The Potential Economic Feasibility of Direct Electrochemical Nitrogen Reduction as a Route to Ammonia

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Abstract

The Haber-Bosch process produces ammonia from hydrogen and nitrogen gases in a globally important energy-intensive process that uses coal or natural gas as a fuel and as a hydrogen source. Direct electrochemical ammonia synthesis from nitrogen and water using renewable energy sources presents an alternative to the Haber-Bosch process that would be more sustainable. Additionally, the different production structure of direct electrochemical nitrogen reduction technology suggests a supply chain alternative to the ammonia industry, and a method for load-leveling of the electrical grid. This alternative route to ammonia from dinitrogen would require smaller capital investments than the Haber-Bosch process, and would not require a fossil fuel supply. The impact of dynamic electrical power pricing is analyzed for a system that could take advantage of pricing volatility. We show that under certain scenarios, at achievable levels of energy efficiency with a future electrocatalyst, direct nitrogen reduction would be economically competitive or advantageous compared with Haber-Bosch-based ammonia production.

Keywords: electrochemical nitrogen reduction; ammonia; sustainable fertilizer production; sustainable nitrogen fixation; dynamic electricity pricing

INTRODUCTION

To meet the world's growing demand for food, an increased input of nutrients, particularly nitrogen, is needed to support the intensification of agricultural production.[1-2] Specifically, ammonia (NH_3) is produced industrially either for direct use as fertilizer or as the feedstock for other fertilizers.[3-4]

Ammonia serves as the nitrogen source for virtually all synthetic fertilizer.[1-6] It is currently synthesized from nitrogen and hydrogen using the Haber-Bosch process (H-B) (eq 1),[1-6] which is projected to support half of the world's food production by 2025, with the share further increasing in subsequent decades.[2] Current ammonia production is ca. 180 million metric tons (mt) per year[7] with a growth rate of ca. 4% projected through 2022.[8]

$$N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3 \qquad (1)$$

H-B is energy-intensive as currently implemented. Natural gas or coal are used as fuel and as the source of hydrogen (via steam reforming). The chemical equilibrium of eq 1 lies far to the left at temperatures required by the current catalytic system; thus, very high pressures (150-300 bar[9]) are used to increase the equilibrium concentration of ammonia. Even at such pressures, however, the conversion to NH_3 is only ca. 12-30%.[9-11] Roughly 2% of the world's fossil fuel is consumed by the process overall, almost half of which is used for energy for fossil fuel reforming and ammonia synthesis above that of the actual product,[12-14] with the carbon released as CO_2. It is therefore critical to develop a sustainable route to ammonia that is not dependent on fossil fuel. H-B is also capital-intensive, requiring large centralized plants to be economical. An ideal fossil-fuel-free alternative to H-B would be a decentralized or distributed method, reducing transportation costs and enabling deployment in locations remote from current ammonia infrastructure.[15] In addition, ammonia has received attention as a potential medium for storage and transportation of energy.[16-24]

Electrolysis of water followed by H-B (hereinafter E/H-B), and direct electrochemical nitrogen reduction (hereinafter ENR),[25-29] represent two methods that can use electricity, potentially from renewable energy sources, as the source of energy required for ammonia synthesis (eq 2). Such processes could significantly reduce the need for fossil fuel and the commensurate emissions of CO_2. E/H-B would still require centralized production, because the electrolysis-generated H_2 would be fed into an H-B plant of the type currently in use. ENR, in contrast, could be more readily decentralized as it obviates the need for H-B. It would thus save the energy and capital costs of H-B, and would permit the use of decentralized facilities and distributed sources of electricity, thereby reducing the cost of transportation of ammonia to agricultural regions.

$$N_2 + 3\ H_2O\ (+\ \text{electrical energy}) \rightarrow 2\ NH_3 + 3/2\ O_2 \qquad (2)$$

