1 2

3

4

Accepted for publication: Journal of Renewable and Sustainable Energy, May 2017

- Towards sustainable agriculture: fossil-free ammonia
- Peter H. Pfromm, Department of Chemical Engineering, Kansas State University,
- 1005 Durland Hall, 1701A Platt Street, Manhattan, Kansas, 66506-5102, U.S.A. (pfromm@ksu.edu)

### 5 6 **Ab**

Abstract 7 About 40% of our food would not exist without synthetic ammonia (NH<sub>3</sub>) for fertilization. Yet, NH<sub>3</sub> 8 production is energy intensive. About 2% of the world's commercial energy is consumed as fossil fuels 9 for NH<sub>3</sub> synthesis based on the century-old Haber-Bosch (H.-B.) process. The state of the art and the 10 opportunities for reducing the fossil energy footprint of industrial H.-B. NH<sub>3</sub> synthesis are discussed. It is 11 shown that even a hypothetical utterly revolutionary H.-B. catalyst could not significantly reduce the 12 energy demand of H.-B. NH<sub>3</sub> as this is governed by hydrogen production. Renewable energy-enabled, 13 fossil-free NH<sub>3</sub> synthesis is then evaluated based on the exceptional and continuing cost decline of 14 renewable electricity. H.-B. syngas  $(H_2, N_2)$  is assumed to be produced by electrolysis and cryogenic air 15 separation, and then supplied to an existing H.-B. synthesis loop. Fossil-free NH<sub>3</sub> could be produced for 16 energy costs of about \$232 per tonne NH<sub>3</sub> without claiming any economic benefits for the avoidance of 17 about 1.5 tonnes of CO<sub>2</sub> released per tonne NH<sub>3</sub> compared to the most efficient H.-B. implementations. 18 Research into alternatives to the H.-B. process might be best targeted at emerging markets with currently 19 little NH<sub>3</sub> synthesis capacity but significant future population growth such as Africa. Reduced capital 20 intensity, good scale-down economics, tolerance for process upsets and contamination, and intermittent 21 operability are some desirable characteristics of  $NH_3$  synthesis in less developed markets, and for 22 stranded resources. Processes that are fundamentally different from H.-B. may come to the fore under 23 these specific boundary conditions.

# 24 Keywords

25 Ammonia; Haber-Bosch; renewable; fossil-free; fertilizer; economical

# 26 Highlights

- There is no motivation for research to improve or replace Haber-Bosch catalysts due to the
  overwhelming impact of hydrogen production on the economics and the energy footprint.
- The cost of electricity from renewables has sharply declined and will likely continue to do so.
- Haber-Bosch ammonia synthesis facilities can be retrofitted with existing technology for
   competitive wind electricity-based feedstock preparation to produce fossil-free ammonia.
- Research for alternatives to the Haber-Bosch process should be directed at emerging market and
   stranded resource requirements instead of attempting to replace existing Haber-Bosch facilities.

34

#### 35 **1 Introduction**

#### 36 The world scale and impact of ammonia synthesis

37 Each year, about 174 million tonnes of ammonia (NH<sub>3</sub>) are synthesized globally (1), making NH<sub>3</sub> the 38 second most produced man made chemical. More than 85% of NH<sub>3</sub> is used in fertilizers, with the 39 remainder used mainly by other areas of the chemical- and process industries.  $NH_3$  is produced by using 40 a significant amount of energy to convert the hydrogen from water, and nitrogen from air to NH<sub>3</sub>. Water 41 is always the hydrogen source, both directly as process steam, and indirectly as the water absorbed by 42 ancient biomass, and now used as hydrogen from methane as natural gas. The prevalent energy source is 43 combustion of natural gas (U.S., Middle East) or coal (mainly in China) to CO<sub>2</sub>. About 600kg of natural 44 gas are consumed to produce 1000 kg NH<sub>3</sub> in the most efficient facilities.(2,3) The total fossil CO<sub>2</sub> 45 emissions from NH<sub>3</sub> synthesis with the current basket of energy sources can be estimated at more than 46 670 million tonnes per year. This estimate is based on the tonnage of ammonia made using natural gas 47 or coal, and the known estimate of  $CO_2$  emission from using either feedstock.(4,5) This amounts to about 48 2.5% of all fossil fuel based  $CO_2$  emissions world wide (6). NH<sub>3</sub> synthesis based on renewable energy 49 and raw materials would therefore be beneficial in moving towards a sustainable future where food and 50 fossil fuels are decoupled.

51 NH<sub>3</sub> is at the intersection of food, energy, and water, and this nexus is attracting increasing interest 52 due to an expected increase of the world population (7), the impact of climate change (8), and an expected 53 world-wide decrease of arable land per capita (9). In the United States, about 30% of commercial energy 54 spent to produce crops is used to synthesize  $NH_3$  (10).  $NH_3$  enables 30-50% of agricultural crop output 55 (11) and conserves water by increasing the crop yield per unit water used (12,13). The escape of unused 56 agricultural fertilizers into the environment is of significant concern. Attempts are being made through 57 precision agriculture (14), and modified application methods (time-release etc., (15)) to address this. 58 Environmental concerns and farmer's interests are aligned since unused fertilizer is a significant financial 59 loss to farmers.

