oxide electrolysis (SOE) with estimated potential difference, current density (*15*, *16*), and productivity per membrane area. The hydrogen/unconverted steam separation via condensation or other means is not shown in detail.

A comprehensive review (*17*) shall serve to cover SOE and solid oxide fuel cells (SOFC) for the interested reader. Briefly, solid oxide electrolysis (SOE) relies on the essentially perfect selectivity of certain crystalline inorganic materials such as yttria stabilized zirconia (YSZ) membranes for the transport of oxygen anions at temperatures of several hundred ºC under the driving force of an imposed electric field. Steam is contacted with one side of a thin (several tens of micrometers, usually deposited on a porous support for mechanical stability) inorganic YSZ type membrane where the water molecules (or oxygen molecules if present, see Figure 1, Approach 3) are split at one surface (feed side). Oxygen ions (from water or molecular oxygen) are driven through the membrane under an applied electrical field and emerge as essentially pure molecular oxygen from the opposite surface of the membrane (permeate side). Hydrogen from water (and any gases such as N_2 if present, not shown in Figure 2) stays behind and is harvested as hydrogen gas (H_2).

Advantageous thermodynamics theoretically allow 20-30% more H_2 to be produced per kilowatt hour (kWh) of renewable electricity using SOE compared to state-of-the-art liquid-phase electrolysis provided that a source of makeup process heat is available to (i) produce steam for the SOE feed, and (ii) supplement SOE with thermal energy (*18*). NH_3 synthesis fortuitously provides some heat of reaction when renewable NH_3 is produced from SOE-derived renewable H_2 via the H.-B. approach. Some additional heat can be obtained when the products from SOE (O_2 and H_2, here assumed at 700°C) are cooled before entering the H.-B. synthesis loop.

SOE can also further simplify renewable NH_3 synthesis overall since water electrolysis to obtain H_2, and oxygen (O_2) removal from air to obtain nitrogen (N_2) can be performed simultaneously in the same SOE unit. This renders a separate unit to derive N_2 from air unnecessary. Additionally, it could be conceived to use the SOE units "in reverse" as fuel cells to produce electricity for more process flexibility and to provide additional income when electricity prices are high.

Realizing SOE at scale has been elusive for many years. Early reports at the pilot scale were encouraging (*19*) but did not lead to widespread full scale adoption. Much important work towards proper materials has been completed over the years in the laboratory at a square centimeter scale. It is a formidable engineering challenge, however, to build devices that package many square meters of perfect and thin inorganic membranes that are quite brittle and are exposed to repeated heating/cooling between room temperature and 500ºC-700ºC. Progress to realize industrial scale implementations is summarized in reports by the U.S. Department of Energy's long-standing effort on solid oxide technology and specifically towards industrial scale SOE (16), and recent public information on efforts in industry (*20*).

State of the Art in SOE, and SOE integrated with Haber-Bosch ammonia synthesis

Cinti et al. (*21*) considered the coupling of SOE for H_2 synthesis with a H.-B. synthesis loop and compared this with conventional electrolysis, and a conventional base case using methane. AspenPlus simulations were performed. They report a specific total energy consumption of 8.3 kWh/kgNH_3 (all electrical) for SOE with heat provided from the H.-B. loop to the SOE. Their results for the other cases are somewhat less meaningful since heat integration of the H.-B. synthesis loop with the upstream processes was only implemented for SOE. Nevertheless, Cinti et al.'s result compares fairly well with the estimate shown below.

Benchmarking published industrial energy demand for SOE based ammonia synthesis

Haldor Topsoe (now Topsoe) is at this time the only world scale company with exceptional experience in catalyst technology and ammonia synthesis that has also announced to make SOE available at the industrial scale. A production facility producing up to 5 gigawatt (GW) of SOE stacks per year with a target date of 2023 has been announced (*22*). While there are other companies working in the SOE space at this time such as Sunfire of Germany, or FuelCell Energy of the U.S., and others, there is little doubt that the experience in world-scale ammonia synthesis that Topsoe represents raises their credibility. Therefore, Topsoe's reported energy consumption for the SOE+air separation+H,-B. case (Approach 2, Figure 1) of 7.7 $MWh_{electrical}$/tonne NH_3 (93% for electrolysis, 2% for air separation, 5% for H.-B., Utilities<1%) shall here be independently verified prior to calculating the energy demand for Approach 2 to 4 in Figure 1. Figure 2 shows a potential difference of 1.25 V as the driving force for oxygen ion transport, based on literature independent of Topsoe (15, 16*)* The number of oxygen ions to be transported then allows calculation of the electrical power demand for oxygen transport

