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## 2 **Towards sustainable agriculture: fossil-free ammonia**

3 Peter H. Pfromm, Department of Chemical Engineering, Kansas State University,  
4 1005 Durland Hall, 1701A Platt Street, Manhattan, Kansas, 66506-5102, U.S.A. (pfromm@ksu.edu)

### 6 **Abstract**

7 About 40% of our food would not exist without synthetic ammonia ( $\text{NH}_3$ ) for fertilization. Yet,  $\text{NH}_3$   
8 production is energy intensive. About 2% of the world's commercial energy is consumed as fossil fuels  
9 for  $\text{NH}_3$  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.  $\text{NH}_3$  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.  $\text{NH}_3$  as this is governed by hydrogen production. Renewable energy-enabled,  
13 fossil-free  $\text{NH}_3$  synthesis is then evaluated based on the exceptional and continuing cost decline of  
14 renewable electricity. H.-B. syngas ( $\text{H}_2$ ,  $\text{N}_2$ ) is assumed to be produced by electrolysis and cryogenic air  
15 separation, and then supplied to an existing H.-B. synthesis loop. Fossil-free  $\text{NH}_3$  could be produced for  
16 energy costs of about \$232 per tonne  $\text{NH}_3$  without claiming any economic benefits for the avoidance of  
17 about 1.5 tonnes of  $\text{CO}_2$  released per tonne  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  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**

- 27 • There is no motivation for research to improve or replace Haber-Bosch catalysts due to the  
28 overwhelming impact of hydrogen production on the economics and the energy footprint.
- 29 • The cost of electricity from renewables has sharply declined and will likely continue to do so.
- 30 • Haber-Bosch ammonia synthesis facilities can be retrofitted with existing technology for  
31 competitive wind electricity-based feedstock preparation to produce fossil-free ammonia.
- 32 • Research for alternatives to the Haber-Bosch process should be directed at emerging market and  
33 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 ( $\text{NH}_3$ ) are synthesized globally (1), making  $\text{NH}_3$  the  
38 second most produced man made chemical. More than 85% of  $\text{NH}_3$  is used in fertilizers, with the  
39 remainder used mainly by other areas of the chemical- and process industries.  $\text{NH}_3$  is produced by using  
40 a significant amount of energy to convert the hydrogen from water, and nitrogen from air to  $\text{NH}_3$ . 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  $\text{CO}_2$ . About 600kg of natural  
44 gas are consumed to produce 1000 kg  $\text{NH}_3$  in the most efficient facilities.(2,3) The total fossil  $\text{CO}_2$   
45 emissions from  $\text{NH}_3$  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  $\text{CO}_2$  emission from using either feedstock.(4,5) This amounts to about  
48 2.5% of all fossil fuel based  $\text{CO}_2$  emissions world wide (6).  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  (10).  $\text{NH}_3$  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  $\text{NH}_3$ -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 nitrogenous 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  
66 animal waste is unlikely to significantly impact the need for synthetic fertilizers (17). Another aspect of  
67 the global impact of the presence or absence of bioavailable nitrogen is lack of bioavailable nitrogen

68 hampering carbon sequestration from the atmosphere as biomass (18). There are considerations of adding  
69 man-made bioavailable nitrogen to natural systems for example for fertilization in the ocean to sequester  
70 fossil CO<sub>2</sub> (19).

71 The capacity of NH<sub>3</sub> to serve as a convenient hydrogen (H<sub>2</sub>) carrier (20), or to be used directly as a  
72 hydrogen-rich fuel or fuel additive in internal combustion engines is an emerging aspect. Compared to  
73 H<sub>2</sub>, NH<sub>3</sub> is liquefied fairly easily and liquid NH<sub>3</sub> exceeds the U.S. Department of Energy's (DOE) target  
74 for hydrogen storage per volume. Bulk NH<sub>3</sub> storage and transport by pipeline, rail, and truck, and  
75 delivery down to the retail scale is well established, as opposed to transport, storage, and distribution of  
76 H<sub>2</sub>. This has been recognized and well described in a recent funding opportunity made available by DOE  
77 (21).