60 Synthetic NH<sub>3</sub>-based fertilizers will remain essential to the survival of a significant and increasing 61 fraction of the world population far into the future (16). Obtaining nitrogeneous fertilizer from animal or 62 human waste at an impactful scale would require collection, transport, storage (due to seasonal demand), 63 and processing of vast amounts of manure with relatively low concentrations of bio-available N, with the 64 concomitant energy- and economic expenditures, and environmental impact. About 5% of U.S. cropland 65 is currently fertilized with manure. Due to the above issues and many additional barriers human and animal waste is unlikely to significantly impact the need for synthetic fertilizers (17). Another aspect of 66 67 the global impact of the presence or absence of bioavailable nitrogen is lack of bioavailable nitrogen

hampering carbon sequestration from the atmosphere as biomass (18). There are considerations of adding man-made bioavailable nitrogen to natural systems for example for fertilization in the ocean to sequester fossil  $CO_2$  (19).

The capacity of  $NH_3$  to serve as a convenient hydrogen (H<sub>2</sub>) carrier (20), or to be used directly as a hydrogen-rich fuel or fuel additive in internal combustion engines is an emerging aspect. Compared to H<sub>2</sub>,  $NH_3$  is liquefied fairly easily and liquid  $NH_3$  exceeds the U.S. Department of Energy's (DOE) target for hydrogen storage per volume. Bulk  $NH_3$  storage and transport by pipeline, rail, and truck, and delivery down to the retail scale is well established, as opposed to transport, storage, and distribution of H<sub>2</sub>. This has been recognized and well described in a recent funding opportunity made available by DOE (21).

In summary, world production of synthetic NH<sub>3</sub> will have to increase significantly from now about
 174 million tonnes per year during the next decades as the world population increases, specifically in
 Africa. Use of NH<sub>3</sub> as a renewable fuel and energy storage mode might further increase this demand.

#### 81 Rising world-wide interest in ammonia

Significant U.S. government programs amounting to in excess of U.S. \$30 million in 2016 alone towards aspects of NH<sub>3</sub> synthesis and applications have recently emerged and will result in an invigorated interest in NH<sub>3</sub> synthesis and applications in the coming years (*21, 22, 23, 24, 25*). Activities in Japan and Europe towards using NH<sub>3</sub> as a mode of energy storage and transport are also on the rise (*26, 27, 28*), often in form of public/private partnerships.

In light of the substantial decline of the cost of renewable electrical energy in the U.S., and due to the rising interest in NH<sub>3</sub> synthesis and applications, it seems timely to estimate if renewable electricity might be an avenue to fossil-free NH<sub>3</sub>, and thereby substantially reduced dependency of food on fossil fuels. The state of the art process is reviewed below, followed by an assessment of renewable electricity enabled Haber-Bosch NH<sub>3</sub> synthesis.

#### 92 Review of the state of the art Haber-Bosch process implementation

There are two major challenges to NH<sub>3</sub> synthesis: first, activating dinitrogen (essentially somehow breaking the exceptionally strong dinitrogen triple bond), and second, obtaining hydrogen to convert activated nitrogen to NH<sub>3</sub>. The former allows a process to exist, but the latter governs the energy demand and economic viability (as shown below). Both tasks must be done at technologically acceptable conditions and at a cost commensurate with the value added by using ammonia in agriculture. Fritz Haber's Nobel Prize (29) was for fundamentally solving the nitrogen activation issue. He secured economical success by patenting recycling of valuable unreacted syngas after separating NH<sub>3</sub>. Carl Bosch's Nobel Prize ((*30*), with F. Bergius) relates in large part to the economical large-scale supply of hydrogen for NH<sub>3</sub> synthesis. Their work created the commercial fertilizer industry and averted imminent worldwide food shortages.(*31*) There were even at the time of Haber's discoveries a number of competing approaches to synthesize NH<sub>3</sub> at the technical scale, but none of them could match the economics of the integrated Haber-Bosch process (*31*). However, these economics are based on fossil fuels and of course do not take the impact of the release of fossil CO<sub>2</sub> into the atmosphere in account.

106 A brief review of the Haber-Bosch (H.-B.) process will show that today's challenge for large-scale 107  $NH_3$  synthesis is no longer the catalytic conversion of dinitrogen and dihydrogen to  $NH_3$ . While the 108 technology is complex, the chemistry is simple: hydrogen and nitrogen combine to produce  $NH_3$ . Figure 109 1 shows both the overall chemical process to produce the syngas ( $H_2$ ,  $N_2$ ) for the H.-B. synthesis, and the 100 chemical reaction taking place in a H.-B. reactor.



111

Figure 1 NH<sub>3</sub> synthesis, top: state of the art overall chemical reaction to produce synthesis gas (syngas)
 from air, water, and natural gas; bottom: the reaction in the Haber-Bosch synthesis reactor proper.
 Figure 2 shows the main sections of what is generally termed the H.-B. process using the most energy

efficient state of the art approach based on natural gas as both feedstock and energy source. The reader is directed to the literature for exhaustive treatment of many variations such as using coal as energy source, sophisticated changes of heat integration of the process steps, catalysts, catalyst fundamentals, and many other issues (*32*, *33*). The discussion below attempts to use the current best available technology characteristics.

The most efficient implementations of the natural gas steam reforming based H.-B. process today at industrial scale use about 600 kg of natural gas per 1000 kg anhydrous NH<sub>3</sub> produced (as used in Figure 2), or about 6.8 Gcal/tonne NH<sub>3</sub> (as natural gas lower heating value, LHV). Various plants may however use significantly more energy depending on the technology in use. If coal is used, the energy demand may approach at best 1.7 times that of an efficient natural gas based plant.