$$\mathbf{P = F * n * V * z} \qquad \textbf{Equation 2}$$

where P is the power in Watt, V is the cross-membrane voltage in volt, n is the number of mols of oxygen (as atomic oxygen) per day transported through the membrane to split water to provide H_2 for 1000 tonnes per day NH_3, and F is Faraday's constant here taken as 96,458 Coulomb/mol univalent ions (C/mol). z is the number of charges per ion transported, equal to two in the case of oxygen. Taking the example of 1000 tonnes of NH_3 produced per day,

$$P = 96{,}458\ \text{C/mol} * 88{,}075{,}000\ \text{mol O} * 1.25\ \text{V} * 2 / (86{,}400\ \text{s}) = 246{,}000{,}000\ \text{W}$$

246 MW is then the estimated electrical demand to transport oxygen through the SOE membranes, neglecting power losses in electrical power conditioning equipment and lines. Steam generation and heating is assumed to be roughly satisfied by heat from the H.-B. reactor (about 31 MW at 1000 tpd NH_3 production (1)), and cooling of the SOE products (Approach 2, O_2 and H_2, Approach 3, O_2, H_2, and N_2) from 700°C towards the H.-B. synthesis temperature. For the overall process, 59 kW is added to supplement the SOE stack operation. This could be via external heat input to SOE, or, as assumed here, via resistive heating in the SOE stack (autothermal operation). Syngas compression and NH_3 recovery by condensation in the H.-B. loop are taken in account as 10 and 6 MW, respectively, for 1000 tonnes NH_3 per day production. This combines to 7.9 $MWh_{electrical}$/tonne NH_3 produced using SOE, independently confirming Topsoe's published 7.7 $MWh_{electrical}$/tonne NH_3. For this work, 7.9 $MWh_{electrical}$/tonne NH_3 will be used for Approach 2, Figure 1 (see also Figure 5).