The discovery of active electrocatalysts for ENR has proceeded rapidly over the last few years although there are still no reported examples that approach a practical level of efficiency. Reported catalysts have a wide range of different chemical compositions, containing Bi, Au, Mo, Ag, Pd, Fe, and numerous other metals,[30-53] implying that there is promise for even more reactive and selective catalysts. The electrochemical overpotential, defined as the applied potential beyond the thermodynamic potential required to reach a certain current density, has been reported to be very low in some cases (as low as 50 mV[50]). A representative leading catalyst uses molybdenum carbide nanorods to yield up to 95 micrograms NH_3 per hour per milligram of catalyst at a cathodic potential of –0.24 V vs. SHE.[54] This catalyst system, like others recently reported, achieves a Faradaic efficiency of about 10% and at –0.24 V vs. SHE (330 mV overpotential), a current density of ~25 mA/cm^2. An ideal catalyst will maximize activity (as measured in current density or turnover frequency), maximize durability (operating time before degradation), and minimize overpotential.

Technoeconomic aspects of ENR have been analyzed from several perspectives.[10, 24, 43, 55-61] In this article we analyze the conditions that affect the potential economics of ENR, particularly relative to H-B-based ammonia production through either the conventional fossil-fuel based route or via H_2 derived from the electrolysis of water (E/H-B). In particular, we estimate costs using micro-level dynamic electricity pricing data[62] to examine how current real-world price fluctuations could affect the costs of ammonia obtained by ENR and by E/H-B. Both ENR and E/H-B are complementary with renewable energy sources such as wind and solar which, due to their intermittency, lead to high variability in pricing due to mismatches between electrical output and demand. By selectively operating when pricing is favorable, such electrochemical processes can take advantage of these supply-demand mismatches. This not only favors their cost, but also allows them to act in a "load-leveling" capacity for an electric grid that is significantly based on renewables, thereby favoring the transition to a renewables-based energy system.[63-64]

AMMONIA PRODUCED VIA THE HABER-BOSCH PROCESS BASED ON FOSSIL FUEL: CURRENT PRACTICES

Overview. The hydrogen feed for H-B can, in principle, be produced via various methods including natural gas reforming or coal gasification (as well as electrolytic splitting of water in the case of E/H-B). Natural gas reformation is the most common source of H_2, currently used for 72% of world ammonia production. About 22% is based on coal gasification, and the remainder mostly based on fuel oil.[18] Compared with the use of natural gas, other fossil fuels are associated with both significantly greater energy consumption per ton NH_3 produced via H-B and, additionally, higher emissions of CO_2 per unit energy consumed.{Giddey, 2017 #12003;FeedingEarthIFA, #12098}

The nitrogen feed for H-B may be produced as a co-product of coal gasification and natural gas reforming or extracted from air using an air separation unit (ASU). The ASU uses a combination of compression, cooling, and expansion to separate the nitrogen from oxygen and other compounds in air, and therefore requires additional energy input.[4, 65]

The values of energy input, monetary costs including capital and operating and maintenance (O&M), and CO_2 emissions, are derived in Appendix A of the supplementary material using existing literature and the U.S. Department of Energy H2A Distributed Hydrogen Production Model (Version 3)[66]. Costs are summarized in Table 1,[67] and are the benchmarks against which the E/H-B and ENR processes will be compared below.

Table 1. Estimated costs of ammonia production (\$/mt-NH_3) via H-B, by natural-gas-based H-B plants of varying capacity (based on a cost of \$2.62/MBTU natural gas)[67]

	H-B plant size (mt-NH_3/day)		
	Large H-B plant (ca. 2000 mt/day)	**Medium H-B plant (545 mt/day)[68]**	**Small H-B plant (91 mt/day)[68]**
Natural gas	\$79	\$79	\$79
Capital	\$55	\$88	\$113
O&M	\$22	\$62	\$133
Total	**\$159**	**\$229**	**\$325**

HABER-BOSCH USING ELECTROCHEMICAL H_2 PRODUCTION (E/H-B)

The economics and energy cost of E/H-B can be viewed in terms of its two major components: (i) electrochemical H_2 production and (ii) the subsequent H-B to synthesize NH_3 according to eq 1. While the energy required for the H-B component of the overall process may be obtained from fossil fuel, in this section we examine the limiting case of a carbon-free (in principle) E/H-B system, in which electric power serves as the source of energy to produce H_2 as well as the energy needed to drive the H-B synthesis.