125 Over the last 100 years, engineering and heat integration of the overall process has led to an approach 126 to the thermodynamic minimum energy demand that is quite impressive. The thermodynamic minimum has been estimated at 4.98 Gcal/tonne  $NH_3$  (as natural gas lower heating value, (*3*)). 5.10 Gcal/tonne  $NH_3$ (product liquid ammonia) has been reported as the thermodynamic minimum elsewhere ((*34*), higher heating value, HHV). Overall, current full scale (1000 tonnes per day  $NH_3$  and larger) energy consumption of the best technology available is therefore only about 20% above the immutable thermodynamic minimum when using the state of the art natural gas based Haber-Bosch process outlined below.



133

Figure 2 The state of the art Haber-Bosch process to produce  $NH_3$  from natural gas (methane). Natural gas is used to provide energy for steam reforming using combustion, and also to provide both hydrogen and nitrogen by steam reforming and subsequent water gas shift (left). (tpd = tonne per day)

The single-pass conversion in the Haber-Bosch reactors depends on a number of operational parameters such as the level of inerts like argon. It is reported often at less than 20%, certainly no more than 30% (4,35). Unreacted hydrogen and nitrogen is always recycled (at pressure) after  $NH_3$  is condensed and separated. The synthesis loop carries an inert load (argon from air, methane from methanation) that is controlled by purging a small stream (not shown). Oxygen or oxides must not enter the synthesis loop since this would inactivate the catalyst. Catalyst charge lifetimes are on the order of many years in industrial practice.

The steam to drive the synthesis loop compressor is generated through heat recovery from the primary reformer and cooling of the highly exothermal NH<sub>3</sub> synthesis reaction, with additional steam left for other purposes such as driving compression for refrigeration to condense ammonia, or for export.

#### 147 The price of ammonia and energy to produce ammonia

The price of ammonia is closely related to the price of the feedstock (36, 2013 data). Labor and other (tax, insurance etc.) add perhaps 25% in the U.S. or Russia, while the high price of feedstock in Europe compared to the U.S. essentially drowns out all other costs. The historically close tracking of  $NH_3$  price and natural gas cost has relaxed in the U.S. since 2008 due to strong demand for  $NH_3$  and the resulting price increase. For 2016, a price of \$500-600 per tonne ammonia has been reported, with a minimum of \$499 per tonne since 2008 (*37*).

Above, the price for natural gas is assumed at a perhaps optimistic \$3/MM BTU. Predictions of the natural gas price would be extremely speculative. Renewable electricity is assumed at \$0.0235/kWh as verified by DOE, and reported to be highly likely to decrease in the future (*38*).

# Further research on Haber-Bosch catalysts has essentially no impact on energy demand per tonne of ammonia

The close approach to thermodynamic limits for the full-scale existing H.-B. process imposes harsh requirements on any aspirations to improve over H.-B. as far as energy consumption per unit NH<sub>3</sub> produced.

162 If one assumes quite hypothetically operating the synthesis loop using a revolutionary catalyst at atmospheric pressure and room temperature and simultaneously improved catalyst performance, then this 163 164 extremely unlikely scenario will only offer a few percent overall energy savings (see Figure 2). This 165 further illustrates that NH<sub>3</sub> synthesis equals hydrogen synthesis from an economic (and thereby energy-) 166 standpoint, as Carl Bosch pointed out. While there may exist academic or scientific reasons to further 167 pursue, for example, improved H.-B. catalysts, there is no need or opportunity to do this for reduction of 168 the energy consumption (39), or to work towards renewable NH<sub>3</sub>. Nevertheless, NSF has called for 169 improved catalysts for the H.-B. process to reduce the energy demand for synthetic NH<sub>3</sub> in two requests 170 for proposals (22, 40) although obtaining  $H_2$  clearly consumes the vast majority of the energy for NH<sub>3</sub>.

#### 171 Research related to Haber-Bosch

172 A number of approaches are under investigation to replace (41,42,43,44,45,46) or improve the H.-B. 173 process. Research on improvement has focused on new catalysts (see above) and scientific advances 174 including a recent Nobel Prize closely related to H.-B. catalysis (47). Current industrial catalysts are already highly optimized and last for many years, while little further practical impact is possible due to 175 176 limitations that cannot be addressed by catalysts (39, also discussion above). Citing Carl Bosch, in 1932, 177 on the importance of further improvements to the catalytic H.-B. loop compared to the cost of obtaining 178 hydrogen feedstock, "... the conversion of the ready-made gas mixture into ammonia is only a minor cost 179 factor"(30). More than 80 years later, this still holds true.

As an example of proposed alternative processes to replace H.-B., one recent approach is the use of a "cold" plasma to produce ammonia from hydrogen and nitrogen (*48*). The "hot" plasma approach using an electrical discharge has been implemented at full scale early in the 20th century and was quickly discarded due to the exceptionally high energy demand compared to H.-B. (*49*). Using the data from the above reference, cold plasma would require about 40,000 MW for a 1000 tonne NH<sub>3</sub> per day production level, while industrial-scale state of the art H.-B. requires about 360 MW. The energy demand of cold plasma for ammonia synthesis appears clearly prohibitive.

187 Electrochemical approaches to replace H.-B. are also being proposed and explored at the laboratory 188 level. Using published data as an example (41) the electrochemical approach would require more than 189 twice the energy per tonne of NH<sub>3</sub> produced compared to H.-B., assuming no loss of energy efficiency 190 from extremely well controlled laboratory conditions to full industrial scale with realistic feedstock and 191 chemicals.