Principle of CLAS

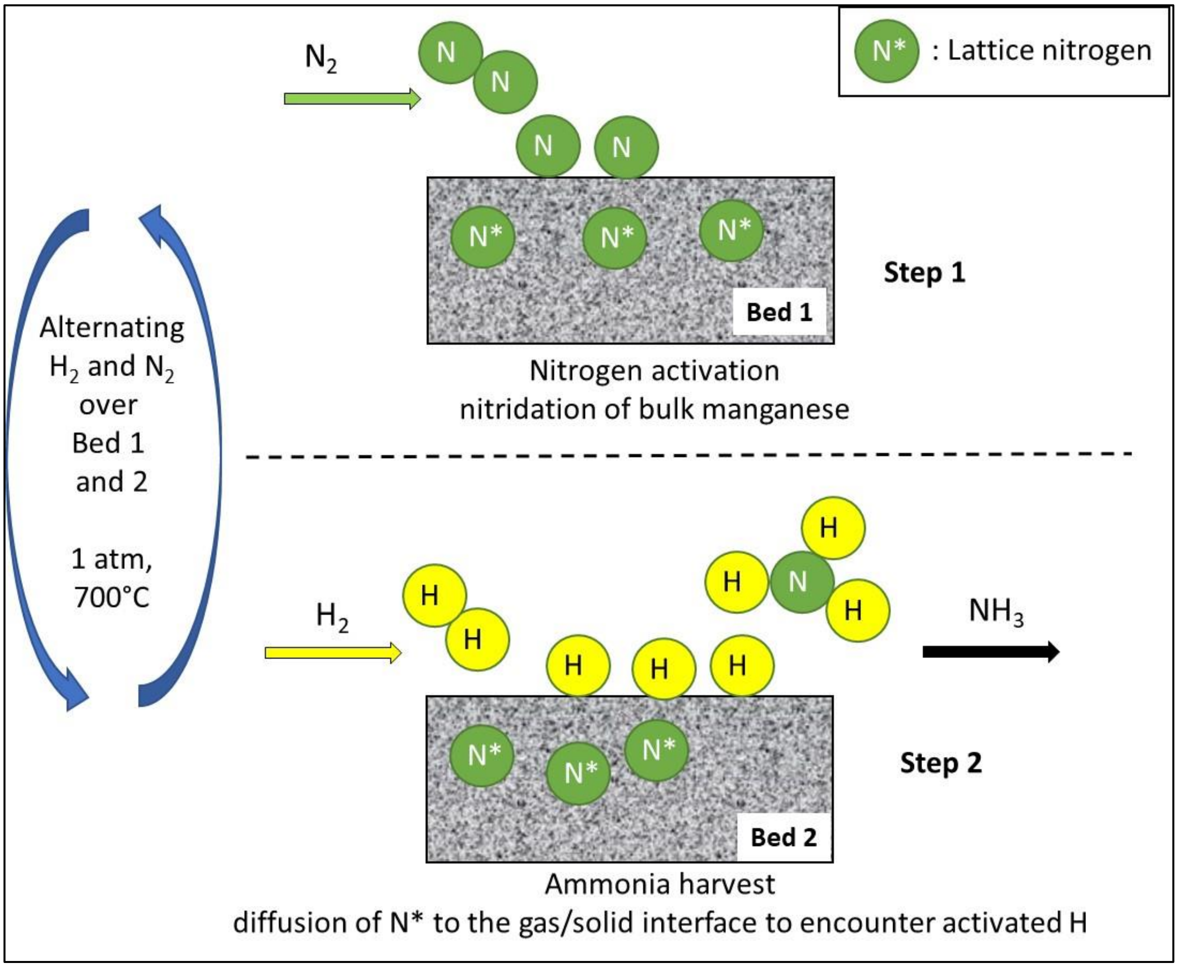

Figure 3: Principle of chemical looping for ammonia synthesis (CLAS) at atmospheric pressure and 700°C. Nitrogen activation by formation of a stable metal (here manganese, Mn) nitride (Bed 1 above) is separated from ammonia harvest (Bed 2, above) by using two separate stationary beds of Mn particles. Activated nitrogen is stored as lattice nitrogen (N*) in the Mn, followed by NH_3 harvest when switching to contacting the solid with H_2.

The principle of CLAS (*23*) is similar to more well-known chemical looping for carbonaceous fuel conversion where oxygen is shuttled between two connected fluidized bed reactors using a solid oxygen carrier (*24*). A significant operational difference between CLAS (chemical looping of nitrogen) as described here and chemical looping of oxygen is that in CLAS different gases are routed alternatingly over two stationary beds of solid particles, while chemical looping with oxygen is generally implemented by physically moving large masses of cyclically oxidized/reduced solids between two fluidized beds, somewhat akin to a catalytic cracker in a refinery. Moving particles can be cumbersome, especially at scale.

Some of the limitations of conventional Haber-Bosch catalysis are removed by separating nitrogen activation from NH_3 harvest. CLAS is fundamentally different from the Haber-Bosch catalytic process. Activated nitrogen arrives from the bulk as atoms at the surface and no competition between nitrogen and hydrogen adsorption exists, among other limitations of H.-B. catalysis caused by surface phenomena.

It is of utmost importance to keep in mind that CLAS is quite unlike the classical heterogeneous catalysis to synthesize NH_3. CLAS in fact represents a fundamentally different approach to molecular nitrogen activation rarely investigated for chemical synthesis in the literature. The process proceeds in two separate steps by directing different gas streams over solid Mn particles:

1. Bulk Mn is converted to Mn nitride under gaseous nitrogen, splitting the nitrogen triple bond, and resulting in nitrogen atoms stored in the crystal structure (N*) of the solid Mn (*25*).

2. When H_2 gas is directed over the surface of the Mn nitride, activated nitrogen diffuses in the nitride to the surface and combines with activated hydrogen atoms to form NH_3.

Step 1 is then repeated to close the loop. It should be emphasized again that nitrogen atoms meet hydrogen at the gas/solid interface during synthesis. This is quite different from heterogeneous catalysis where both nitrogen and hydrogen need to be activated simultaneously on the surface of a catalyst, leading to competition and well-recognized tradeoffs and limitations. The synthesis reaction in classical H.-B. catalysis is the equilibrium

$$\mathbf{N_2 + 3\ H_2 \leftrightarrow 2\ NH_3} \qquad \textbf{Equation 3}$$

where N_2, H_2, and NH_3 are all present in the gas phase, and activated species and intermediates (not shown) are present on the solid catalyst surface. The reaction for nitrogen activation in CLAS is

$$\mathbf{N_2 \rightarrow 2\ N^*} \qquad \textbf{Equation 4}$$

where N* stands for nitrogen atoms in the manganese crystal lattice. Nitrogen can be seen as partially ionized (hybrid bond) when present as nitride in the solid.

The reaction for NH_3 synthesis in CLAS is then

$2\ N^*+3\ H_2 \rightarrow 2\ NH_3$ Equation 5

where N* is present only in the solid and no N2 is needed in the gas phase. It is acknowledged that hydrogen molecules will adsorb and likely exist as activated hydrogen on the solid surface before conversion to NH_3. The decoupling of nitrogen- and hydrogen activation allows CLAS to proceed at atmospheric pressure and (preferred) 700°C. The solid Mn depleted of nitrogen is loaded again with activated nitrogen after ammonia harvest, closing the loop.