Total costs of ammonia production, including capital and O&M from E/H-B plants that use electrochemically produced H_2 for feed and fuel are estimated. The values obtained are based on a benchmark electric power price of \$50/MWh and are summarized in Table 2.[67] At the largest economy of scale, the total cost is estimated as \$629/mt-NH_3, with higher costs incurred with smaller-scale accompanying H-B plants.

Table 2. Estimated costs of ammonia production (\$/mt-NH_3) via E/H-B, based on H2A model,[66-67] PEM electrolyzer system with capacity 50 mt-H_2/day, with accompanying H-B plants of varying capacity, at a fixed benchmark electric power cost of \$50/MWh

	H-B plant size (mt-NH_3/day)		
	Large H-B (ca. 2000 mt/day)	**Medium H-B (545 mt/day)**	**Small H-B (91 mt/day)**
Electricity to produce H_2 feed (80% electrical efficiency)	\$441	\$441	\$441
Capital cost (electrolyzer only) to produce H_2 feed	\$33	\$33	\$33
O&M expenses (electrolyzer only) to produce H_2 feed	\$41	\$41	\$41
Electricity to run accompanying H-B plant	\$67	\$67	\$67
Capital cost for H-B plant and ASU unit (58% of full gas-based H-B plant)	\$34	\$51	\$66
O&M expenses for H-B plant (58% of full gas-based H-B plant)	\$13	\$36	\$77
Total	**\$629**	**\$669**	**\$725**

DIRECT ELECTROCHEMICAL NITROGEN REDUCTION (ENR)

Overview. The ENR process comprises oxidation of water at the anode to yield O_2 and H^+ (eq 3) and reduction of N_2 at the cathode and protonation to yield ammonia (eq 4) (Fig. 1).

At the anode: $$3H_2O \rightarrow \frac{3}{2}O_2 + 6e^- + 6H^+ \quad (3)$$

At the cathode: $$6e^- + 6H^+ + N_2 \rightarrow 2NH_3 \quad (4)$$

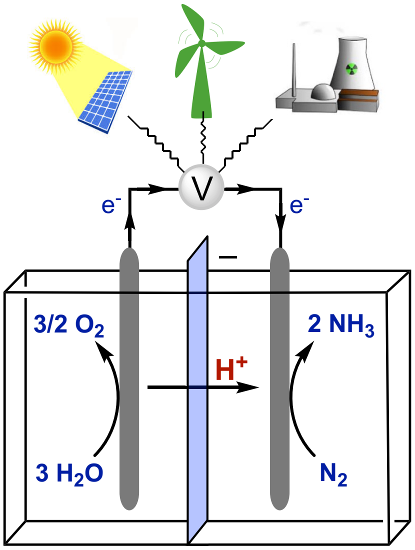

Figure 1. Schematic of sustainable electrochemical nitrogen reduction

The electrochemical potentials at standard state (1 M solutes, 1 atm gases, 298 K) for these half-reactions, and the potential for the overall reaction, are given in equations 7-9.[69-70] All potentials are presented versus the standard hydrogen electrode, SHE.