78 In summary, world production of synthetic NH<sub>3</sub> will have to increase significantly from now about  
79 174 million tonnes per year during the next decades as the world population increases, specifically in  
80 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**

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

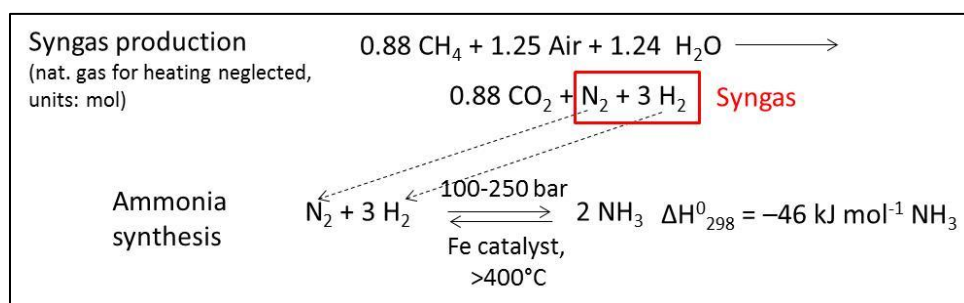
87 In light of the substantial decline of the cost of renewable electrical energy in the U.S., and due to the  
88 rising interest in NH<sub>3</sub> synthesis and applications, it seems timely to estimate if renewable electricity might  
89 be an avenue to fossil-free NH<sub>3</sub>, and thereby substantially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

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

93 There are two major challenges to NH<sub>3</sub> synthesis: first, activating dinitrogen (essentially somehow  
94 breaking the exceptionally strong dinitrogen triple bond), and second, obtaining hydrogen to convert  
95 activated nitrogen to NH<sub>3</sub>. The former allows a process to exist, but the latter governs the energy demand  
96 and economic viability (as shown below). Both tasks must be done at technologically acceptable  
97 conditions and at a cost commensurate with the value added by using ammonia in agriculture. Fritz  
98 Haber's Nobel Prize (29) was for fundamentally solving the nitrogen activation issue. He secured  
99 economical success by patenting recycling of valuable unreacted syngas after separating NH<sub>3</sub>. Carl

100 Bosch's Nobel Prize ((30), with F. Bergius) relates in large part to the economical large-scale supply of  
 101 hydrogen for NH<sub>3</sub> synthesis. Their work created the commercial fertilizer industry and averted imminent  
 102 worldwide food shortages.(31) There were even at the time of Haber's discoveries a number of  
 103 competing approaches to synthesize NH<sub>3</sub> at the technical scale, but none of them could match the  
 104 economics of the integrated Haber-Bosch process (31). However, these economics are based on fossil  
 105 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<sub>3</sub> synthesis is no longer the catalytic conversion of dinitrogen and dihydrogen to NH<sub>3</sub>. While the  
 108 technology is complex, the chemistry is simple: hydrogen and nitrogen combine to produce NH<sub>3</sub>. Figure  
 109 1 shows both the overall chemical process to produce the syngas (H<sub>2</sub>, N<sub>2</sub>) for the H.-B. synthesis, and the  
 110 chemical reaction taking place in a H.-B. reactor.



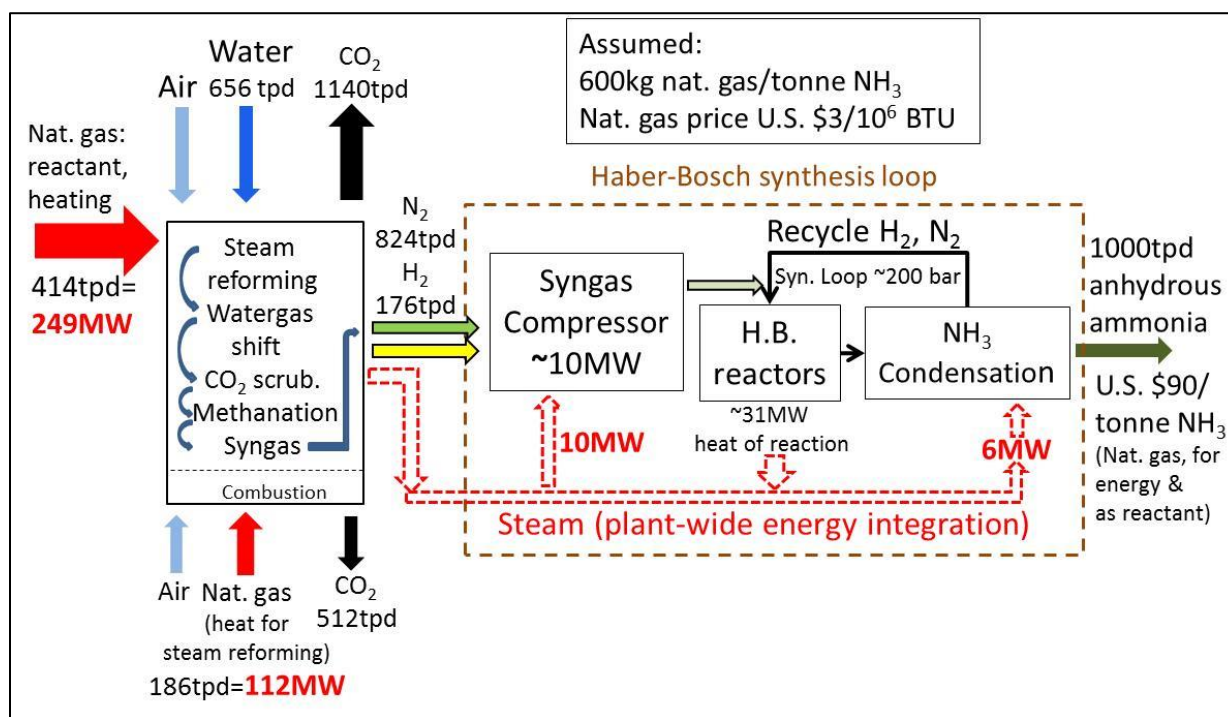
111  
 112 **Figure 1** NH<sub>3</sub> synthesis, top: state of the art overall chemical reaction to produce synthesis gas (syngas)  
 113 from air, water, and natural gas; bottom: the reaction in the Haber-Bosch synthesis reactor proper.