Several simplified assumptions will be made for CLAS:

1. The conversion of nitride N* to NH_3 is without loss to parasitic recombined N_2. Rationale: the use of promoters such as sodium has already improved the conversion of N* to NH_3 (*26*Further research may arrive at negligible parasitic N_2 formation.

2. NH_3 recovery from the CLAS product gas (and unconverted H_2 recycling) is accounted for with the same energy demand as NH_3 separation in H.-B. processes. Rationale: This is taken as a worst case. The inexpensive Mn solid could be used in excess to allow complete conversion of all H_2. Partial removal of nitride N* to form NH_3 in each cycle introduces a nitride deadload in the solid but is not prohibitive.

3. For the overall energy balance, the same amount of energy is assumed recovered from CLAS as from H.-B. since the overall reaction (Eq. 3) is the same. Rationale: the overall reaction is identical for H.-B. and CLAS. Energy can be recovered from CLAS as from H.-B.

Preliminary design of solid oxide electrolysis vs. liquid water electrolysis at the scale of 1000 tonnes per day ammonia produced.

The specific current density (milliampere per area of membrane and time, $mA/cm^2_{membrane}$) is a dominating design parameter for electro-membrane processes since it determines the membrane area. It shall be assumed that 176 tonnes of H_2 per day are to be produced to feed a 1000 tonnes NH_3 per day synthesis . It is assumed that no parasitic electrical current losses occur in the electrolysis processes (100% current efficiency).

With a typical specific current density of 300 $mA/cm^2_{membrane}$ for liquid water electrolysis, about 66,000 m^2 of membrane area are needed. Typical industrial scale liquid water electrolysis stacks may have a cross sectional area on the order of 3 m^2, with hundreds of repeat units in a stack. The 1000 tpd NH_3 facility envisioned here would then have an electrolysis section consisting of on the order of 70 electrolysis stacks with each stack having a length of several tens of meters and a diameter of on the order of 4 m.

Assuming 500 $mA/cm^2{}_{membrane}$ for SOE, a membrane area of about 39,000 m^2 is needed to produce the H_2 for 1000 tpd NH_3. SOE has never been practiced at more than perhaps a few square meters of membrane area or less . Typical SOE stacks have a cross sectional area of perhaps 0.01 m^2, with several tens of membranes stacked. To achieve the 1000 tpd NH_3 scale one would reasonably expect several years of development after industrial scale production of such SOE stacks is operating and validated.

In summary, liquid electrolysis to provide hydrogen for 1000 tpd scale ammonia plants is readily available at scale and has been used in such plants at this scale for many decades for example in Zimbabwe, Egypt, and Peru due to exceptionally low cost electrical energy in specific locations (*27*). SOE clearly will require several levels of scaleup development if and when industrial stacks become available. SOE would be first reasonably used in ton per day NH_3 or smaller facilities.

Results and Discussion

Capital expense

The capital expense for a complete 1000 tonne per day NH_3 facility based on liquid water electrolysis has been reported by Grundt et al. of Norsk Hydro at U.S.$200 million (2016 Dollars) (*28*). While no sophisticated economic analysis is attempted here, suffice it to say that with energy costs (which represents the largest portion of operating costs for NH_3 synthesis) at about U.S.$200 per tonne NH_3, and market prices at over U.S.$1,400 per tonne NH_3 early in 2022, a gross overall nominal payback is attractive at about 0.5 years. Even at a price of U.S.$600-800 per tonne NH_3 (an approximate average 2009-2020 (*29*)) renewable electrolysis-based NH_3 is certainly worthy of consideration by investors, even before any possible credit for fossil CO_2. As pointed out above, the global NH_3 market is poised to grow significantly due to population increase, growing consumer demand for protein for example in Asia, and emerging NH_3-for-energy applications. Some caution is needed since the tight relation of NH_3 and crop yield could devolve this into a food vs. fuel debate if NH_3 synthesis capacity is not ramped up along with emerging NH_3 energy applications. The continuous world supply of fertilizer is absolutely paramount to possible energy applications.

While capital cost of an emerging technology such as SOE is much more difficult to estimate one may perhaps reasonably expect that when SOE is produced at large scale capital cost may not differ significantly from liquid water electrolysis.

Estimating capital cost for a laboratory scale technique such as CLAS is even more difficult, but the absence of a need for compression of the syngas may reduce capital cost. However, the gas handling for chemical looping does introduce other hardware demands. An early estimate put the CLAS process capital cost as perhaps similar to conventional natural gas based NH_3 synthesis (*30*).