$$N_2 + 6\,e^- + 6\,H^+ \rightarrow 2\,NH_3(aq);\ E^0 = +0.092V \quad (5)$$

$$3\,H_2O \rightarrow 1.5\,O_2 + 6\,e^- + 6\,H^+;\ -(E^0 = +1.229V) \quad (6)$$

$$N_2 + 3\,H_2O \rightarrow 2\,NH_3 + 1.5\,O_2;\ E^0 = -1.137V \quad (7)$$

From equation 7 and the Nernst equation we can obtain the baseline thermodynamic free-energy requirements for ENR, which corresponds to a minimum energy input of 5.37 MWh/mt-NH_3.[71] Note that equations 5 and 6 correspond to the thermodynamics of the hypothetical situation where NH_3 is produced at pH 0. This convention was chosen to enable direct comparison of the product of HB, E/HB, and ENR. However, it should be recognized that aqueous N_2 reduction would, in practice, produce NH_4^+ under acidic conditions (pH < 10) or NH_3 under basic conditions (pH >10). Alternatively, some catalysts being explored utilize organic, non-aqueous solvents and low acidity which would also produce NH_3. In practice, ENR and HB might have distinct separation strategies or even distinct end products, based on the dramatic differences in the type of chemical processes involved.

On the basis of literature values for independent studies of the half-reactions of eq 5 and eq 6, we consider 0.6 V to be a feasible aspirational full cell overpotential for eq 7,[72] and 1.2 V to be a likely upper limit (if greater cathodic overpotentials are used, there is likely to be substantial undesired proton reduction to H_2). We combine the full cell overpotential and Faradaic efficiency to define a total energy efficiency according to eq 8, where FE denotes Faradaic efficiency, TE denotes thermodynamic voltage requirement which equals 1.137 V, and TV denotes total voltage (TE plus full-cell overpotential).

$$EE = FE \times \frac{TE}{TV} \tag{8}$$

For benchmarking purposes, we consider aspirational values of 95% Faradaic efficiency and 0.60 V overpotential, at which EE is 62.2%. With a hypothetical electricity cost of \$50/MWh this yields an energy cost of \$432 per mt-NH_3 produced.

Economics of ENR at a fixed price of electrical power. We estimate projections of capital and operation costs for an ENR system based on the same values as used for electrochemical H_2 production, using the same costs per unit of current, and assuming a fixed-proportion relation between cost structure and electric current. Thus, an ammonia plant would produce 5.63 g NH_3 as compared with 1.0 g H_2 per unit current from a hydrogen plant. The H2A Project[66] capacity of 50 mt-H_2/day thus implies 282 mt-NH_3/day produced with comparable investments and costs. Additionally, an air separation unit would be required for the ENR plant. Based on data from Andersson,[55] we estimate the cost of the ASU unit for such a plant to be \$4.6 M, which we add to the total capital cost of \$67.4 M for the corresponding PEM electrolyzer system with hydrogen capacity of 50 mt-H_2/day, for a total of \$72.0 M. O&M expenses, as given above for the E/H-B system, are \$4.2 M/year. This baseline scenario gives a cost of \$508/mt-NH_3, assuming the same parameters as applied to the cost estimates for ammonia production via H-B and E/H-B, including electricity priced at \$50/MWh (Table 3).

Table 3. Estimated costs of ammonia production (\$/mt-NH_3) via ENR, at 62.2% EE and a fixed benchmark electric power cost of \$50/MWh

	Cost (\$/mt-NH_3)
Electricity to reduce N_2 (62% EE)	\$432
Capital	\$35
O&M	\$41
Total	**\$508**

Effects of fluctuations in electricity prices. Wholesale electricity prices depend on numerous factors, and can fluctuate significantly within a day, over a week, and across seasons. We next investigate the economic viability of a simulated ENR ammonia plant while allowing production of NH_3 to vary depending on fluctuation in electricity prices, using pricing obtained from the Electric Reliability Council of Texas (ERCOT) in the U.S.[73] ERCOT manages the flow of electricity in most of Texas, performs financial settlement for the competitive wholesale bulk-power market, and administers retail switching. Quarter-hourly wholesale ERCOT real-time market price data for the period January – December 2019 were used. Variability in pricing is significant. For example, for the ERCOT West Hub, the average price was $34.60/MWh ($0.0346/kWh) while the price at the 99-percentile level was $297/MWh and at the 1-percentile level was negative, at -$2.81/MWh.