Ammonia synthesis based on nitrides and solar energy has been estimated to be competitive to existing state of the art H.-B. facilities (*50*). The advantages of the process, however, relate more to operation near ambient pressure vs. several hundred atmospheres for H.-B., and the use of rugged bulk chemical conversions instead of the sensitive H.-B. heterogeneous catalysts.

Below it is shown that renewable H.-B. NH<sub>3</sub>, based on available full-scale electrolysis technology to produce hydrogen and cryogenic air separation to produce nitrogen, is now becoming economically attractive due to the exceptional decrease in the cost of renewable electricity (*38*). The basic approach is to take full advantage of the highly optimized H.-B. process and existing installed capital, with a bolt-on solution to provide syngas.

#### 201 Realistic opportunities for Haber-Bosch alternatives

A need for new simple, rugged, and down-scaleable processes exists where H.-B. is not economical or practical: small scale, with operation on intermittent renewable electricity, in less developed countries without an existing NH<sub>3</sub> industry or reliable infrastructure, and where upsets may be more frequent.

From an economical perspective, commodities such as NH<sub>3</sub> produced in capital-intensive facilities at large volumes with modest profit per unit, suffer from significant barriers to entry for proposed novel greenfield processes. This is especially true in markets such as the U.S., Europe, China, or the Middle East where a large base of installed, conventional H.-B. capital is present and growing, and will operate for decades to come absent regulatory intervention. Taking advantage of the installed capital base of H.-B. ammonia facilities, with about 29 facilities in the U.S. alone (*1*), retrofitting would lower the barriers for renewable ammonia to enter the market. This approach is taken below.

#### 212 **2 Results and Discussion**

The basis for the proposed renewable ammonia process evaluated herein is 1000 tonnes of anhydrous ammonia produced per day (1000 tpd), a representative size of a commercial unit (Figure 2). Renewable hydrogen can be derived from water by solar thermal processes (*51*). However, electrolysis of water for hydrogen production is commercially available at scale and is therefore assumed here as the hydrogen source for ammonia synthesis from renewable electricity.

The overall premise is to retain the existing H.-B. synthesis loop to make use of installed capital investments. The hydrogen and nitrogen generation from natural gas (steam reforming/watergas shift, state of the art Haber-Bosch plants) is replaced with electrolytic hydrogen, and cryogenic nitrogen is made using renewable electricity. This replacement could also be done step-wise in form of incremental capacity, or debottlenecking if steam reforming of natural gas limits capacity.

223 The methodology applied here concentrates on the energy input to produce a unit of anhydrous 224 ammonia. This is quite simple when electrical energy is used to produce syngas by electrolysis of water, 225 and cryogenic air separation, respectively, especially since energy for the H.-B. synthesis loop is 226 essentially negligible. The feedstock is either available at no cost (air), or at marginal energy input (water 227 purification, see below). The reference case for natural gas-based state of the art NH<sub>3</sub> production 228 intertwines energy and chemical feedstock somewhat since some hydrogen is derived from water (steam), 229 and some from natural gas that also supplies energy. The operating cost, however, can be compared 230 through the price per unit of energy, either as natural gas or as electricity. This is done below.

#### 231 Hydrogen and nitrogen production

In the proposed system, renewable  $NH_3$  is produced by electrolyzing water to obtain highly pure hydrogen (alkaline electrolysis or proton-exchange membrane electrolysis, assumed at 54 kWh per kg  $H_2$ delivered at 30 bar (*52,53*)). Electrolytic hydrogen has the added advantage of not containing catalyst poisons (especially sulfurous compounds), compared to using natural gas. Purified nitrogen is produced by a cryogenic air separation unit (243 kWh per tonne  $N_2$  delivered at 285K, 40 bar (*54*)). A conventional oxygen-removal step (not shown) to purify the cryogenic nitrogen is needed due to the great oxygen sensitivity of H.-B. catalysts.

#### 239 Synthesis loop compressor

A single multi-stage centrifugal syngas compressor used in state of the art existing H.-B. synthesis loops is typically driven by a steam turbine and requires about 10 MW to compress the synthesis gas for the assumed 1000 tpd  $NH_3$  production (55). Steam is conventionally derived from the natural gas steam reforming process, and from cooling the H.-B. reactors. The conceptual cryogenic air separation and electrolysis assumed here do not produce significant amounts of steam to drive the compressor. However, up to 31 MW of heat of reaction is still available as high-pressure steam from required cooling of the Haber-Bosch synthesis reactors (*3*, *56*). Estimating 30% efficiency for the use of the high-pressure steam in the syngas compressor, the available steam would nominally suffice to drive the syngas compressor. An amount of renewable energy may be needed to raise additional steam for the compressor, but even an electrical drive would have marginal impact compared to the energy for H<sub>2</sub> generation.

As their relative contributions are small, energy for the following is neglected: gas recycling inside of the Haber-Bosch synthesis loop, and motive force to transport various gases and liquids.



252

Figure 3 Hydrogen generation governs the energy demand for the synthesis of 1000 tonnes per day (tpd)
of renewable ammonia in a "bolt-on" concept. Renewable cryogenic N<sub>2</sub> and renewable H<sub>2</sub> from water
electrolysis are fed to an existing Haber-Bosch synthesis loop. Electrolysis is assumed at 54 kWh/kg H<sub>2</sub>.
Cryogenic N<sub>2</sub> is assumed at 243 kWh per tonne N<sub>2</sub>. Wind turbines are assumed operating at 3 MW each
for a simple illustration, disregarding the capacity factor.