Cost of energy

The cost of renewable electricity was taken for a wind energy Power Purchase Agreement (PPA) as \$0.020/kWh (*31*). Prices for renewable energy vary geographically, and with a number of other parameters. 2014-2021 data for executed PPA's (p. 46 of the 2021 report cited above) seems to indicate that \$0.020/kWh as an average may be used to arrive at estimated energy costs at this time. The results shown below simply scale linearly with the cost of renewable energy, a doubling of the cost of renewable energy would simply double the energy cost per tonne of renewable NH_3, for example. Scenarios are therefore easily explored by the reader as costs change.

In this paper the number of wind turbines for the renewable power generation (see Figures for Approaches 1-4) is based on a name plate capacity of 2.75 MW (average of newly installed turbines in 2021 per the U.S. Department of Energy). No capacity factor was applied.

The cost of natural gas fluctuates, and sometimes very significantly so. This is a concern for example for farmers since the risk of fossil energy-based fertilizer cost fluctuations or even the availability of fossil fuel in some parts of the world to produce fertilizer impacts farm economics very significantly.

Renewable ammonia by conventional liquid water electrolysis, air separation, and Haber-Bosch synthesis

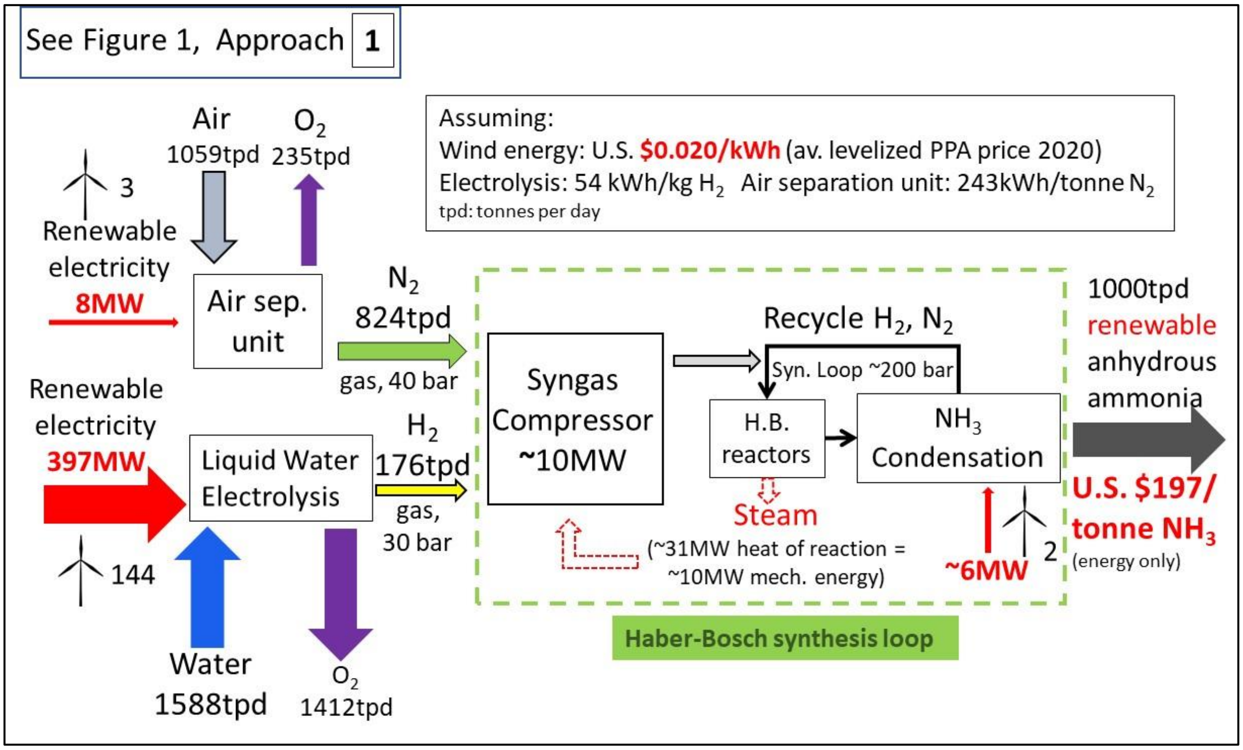

Figure 4: Approach 1 (see Figure 1): Renewable NH_3 production via conventional liquid water electrolysis, air separation, and Haber-Bosch synthesis. All energy inputs are via renewable electrical energy. Approximate number of wind turbines is indicated for scale. Update from (1).

This approach has been presented previously (1) and is here only updated for energy costs. The overwhelming impact of H_2 production regarding the energy demand for NH_3 synthesis is quite obvious. The H.-B. synthesis loop is not a useful target for energy efficiency work in NH_3 synthesis.