114 Figure 2 shows the main sections of what is generally termed the H.-B. process using the most energy  
 115 efficient state of the art approach based on natural gas as both feedstock and energy source. The reader is  
 116 directed to the literature for exhaustive treatment of many variations such as using coal as energy source,  
 117 sophisticated changes of heat integration of the process steps, catalysts, catalyst fundamentals, and many  
 118 other issues (32, 33). The discussion below attempts to use the current best available technology  
 119 characteristics.

120 The most efficient implementations of the natural gas steam reforming based H.-B. process today at  
 121 industrial scale use about 600 kg of natural gas per 1000 kg anhydrous NH<sub>3</sub> produced (as used in Figure  
 122 2), or about 6.8 Gcal/tonne NH<sub>3</sub> (as natural gas lower heating value, LHV). Various plants may however  
 123 use significantly more energy depending on the technology in use. If coal is used, the energy demand  
 124 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

127 has been estimated at 4.98 Gcal/tonne NH<sub>3</sub> (as natural gas lower heating value, (3)). 5.10 Gcal/tonne NH<sub>3</sub>  
 128 (product liquid ammonia) has been reported as the thermodynamic minimum elsewhere ((34), higher  
 129 heating value, HHV). Overall, current full scale (1000 tonnes per day NH<sub>3</sub> and larger) energy  
 130 consumption of the best technology available is therefore only about 20% above the immutable  
 131 thermodynamic minimum when using the state of the art natural gas based Haber-Bosch process outlined  
 132 below.



133  
 134 **Figure 2** The state of the art Haber-Bosch process to produce NH<sub>3</sub> from natural gas (methane). Natural  
 135 gas is used to provide energy for steam reforming using combustion, and also to provide both hydrogen  
 136 and nitrogen by steam reforming and subsequent water gas shift (left). (tpd = tonne per day)

137 The single-pass conversion in the Haber-Bosch reactors depends on a number of operational  
 138 parameters such as the level of inerts like argon. It is reported often at less than 20%, certainly no more  
 139 than 30% (4,35). Unreacted hydrogen and nitrogen is always recycled (at pressure) after NH<sub>3</sub> is  
 140 condensed and separated. The synthesis loop carries an inert load (argon from air, methane from  
 141 methanation) that is controlled by purging a small stream (not shown). Oxygen or oxides must not enter  
 142 the synthesis loop since this would inactivate the catalyst. Catalyst charge lifetimes are on the order of  
 143 many years in industrial practice.

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

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

148 The price of ammonia is closely related to the price of the feedstock (36, 2013 data). Labor and other  
149 (tax, insurance etc.) add perhaps 25% in the U.S. or Russia, while the high price of feedstock in Europe  
150 compared to the U.S. essentially drowns out all other costs. The historically close tracking of NH<sub>3</sub> price  
151 and natural gas cost has relaxed in the U.S. since 2008 due to strong demand for NH<sub>3</sub> and the resulting  
152 price increase. For 2016, a price of \$500-600 per tonne ammonia has been reported, with a minimum of  
153 \$499 per tonne since 2008 (37).

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

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

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

162 If one assumes quite hypothetically operating the synthesis loop using a revolutionary catalyst at  
163 atmospheric pressure and room temperature and simultaneously improved catalyst performance, then this  
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<sub>2</sub> 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  
175 already highly optimized and last for many years, while little further practical impact is possible due to  
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.