258 Detailed discussion of costs

Hydrogen production by electrolysis consumes 94% of the renewable electricity required according to Figure 3. The U.S. nationwide average electricity price to industrial customers in 2014 was \$0.071 per kWh (*57*). Renewable energy prices have declined precipitously, with an average of \$0.0235 per kWh for power-purchase agreements from wind energy reported for 2014 in the U.S.(*58*) If a total of 411 MW is required (Figure 3) for the benchmark 1000 tpd ammonia production, then the energy cost for renewable electricity would be \$232 per tonne of ammonia produced. No significant amount of fossil fuel would be needed. 266 Transportation costs in the U.S. are negligible compared to the cost of producing  $NH_3$  (59,60). Feed 267 water for the electrolysis can be produced from seawater (worst-case / highest-cost scenario) by reverse 268 osmosis for 1.20 per tonne of ammonia including maintenance and capital expense charges (61), at about 269 3 kWh per cubic meter of water produced, resulting in a total cost of \$233 per tonne of anhydrous 270 renewable NH<sub>3</sub>. Seventy to eighty-five percent of ammonia production cash cost resides in the cost of 271 energy (62), with the U.S. at the top of this range (energy as natural gas, for the state-of-the-art H.-B. 272 process). Taking this in account, it can be estimated that cash costs would be \$251 per tonne of 273 anhydrous renewable ammonia based on electricity from wind. The market price of ammonia is quite 274 variable but for comparison, the minimum price of ammonia was reported at \$499/tonne for the time period of 2008-2016 (37). 275

Any credit for eliminating the current minimum of about 1.5 tonnes of  $CO_2$  emissions per tonne of ammonia produced would improve fossil-free ammonia economics. Further improvement would result if the high-purity oxygen by-product could be used, perhaps for oxygen-blown fossil fuel combustion to enable carbon capture/sequestration, or for other purposes such as steel making or bleaching for the pulp and paper industries.

#### 281 Comparison to previous work on electrolysis based ammonia

282 The calculations above are verified against earlier work by Grundt et al. at Norsk Hydro a. s. (63). Grundt et al. reported an overall energy demand of 416MW for 1000 tpd for a Haber-Bosch ammonia 283 284 plant design using water electrolysis and air separation. This resulted in energy costs of U.S. \$217 per 285 tonne of ammonia produced, using today's \$0.0235 per kWh, nearly identical to the result above. 286 Elsewhere (64), Dubey evaluated a technically similar but energy-island-based scenario for small-scale, 287 wind- and electrolysis based H.-B. NH<sub>3</sub> (77 tonnes per day or less). This included hydrogen storage to 288 continuously generate electricity using generators (for air separation etc.), and NH<sub>3</sub> when wind would be 289 not available. Simply extrapolating Dubey's small-scale data to the benchmark 1000tpd results in about 290 twice the electrical energy demand compared to Grundt et al. and the calculations above. This difference 291 is mainly due to the added H<sub>2</sub> storage/usage, and the less efficient small-scale cryogenic nitrogen-292 generation system.

Grundt et al. estimated capital expenses of U.S. \$200 million (corrected to 2016 dollars) for a 1000tpd ammonia facility (H.-B. synthesis loop, water electrolysis, and cryogenic air separation). Applying the six-tenths rule of plant design, a 2000tpd facility would have estimated capital costs of \$329 million. Capital investment for conventional H.-B. facilities are essentially equivalent at U.S. \$312 million for 2000-tpd capacity (natural gas-based, state-of-the-art, greenfield H.-B. facility (*65*)). Thus, even for a greenfield facility, renewable ammonia capital costs are competitive with natural gas-based ammonia. Grundt et al.'s capital investment figure will obviously be significantly reduced if an existing Haber-Bosch synthesis loop is retrofitted with renewable syngas production.

#### **301 Avenues to renewable ammonia:**

The very significant existing capital investments in natural gas- or coal-based ammonia synthesis via H.-B. in countries such as China and the U.S. causes an amount of inertia to technological change that is hard to overcome. The "bolt-on" conversion or partial conversion to hydrogen and nitrogen from water and air based on renewable electricity, however, can perhaps overcome this inertia through strong payback as demonstrated here, or perhaps by marketing renewable fertilizer or NH<sub>3</sub> that may be attractive even at a premium for organic food production or energy storage/transportation (*26*).

308 The capital investment inertia in Africa is much lower since little ammonia is used or synthesized on the continent, relative to the current and future population. However, the technical complexity, economic 309 310 barriers to down-scaling, and capital intensity of state-of-the-art H.-B. facilities makes the process less 311 compatible with the economic, technological, and infrastructure realities in Africa. Research for  $NH_3$ 312 synthesis completely different from H.-B. should address enabling factors of future markets like Africa: 313 economical down-scaling to regional or local scale to avoid the need for transport networks, robustness 314 and resilience to upsets or utility interruptions, intermittent operability from intermittent renewable 315 resources, and technological simplicity.