Renewable ammonia synthesis by solid oxide electrolysis of steam and air separation, followed by Haber Bosch synthesis of NH_3

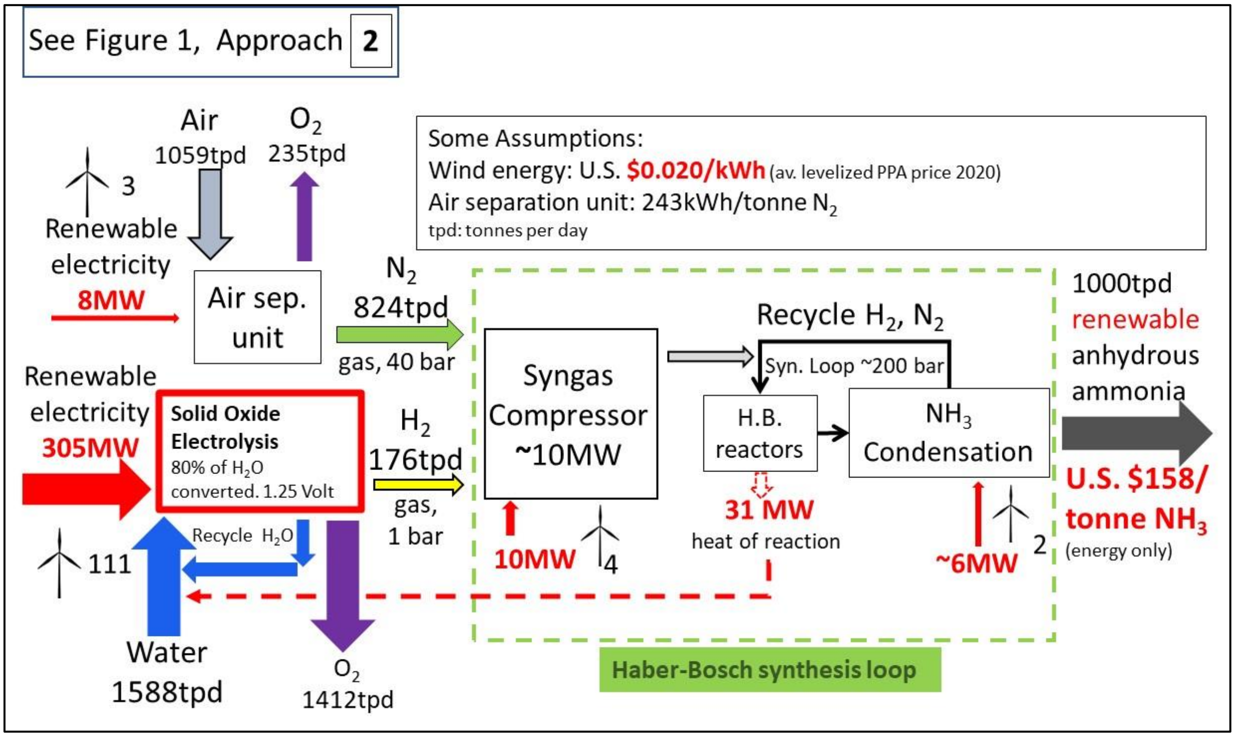

Figure 5: Approach 2 (see **Figure 1**): Renewable NH_3 production via solid oxide electrolysis (SOE), air separation, and Haber-Bosch (H.-B.) synthesis. All energy inputs via electrical energy. Approximate number of wind turbines is indicated for scale.

The data regarding all operations except SOE was previously shown and verified (1). An overall energy demand of 339 MW for 1000 tonnes per day production converts to 7.9 $MWh_{electrical}$/tonne NH_3. With the SOE voltage assumed here it is clear that the overall energy demand is reduced by about 20% compared to conventional water electrolysis. This is before taking issues such as energy demand for separation and recycling of unconverted steam in account (Figure 2).

Overall, the energy savings accrued by implementing a technology such as SOE that is not proven at the required scale selected here is modest compared to the risks.

Renewable ammonia synthesis by simultaneous solid oxide electrolysis of steam and air, followed by Haber Bosch synthesis of NH_3