For purposes of this analysis we assume that the difference between industrial and wholesale ERCOT prices is fixed and therefore equal to the difference between the average annual industrial price and the average wholesale price. We use the U.S. EIA annual industrial electricity price data for Texas[74] together with ERCOT wholesale prices[73] (i.e., $p_{wholesale}^{ERCOT}$), to calculate this difference.

$$\Delta = annual\ p_{Industrial} - annual\ p_{wholesale} \tag{9}$$

We assume that the price obtained by the ENR ammonia plant would be less than or equal to the standard industrial price, $p_{Industrial}^{Calculated}$ (eq 10).

$$p_{Industrial}^{Calculated} = \Delta + p_{wholesale}^{ERCOT} \tag{10}$$

The average industrial electricity price paid in Texas in 2019 was $56.2/MWh[74] while the average wholesale electricity price the same year, for all hubs/loading zones in the ERCOT system, was $35.8/MWh[73]. Thus, the average value of Δ is approximately $20/MWh. We will consider this value, but we will also consider the likelihood that an ammonia plant, due to large scale, and especially by choosing a favorable location, might obtain a significantly more favorable price for delivery of electric power.

Based on quarter-hourly rates and Δ we calculate the annual cost of ammonia production by an ENR plant, assuming that production is discontinued when electricity costs rise above various values ("cut-offs"). These values correspond to various pricing percentiles; selected percentiles are shown in Table 4. The total cost per mt-NH_3, including electricity, capital, and O&M, is calculated according to eq 11.

$$\text{total cost/mt-NH}_3 = 5.37\ \text{MWh}(PE_{cut} + \Delta)/EE + FC/OT \tag{11}$$

- PE_{cut}: average price paid for electrical energy (per MWh) for operation times (i.e. when price per MWh is below the given cut-off)
- FC: Fixed annual costs (capital cost plus O&M) divided by full capacity in mt-NH_3/year
- OT: Operating time as fraction of full time (equal to percentile value corresponding to price cut-off)

Lower price cut-offs will of course correspond to lower electricity costs per unit ammonia production, but fixed costs (capital and operating) will then be greater calculated on a per-ton basis. Here we consider the lowest possible total cost per ton at which ammonia can be produced (including capital and O&M costs), at various assumed levels of EE, Δ, and fixed costs. This would allow a potential investor to determine if a plant could be profitable in the scenario of a given distribution of electrical pricing and a given ammonia price. Once the plant is operational, however, under this very simple model scenario, it would in principle produce ammonia whenever the cost of electricity (the marginal production cost) is less than the price for which the ammonia could be sold, allowing it to maximize profit.

Table 4. Total cost (USD, energy plus fixed costs) per mt-NH_3 produced via ENR as a function of EE, electricity cost, capital and operating expenses, with varying electricity pricing cut-offs for operation using 2019 ERCOT real-time market prices (ERCOT West Hub).

			1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
		Energy Efficiency	**100%**	**100%**	**62%**	**62%**	**62%**	**39%**	**29%**	**62%**	**62%**
		Δ ($/MWh)[a]	10	20	10	15	20	20	20	20	20
	Fixed costs[b] ($/mT) (24/7)		**75.7**	**75.7**	**75.7**	**75.7**	**75.7**	**75.7**	**75.7**	**151.4**	**37.9**
energy cost cut-off ($/MWh)[c]	**% time operating[d]**	**average energy cost ($/MWh)[e]**									
	100	34.60	315	369	461	504	547	829	1080	623	509
71.3	97	19.17	235	288	330	373	416	619	799	494	377
43.2	94	18.07	231	285	323	366	409	606	781	490	369
33.6	90	17.21	230	284	319	362	405	598	769	490	363
28.9	85	16.41	231	285	317	360	403	591	759	493	359
26.2	80	15.70	233	286	317	360	403	587	751	498	356
22.5	70	14.49	240	293	320	363	406	584	743	514	352
20.2	60	13.33	251	305	328	371	414	586	739	540	351
18.8	50	12.16	270	324	343	386	429	595	743	581	353
7.0	10	0.89	815	869	851	894	937	1045	1141	1694	559
-2.8	1	-7.90	7581	7635	7588	7631	7675	7737	7793	15245	3890
	per ton cost energy only (24/7)[f]		186	186	299	299	299	477	636	299	299
	per ton cost energy + Δ (24/7)[g]		239	293	385	428	472	753	1004	472	472
	per ton fixed costs (24/7)[h]		76	76	76	76	76	76	76	151	38
	per ton total costs (24/7)		315	369	461	504	547	829	1080	623	509