#### 316 **3 Conclusions**

317 The precipitous decline in the cost of renewable electricity renders electrolysis of water and cryogenic 318 nitrogen from air a feedstock supply route for Haber-Bosch ammonia synthesis gas that is increasingly 319 competitive with natural gas-based Haber-Bosch ammonia. Using available industrial-scale technology, 320 the energy demand for a process based on electrical energy to provide hydrogen and nitrogen is about 321 14% higher than for the conventional natural gas based process. Existing Haber-Bosch synthesis loops in 322 ammonia synthesis facilities in the U.S. and worldwide could be incrementally or completely retrofitted. 323 Developing retrofit technology would perhaps also be useful for the Chinese market for the future (66). 324 There is now a clear, economically attractive and relatively rapid path to decouple ammonia synthesis as a 325 major energy component of food production from fossil fuel, especially where renewable electricity 326 already is increasingly inexpensive, such as in the U.S. and Europe.

Research into Haber-Bosch catalysts or replacements for those catalysts will have little to no impact on the energy demand or fossil fuel footprint of ammonia synthesis since hydrogen production consumes the Lyon's share of energy. Even a hypothetical catalyst allowing room temperature operation at atmospheric pressure with superior performance compared to existing Haber-Bosch catalysts will haveessentially no impact on the energy footprint.

Research into fundamental alternatives to the Haber-Bosch process should therefore concentrate on conditions in future markets such as Africa where farmers use little fertilizer, ammonia production is at a low level, and future population growth and increase in food demand is expected to be the most significant. Issues such as economical down-scaling, reduced complexity by atmospheric pressure operation, lower capital expense, tolerance to upsets, and ease of intermittent operability would enable future greenfield ammonia production in Africa.

## 338 Acknowledgments

This material is partially based upon work supported by the National Science Foundation Grant, "From Crops to Commuting: Integrating the Social, Technological, and Agricultural Aspects of Renewable and Sustainable Biorefining (I-STAR)," NSF Award No.: DGE-0903701.

This material is partially based upon work supported by the U.S. Department of Energy, Office of
 Science, Office of Basic Energy Sciences, EPSCoR, under Award Number DESC0016453

Funding by the Center for Sustainable Energy, Kansas State University, is gratefully acknowledged.

## 345 **References**

1 U.S. Geological Survey, Mineral commodity summaries, 112-113, 2014

2 E. Worrell, D. Phylipsen, D. Einstein, N. Martin, "Energy Use and Energy Intensity of the U.S.

Chemical Industry" (Lawrence Berkeley National Laboratory, LBNL-44314, 2000);

https://www.energystar.gov/ia/business/industry/industrial\_LBNL-44314.pdf

*3* Uhde, "Ammonia," (Company brochure);

http://www.thyssenkrupp-industrial

 $solutions.com/fileadmin/documents/brochures/uhde\_brochures\_pdf\_en\_5.pdf$ 

4 European Fertilizer Manufacturers' Association, "Best Available Techniques for Pollution

Prevention and Control in the European Fertilizer Industry" (Booklet No. 1 of 8: Production of

Ammonia,2000);

http://www.fertilizerseurope.com/fileadmin/user\_upload/user\_upload\_prodstew/documents/Book let\_nr\_1\_Production\_of\_Ammonia.pdf

5 International Fertilizer Industry Association, Production and International Trade Committee,

"Ammonia Feedstock Evolution" (2013)

http://www.fssa.org.za/Journals/2014/deSousa\_slides.pdf

6 IPCC Fourth Assessment Report: Climate Change, 2007, p. 4

https://www.ipcc.ch/pdf/assessment-report/ar4/wg3/ar4\_wg3\_full\_report.pdf

7 "World Population to 2300" (United Nations Department of Economic and Social Affairs, United Nations, New York, 2004).

8 T. Wheeler, J. von Braun, Climate change impacts on global food security. *Science* **341**(6145), 508-513 (2013).

9 J. Bruinsma, "The resources outlook: by how much do land, water and crop yield need to increase by 2050?", in: *Looking Ahead in World Food and Agriculture*, P. Conforti, Ed., Food and Agriculture Organization of the United Nations (2011);

http://www.fao.org/docrep/014/i2280e/i2280e00.pdf

10 B. A. Stout, Handbook of Energy for World Agriculture (Elsevier, New York, 1989).

11 W. M. Stewart, A. E. Dibb, A. E. Johnston, T. J. Smyth, The Contribution of Commercial Fertilizer Nutrients to Food Production. *Agronomy Journal* **97**(1), 1-6 (2005).

*12* A. Lerna, G. Pandino, S. Lombardo, G. Mauromicale, Tuber yield, water and fertilizer productivity in early potato as affected by a combination of irrigation and fertilization. *Agricultural Water Management* **101**(2011), 35-41.

*13* I. Kisekka, F. Lamm, J. D. Holman, "Response of Drought-Tolerant and Conventional Corn to Limited Irrigation," (Kansas Agricultural Experiment Station Research Report, Volume 1, Issue 5, Article 21, 2015);

http://newprairiepress.org/cgi/viewcontent.cgi?article=1088&context=kaesrr

*14* C. Hedley, The role of precision agriculture for improved nutrient management of farms. *Journal of the Science of Food and Agriculture*, **95**(1), 12-19 (2015)

*15* Y. P. Timilsena, R. Adhikari, P. Casey, T. Muster, H. Gill, B. Adhukari, Enhanced efficiency fertilisers: a review of formulation and nutrient release patterns. *Journal of the Science of Food and Agriculture*, **95**(6), 1131-1142 (2015).

16 V. Smil, Enriching the Earth: Fritz Haber, Carl Bosch, and the Transformation of World Food Production (MIT Press, Cambridge, MA, 2004).