180 As an example of proposed alternative processes to replace H.-B., one recent approach is the use of a  
181 "cold" plasma to produce ammonia from hydrogen and nitrogen (48). The "hot" plasma approach using  
182 an electrical discharge has been implemented at full scale early in the 20th century and was quickly  
183 discarded due to the exceptionally high energy demand compared to H.-B. (49). Using the data from the  
184 above reference, cold plasma would require about 40,000 MW for a 1000 tonne NH<sub>3</sub> per day production  
185 level, while industrial-scale state of the art H.-B. requires about 360 MW. The energy demand of cold  
186 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.

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

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

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

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

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

## 212 **2 Results and Discussion**

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

218 The overall premise is to retain the existing H.-B. synthesis loop to make use of installed capital  
219 investments. The hydrogen and nitrogen generation from natural gas (steam reforming/watergas shift,  
220 state of the art Haber-Bosch plants) is replaced with electrolytic hydrogen, and cryogenic nitrogen is  
221 made using renewable electricity. This replacement could also be done step-wise in form of incremental  
222 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**

232 In the proposed system, renewable NH<sub>3</sub> is produced by electrolyzing water to obtain highly pure  
233 hydrogen (alkaline electrolysis or proton-exchange membrane electrolysis, assumed at 54 kWh per kg H<sub>2</sub>  
234 delivered at 30 bar (52,53)). Electrolytic hydrogen has the added advantage of not containing catalyst  
235 poisons (especially sulfurous compounds), compared to using natural gas. Purified nitrogen is produced  
236 by a cryogenic air separation unit (243 kWh per tonne N<sub>2</sub> delivered at 285K, 40 bar (54)). A conventional  
237 oxygen-removal step (not shown) to purify the cryogenic nitrogen is needed due to the great oxygen  
238 sensitivity of H.-B. catalysts.

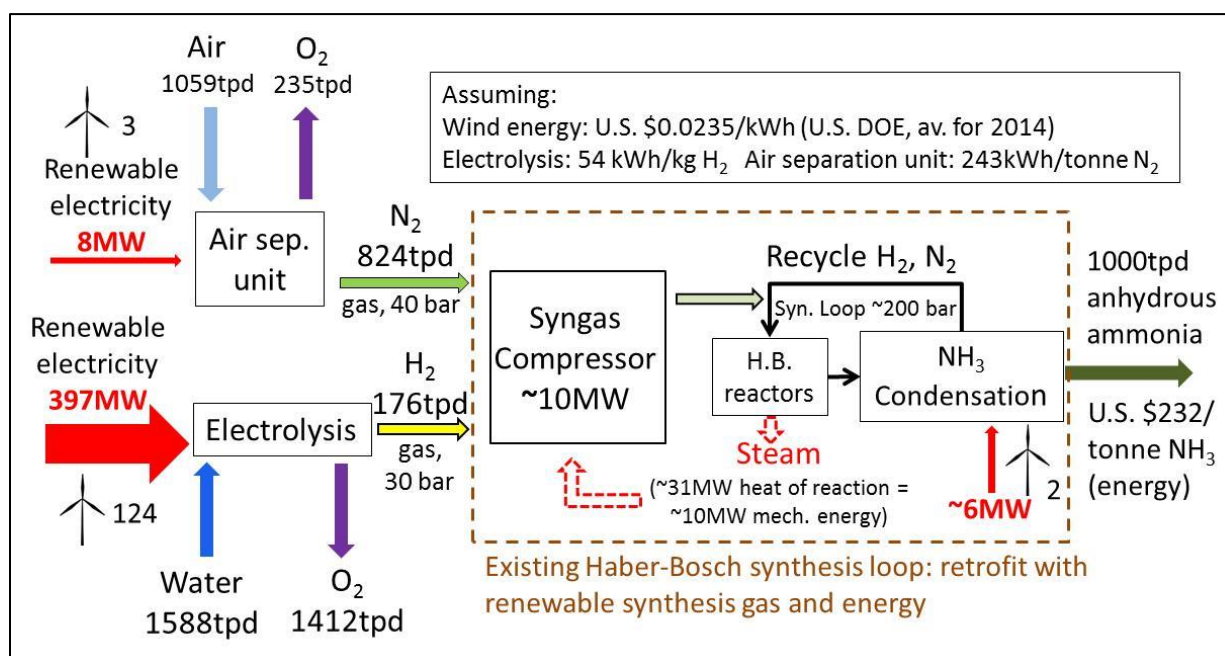
### 239 **Synthesis loop compressor**

240 A single multi-stage centrifugal syngas compressor used in state of the art existing H.-B. synthesis  
241 loops is typically driven by a steam turbine and requires about 10 MW to compress the synthesis gas for  
242 the assumed 1000 tpd NH<sub>3</sub> production (55). Steam is conventionally derived from the natural gas steam  
243 reforming process, and from cooling the H.-B. reactors. The conceptual cryogenic air separation and