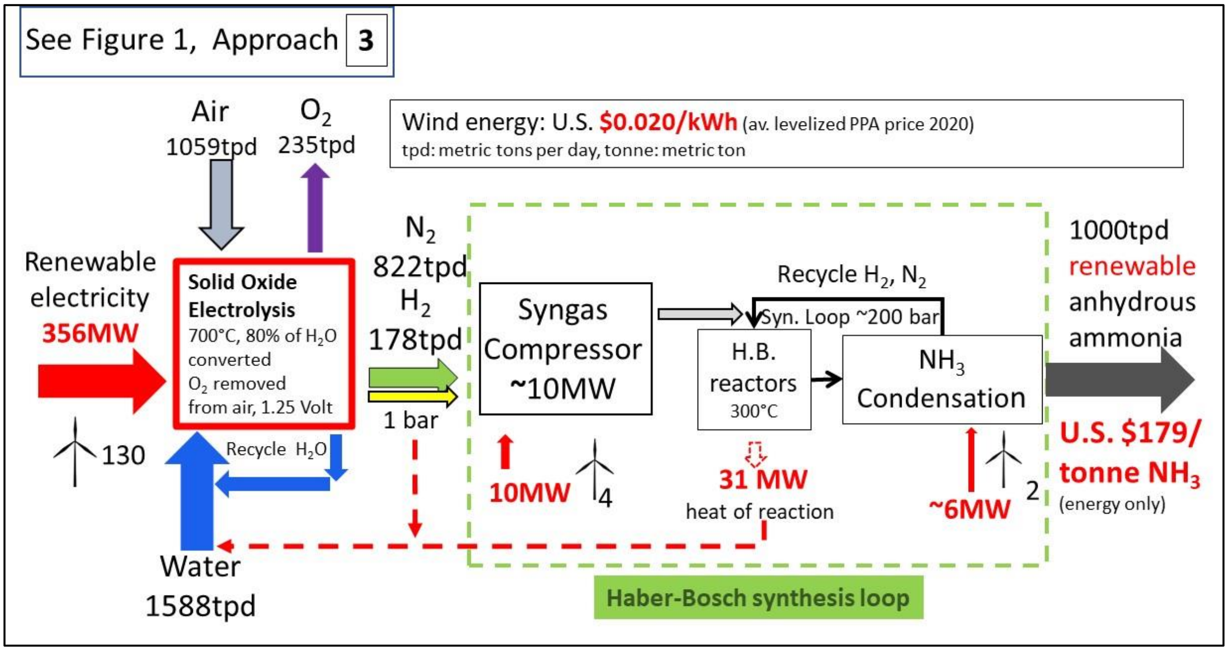

Figure 6: Approach 3 (see **Figure 1**): Renewable NH_3 production via solid oxide electrolysis (SOE), and Haber-Bosch (H.-B.) synthesis. All energy inputs are via electrical energy. The approximate number of wind turbines is indicated for scale. Removing oxygen from air via SOE instead of a separate air separation process leads to a small increase in energy demand. Process simplification is a benefit of combined air/steam SOE.

A unique feature of SOE compared to liquid water electrolysis is the option to feed a mixture of steam and air to SOE with the goal of removing both the oxygen from water, and oxygen from air, to arrive at a stoichiometrically balanced feed stream for NH_3 synthesis in a single unit operation. The removal of the oxygen from air, however, is slightly less energy efficient using SOE than for conventional air separation . This results in a somewhat higher energy price of NH_3. The process simplification afforded by this approach, however, may be sufficient motivation. This may be especially true for down-scaling and modularization, or stranded renewable energy, especially in countries with less developed infrastructure.

Renewable ammonia synthesis by separate solid oxide electrolysis of steam and air, followed by Chemical Looping Ammonia synthesis