*17* USDA ERS, Manure Use for Fertilizer and for Energy, Report to Congress United States Department of Agriculture, June 2009

18 Y. Luo, B. Su, W. S. Currie, J. S. Dukes, A. Finzi, U. Hartwig, B. Hungate, R. E. McMurtrie,
R. Oren, W. J. Parton, D. E. Pataki, R. M. Shaw, D. R. Zak, C. B. Field, Progressive Nitrogen
Limitation of Ecosystem Responses to Rising Atmospheric Carbon Dioxide. *Bio Science*, 54(8),
731-739 (2004).

*19* I. S. F. Jones, The cost of carbon management using ocean nourishment. *International Journal of Climate Change Strategies and Management*, **6**(4), 391-400 (2014).

20 T. Lipman, N. Shah, "Ammonia As an Alternative Energy Storage Medium for Hydrogen Fuel Cells" (Final Report Caltrans/UC Berkeley Contract #22A0418, Task Order 1, U.C. Berkeley Transportation Sustainability Research Center, 2007);

http://escholarship.org/uc/item/7z69v4wp

21 "ARPA-E Announces \$30 Million in Funding for New Technologies to Produce Renewable Liquid Fuels", (Arpa-E Press and Public Affairs, 2016); http://arpa-e.energy.gov/?q=news-item/arpa-e-announces-30-million-funding-new-technologies-produce-renewable-liquid-fuels
22 Innovations at the Nexus of Food, Energy and Water Systems (INFEWS), (U.S. National Science Foundation, 2016); http://www.nsf.gov/pubs/2016/nsf16524/nsf16524.htm
23 114th Congress of the United States, Report 114-54 to accompany H.R. 2028, p. 90, 2015
24 J. Norskov, J. Chen, (Co-Chairs), "Sustainable Ammonia Synthesis" (DOE Roundtable Report, 2-2016); http://science.energy.gov/~/media/bes/csgb/pdf/docs/2016/NH3\_Report
25 Sustainable Ammonia Synthesis (U. S. Department of Energy Office of Science Basic Energy

Sciences, DE-FOA-0001569 and 1572, 2016);

http://science.energy.gov/~/media/grants/pdf/foas/2016/SC\_FOA\_0001569.pdf

*26* D. Howell, "Revolutionary disruption coming to the energy sector, The Japan Times, March 10, 2017.

http://www.japantimes.co.jp/opinion/2017/03/10/commentary/world-commentary/revolutionarydisruption-coming-energy-sector#.WO-VqYN3Hmg 27 "Green" Ammonia is the key to meeting the twin challenges of the 21st century, Siemens United Kingdom

http://www.siemens.co.uk/en/insights/potential-of-green-ammonia-as-fertiliser-and-electricitystorage.htm

28 "Dutch gas plants made fossil-free?", Vattenfall, March 2016

http://news.vattenfall.com/en/article/dutch-gas-plants-made-fossil-free

29 F. Haber, The synthesis of ammonia from its elements, Nobel lecture, June 3, 1920.

*30* C. Bosch, The development of the chemical high-pressure method during the establishment of the new ammonia industry, Nobel lecture, May 21, 1932.

31 A. Mittasch, "Geschichte der Ammoniak-Synthese" (Verlag Chemie, Weinheim, 1957).

*32* M. Appl, "Ammonia", in: Ullmann's Encyclopedia of Industrial Chemistry (Wiley VCH, 2006)

*33* T. Eggemann, "Ammonia", in: Kirk-Othmer Encyclopedia of Chemical Technology (John Wiley and Sons, 2010)

34 J. W. Geus, K. C. Waugh, Ammonia Synthesis Commercial Practice. In: J. R. Jennings (ed.),
Catalytic Ammonia Synthesis, Fundamentals and Practice. Plenum Press, New York, 1991, 253283.

35 M. Appl, "Ammonia: principles and industrial practice" (Wiley VCH Verlag GmbH, Weinheim, 1999) p. 146.

*36* A. Boulamanti, J. A. Moya, Production costs of the chemical industry in the EU and other countries: Ammonia, methanol, and light olefins. *Renewable and Sustainable Energy Reviews* (2016), http://dx.doi.org/10.1016/j.rser.2016.02.021i

37 G. Schnitkey, Anhydrous Ammonia, Corn, and Natural Gas Prices Over Time, Farmdoc Daily(6)112, University of Illinois at Urbana-Champaign, June 14 2016

38 L. Tillemann, "Revolution Now – The Future Arrives for Four Clean Energy Technologies"(U.S. Department of Energy, September 17, 2013);

http://energy.gov/sites/prod/files/2013/09/f2/200130917-revolution-now.pdf

*39* R. Schlögl, Catalytic synthesis of ammonia – a "never ending story?". *Angew. Chem. Int. Ed.* 42(18), 2004-2008 (2003).

40 NSF 17-013, Dear Colleague Letter: FY 2017 Innovations at the Nexus of Food, Energy and Water Systems (INFEWS) Funding Opportunity on Nitrogen, Phosphorus, and Water

https://www.nsf.gov/pubs/2017/nsf17013/nsf17013.jsp

41 S. Licht, B. Cui, B. Wang, F.-F. Li, J. Lau, S. Liu, Ammonia synthesis by N<sub>2</sub> and steam electrolysis in molten hydroxide suspensions of nanoscale Fe<sub>2</sub>O<sub>3</sub>. *Science* 345(2014), 637-640.
42 Skodra, A., Stoukides, M., Electrocatalytic synthesis of ammonia from steam and nitrogen at atmospheric pressure". *Solid State Ionics* 180(2009), 1332-1336.