244 electrolysis assumed here do not produce significant amounts of steam to drive the compressor.  
 245 However, up to 31 MW of heat of reaction is still available as high-pressure steam from required cooling  
 246 of the Haber-Bosch synthesis reactors (3, 56). Estimating 30% efficiency for the use of the high-pressure  
 247 steam in the syngas compressor, the available steam would nominally suffice to drive the syngas  
 248 compressor. An amount of renewable energy may be needed to raise additional steam for the compressor,  
 249 but even an electrical drive would have marginal impact compared to the energy for H<sub>2</sub> generation.

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



252  
 253 **Figure 3** Hydrogen generation governs the energy demand for the synthesis of 1000 tonnes per day (tpd)  
 254 of renewable ammonia in a "bolt-on" concept. Renewable cryogenic N<sub>2</sub> and renewable H<sub>2</sub> from water  
 255 electrolysis are fed to an existing Haber-Bosch synthesis loop. Electrolysis is assumed at 54 kWh/kg H<sub>2</sub>.  
 256 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  
 257 for a simple illustration, disregarding the capacity factor.

258 **Detailed discussion of costs**

259 Hydrogen production by electrolysis consumes 94% of the renewable electricity required according to  
 260 Figure 3. The U.S. nationwide average electricity price to industrial customers in 2014 was \$0.071 per  
 261 kWh (57). Renewable energy prices have declined precipitously, with an average of \$0.0235 per kWh for  
 262 power-purchase agreements from wind energy reported for 2014 in the U.S.(58) If a total of 411 MW is  
 263 required (Figure 3) for the benchmark 1000 tpd ammonia production, then the energy cost for renewable  
 264 electricity would be \$232 per tonne of ammonia produced. No significant amount of fossil fuel would be  
 265 needed.

266 Transportation costs in the U.S. are negligible compared to the cost of producing NH<sub>3</sub> (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  
275 period of 2008-2016 (37).

276 Any credit for eliminating the current minimum of about 1.5 tonnes of CO<sub>2</sub> emissions per tonne of  
277 ammonia produced would improve fossil-free ammonia economics. Further improvement would result if  
278 the high-purity oxygen by-product could be used, perhaps for oxygen-blown fossil fuel combustion to  
279 enable carbon capture/sequestration, or for other purposes such as steel making or bleaching for the pulp  
280 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).  
283 Grundt et al. reported an overall energy demand of 416MW for 1000 tpd for a Haber-Bosch ammonia  
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.

293 Grundt et al. estimated capital expenses of U.S. \$200 million (corrected to 2016 dollars) for a 1000-  
294 tpd ammonia facility (H.-B. synthesis loop, water electrolysis, and cryogenic air separation). Applying  
295 the six-tenths rule of plant design, a 2000tpd facility would have estimated capital costs of \$329 million.  
296 Capital investment for conventional H.-B. facilities are essentially equivalent at U.S. \$312 million for  
297 2000-tpd capacity (natural gas-based, state-of-the-art, greenfield H.-B. facility (65)). Thus, even for a  
298 greenfield facility, renewable ammonia capital costs are competitive with natural gas-based ammonia.

299 Grundt et al.'s capital investment figure will obviously be significantly reduced if an existing Haber-  
300 Bosch synthesis loop is retrofitted with renewable syngas production.

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

302 The very significant existing capital investments in natural gas- or coal-based ammonia synthesis via  
303 H.-B. in countries such as China and the U.S. causes an amount of inertia to technological change that is  
304 hard to overcome. The "bolt-on" conversion or partial conversion to hydrogen and nitrogen from water  
305 and air based on renewable electricity, however, can perhaps overcome this inertia through strong  
306 payback as demonstrated here, or perhaps by marketing renewable fertilizer or  $\text{NH}_3$  that may be attractive  
307 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  
309 the continent, relative to the current and future population. However, the technical complexity, economic  
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  $\text{NH}_3$   
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.

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

330 atmospheric pressure with superior performance compared to existing Haber-Bosch catalysts will have  
331 essentially no impact on the energy footprint.

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

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