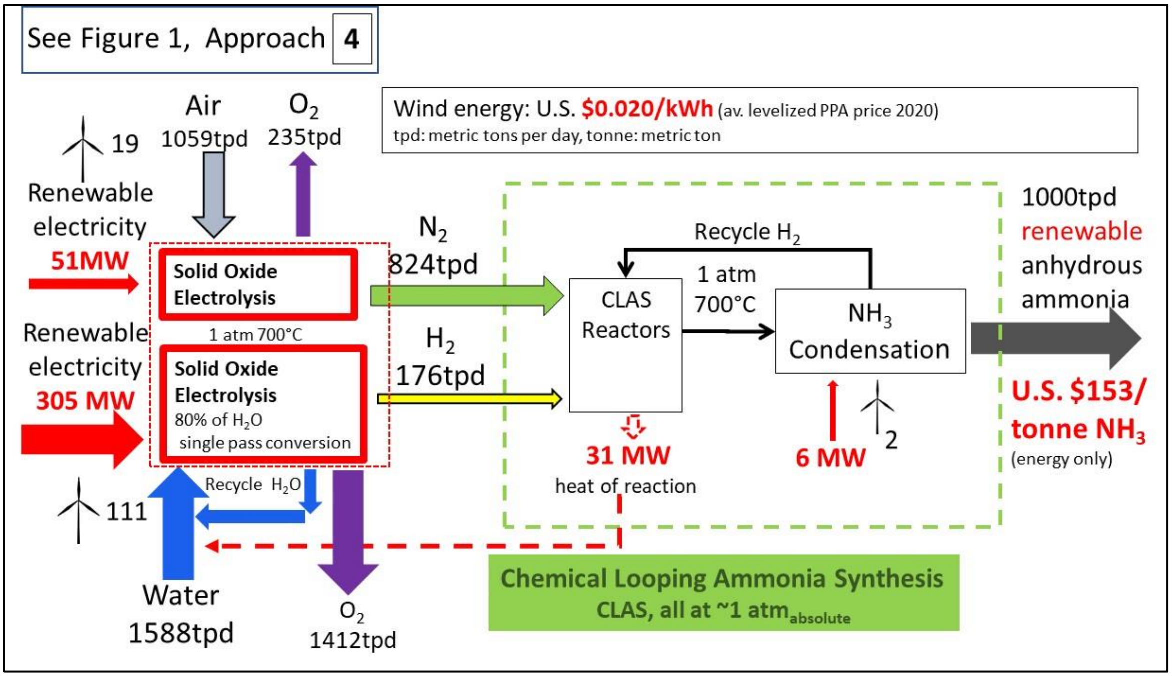

Figure 7: Approach 4 (see Figure 1): Renewable NH_3 production via separate solid oxide electrolysis (SOE) of steam and air, and Chemical Looping Ammonia Synthesis (CLAS). All energy inputs are via electrical energy. The approximate number of wind turbines is indicated for scale.

CLAS requires separate generation of H_2 and N_2 since the looping process alternates solids between being contacted with H_2 (ammonia harvest) and N_2 (nitridation, nitrogen activation). Both CLAS and SOE are assumed to be operated at 700°C. Energy to recycle unconverted steam to SOE is again neglected. The overall energy cost is lowest by a small margin in this comparison for the SOE/CLAS approach compared to all other approaches and the reference natural gas reforming, but the uncertainty is the highest due to the limited level of experience and scaleup for SOE and CLAS.

The needed amount of Mn for the CLAS reactors can be estimated at an order-of-magnitude level. 3.52 kgNH_3 produced per tonne Mn and day has been estimated (*32*). For 1000 tonne NH_3 per day production, 284,000 tonnes of Mn would be needed. Particle size optimization and mass transfer improvements through reactor design may reduce this significantly but a 1 tonne per day scale (284 tonnes of Mn) might be a better target for the most simplified (two main unit operations at identical temperature, all at atmospheric pressure) ammonia synthesis process considered here.

Overall comparison

It does not seem that there is a compelling energy cost argument to abandon liquid water electrolysis for SOE, or conventional H.-B. synthesis for CLAS considering the uncertainties in the above calculations, especially regarding SOE (emerging at industrial scale) and CLAS (currently at gram per hour scale in the laboratory). The combination of SOE and CLAS (Approach 4) is attractive because it is simple and takes place all at atmospheric pressure. CLAS certainly has ample room for optimization through thermochemistry, chemistry, and reactor design.

The simplest system for down scaling and modularization may be at this time and for some years to come simultaneous air separation and steam electrolysis in an SOE stack, followed by a conventional H.-B. synthesis loop, especially in light of recent efforts to commercially produce SOE at the Megawatt scale.

Conclusions and Outlook

The energy cost of ammonia synthesis, does not differ very significantly with the technologies considered here: liquid water electrolysis or solid oxide electrolysis (SOE) to replace natural gas reforming, and chemical looping for ammonia synthesis (CLAS) to replace the Haber-Bosch synthesis loop. Hydrogen production is always the lion's share of the energy demand or cost with any approach, and any further research and development regarding heterogeneous Haber-Bosch type catalysts for the reaction of N_2 and H_2 to NH_3 is, from an applied impact point of view, misplaced. No significant amount of energy regarding NH_3 production can be saved in the Haber-Bosch synthesis loop. Process simplification, down-scaling, and modularization may be drivers for alternatives to Haber-Bosch, and alternatives to liquid water electrolysis, but not energy demand.

Renewable ammonia can certainly be made at competitive energy consumption- and energy cost levels compared to even the most efficient state of the art fossil fuel based ammonia with current energy costs for natural gas and wind electricity. This is without taking credit for the very significant savings in fossil CO_2 release of at least about 1.5 tonnes CO_2 per tonne of ammonia comparing fossil based vs. green ammonia.

The most significant conclusions can be summarized as follows: (i) energy cost is not a significant driver of process design considering the design alternatives investigated here (ii) design alternatives may be selected due to simplicity rather than marginal energy cost advantages when designing small scale installations for example using stranded resources, or for local supply of fertilizers etc..

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Data Availability Statement

The data that supports the findings of this study are available within the article and its supplementary material.

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