43 J. A. Pool, E. Lobkovsky, P. J. Chirik, Hydrogenation and cleavage of dinitrogen to ammonia with a zirconium complex. *Nature* **427**(2004), 527-530.

44 D. V. Yandulov, R. R. Schrock, Catalytic reduction of dinitrogen to ammonia at a single

molybdenum center. *Science* **301**(2003), 76-78.

45 R. Michalsky, P. H. Pfromm, An Ionicity Rationale to Design Solid-Phase Metal-Nitride Reactants for Solar Ammonia Production. *J. Phys. Chem. C.* **116**(44), 23243-2325 (2012).

*46* R. Michalsky, A. M. Avram, B. A. Peterson, P. H. Pfromm, A. A. Peterson, Chemical looping of metal-nitride catalysts: low-pressure ammonia synthesis for energy storage. *Chemical Science* **6**(2015), 3965-3974.

47 G. Ertl, Reactions at surfaces: from atoms to complexity, Nobel lecture, December 8, 2007.

48 P. Peng , Y. Li, Y. Cheng, S. Deng, P. Chen, R. Ruan, "Atmospheric Pressure Ammonia Synthesis Using Non-thermal Plasma Assisted Catalysis", *Plasma Chemistry and Plasma Processing*, **36**(5), 1201-1210 (2016).

49 A. S. Travis, "The Synthetic Nitrogen Industry in World War I – its emergence and expansion" (Springer Verlag, New York, 2015).

*50* R. Michalsky, B. J. Parman, V. Amanor-Boadu, P. H. Pfromm, Solar thermochemical production of ammonia from water, air and sunlight: thermodynamic and economic analyses. *Energy*, **42**(1), 251-260 (2012).

51 A. Steinfeld, Solar thermochemical production of hydrogen – a review. *Solar Energy* 78(5),
603-615 (2005).

52 L. Bertuccioli, A. Chan, D. Hart, F. Lehner, B. Madden, E. Standen, "Study of development of water electrolysis in the European Union" (Final Report, Fuel Cells and Hydrogen Joint Undertaking, February 2014)

;http://www.fch.europa.eu/sites/default/files/study%20electrolyser\_0-Logos\_0\_0.pdf

53 J. Genovese, K. Hark, M. Pater, J. Turner, "Current (2009) State-of-the-Art Hydrogen Production Cost Estimate Using Water Electrolysis" (U.S. Department of Energy National Renewable Energy Laboratory, Report NREL/BK-6A1-46676, 2009);

http://www.osti.gov/bridge

54 European Industrial Gases Association, "Indirect CO<sub>2</sub> Emissions Compensation: Benchmark Proposal for Air Separation Plants" (Position Paper PP-33, 2010);

https://www.eiga.eu/fileadmin/docs\_pubs/PP-33-

 $Indirect\_CO2\_emissions\_compensation\_Benchmark\_proposal\_for\_Air\_Separation\_Plants.pdf$ 

55 C. W. Hooper, Ammonia Synthesis: commercial Practice, in: J. R. Jennings (ed.) Catalytic Ammonia Synthesis, Plenum Press, NY, 1991, p. 265 (1991)

*56* Appl, M., The Haber-Bosch Heritage: The Ammonia Production Technology. *50*th Anniversary of the IFA Technical Conference, September 25–26 1997, Sevilla, Spain.

*57* U.S. Energy Information Administration, "Electricity-Electrical Power Annual" (2016); http://www.eia.gov/electricity/annual/html/epa\_02\_10.html

*58* "Revolution...Now The Future Arrives for Five Clean Energy Technologies – 2015 Update" (Report, U.S. Department of Energy, November 2015);

http://energy.gov/sites/prod/files/2015/11/f27/Revolution-Now-11132015.pdf

*59* J. R. Bartels, M. P. Pate, "A feasibility study of implementing an ammonia economy" (Final Report, Iowa Energy Center Project Grant Number: 07S-01, 2008);

http://www.iowaenergycenter.org/wp-content/uploads/2012/03/Bartels\_07S-01.pdf

60 T. Eggemann, "Ammonia", in: Kirk-Othmer Encyclopedia of Chemical Technology (John Wiley and Sons, 2010)

61 Y. Zhou, Y., R. S. J. Tol, Evaluating the Costs of Desalination and Water Transport. *Water Resources Res.* **41**(2005), W03003.

62 PotashCorp, "Nitrogen Overview," (2014).

http://www.potashcorp.com/overview/nutrients/nitrogen/overview/nitrogen-production-cashcosts

*63* T. Grundt, K. Christiansen, Hydrogen by water electrolysis as basis for small-scale ammonia production. A comparison with hydrocarbon -based technologies. *International Journal of Hydrogen Energy*, **7**(3), 247-257 (1982).

64 M. B. Dubey, "Conversion and storage of wind energy as nitrogeneous fertilizer" (Final Report, The National Science Foundation, Contract NSF C75-22186, 1977).

65 D. Lippmann, D., Larsen, J., "Uhde dual-pressure process for large-scale ammonia plants" (Thyssenkrupp techforum, 56-61, July 2004);

https://www.thyssenkrupp.com/documents/Publikationen/Techforum/techforum\_e\_7\_2004.pdf

66 B. Spiegele, China's State Grid Envisions Global Wind-and-Sun Power Network. The Wall Street Journal, March 30, 2016

http://www.wsj.com/articles/chinas-state-grid-envisions-global-wind-and-sun-power-network-1459348941