a) Δ: difference between wholesale electricity price and price paid
b) Fixed costs (capital and operating expenses) per mt assuming full-time operation at capacity
c) Greatest wholesale electricity price at percent operating time indicated (i.e. pricing at percentile indicated)
d) Percent time operating, assuming full operation at indicated pricing level or lower
e) Average cost of energy during time operating
f) Energy cost (not including Δ) per mt assuming full-time operation at capacity
g) Energy cost (including Δ) per mt assuming full-time operation at capacity

Assuming the various levels of energy efficiency given in Table 4, and various values of Δ, we calculate the annual per-ton cost of ammonia production at various electricity price cut-offs, each corresponding to a certain percentage (OT) of continuous operation. Because the share of energy consumed which is renewably produced (primarily by wind) is by far the greatest in the West Hub region within the ERCOT system, and because of the relevance of this study to renewably produced energy, we will focus on ammonia cost obtained using pricing from the ERCOT West Hub (Table 4). The minimum per-mt-NH_3 production cost for each set of conditions is highlighted, and the minima for the aspirational 62.2% energy efficiency are shown in red.

Considering first the purely theoretical case of a 100% energy-efficient process, and Δ = $20/MWh, the production cost of ammonia in this scenario is $369/mt-$NH_3$ (Table 4, column 2) if the plant operates without interruption throughout the year ("24/7"). By discontinuing operation when prices are above \$71.3/MWh (corresponding to 97% operation) a lower production cost of \$288/mt-NH_3 can be achieved, with a slightly lower minimum (\$284/mt-NH_3) achieved by operating about 90% of the time.[75] If it is assumed that Δ = \$10/MWh (column 1) instead of \$20/MWh, the cost will be less by \$53.7/mt-NH_3 at 100% efficiency. (We note again that these costs include per-tonne capital and O&M expenses.)

Assuming a feasible energy efficiency of 62.2% (corresponding to the aspirational values of 0.6 V overpotential and 95% FE) the cost of 24/7 production is \$461/mt, \$504/mt and \$547/mt at Δ values of \$10/MWh, \$15/MWh and \$20/MWh respectively (columns 3-5). A greater savings is now achieved by taking advantage of dynamic electricity pricing since more energy is required to produce a given quantity of ammonia [(5.37/0.622)MWh/mt-NH_3]. Operating only 80% of the time, production costs that are 26-31% lower can be achieved.

Even in less favorable scenarios the cost of ammonia production via ENR is not exorbitantly high. With an energy efficiency of only 39% (corresponding, for example, to an overpotential of 1.2 V and FE = 80%) and Δ = \$20/MWh, ammonia production can be achieved at a cost of \$584/mt with an operating-time percentage of 70% (column 6). (Note that at these lower FEs a substantial quantity of H_2 is produced, which could have significant value, discussed below, partially offsetting the increased cost due to the "wasted" electrical current.) We also considered the possibility that the fixed cost (capital and operating costs) would be much higher than our estimates. Increasing this total by a factor of two, with an EE of 62% and Δ = \$20/MWh, allows ammonia production at a total cost of \$490/mt, operating at 90% capacity (column 8). Conversely, lower fixed costs would allow the plant to take greater advantage of dynamic power pricing; decreasing fixed costs by a factor of two permits ammonia production at \$351/mt, operating at 60% capacity. It should be noted, however, that a greater quantity could be produced at an only slightly higher average cost (e.g. operating at 90% of capacity, the total average cost is \$363/mt-NH_3; Column 9); the actual optimum electricity price cut-off on any given day would presumably be dictated by ammonia prices.

The values in Table 4, as noted above, were obtained using electricity prices from the ERCOT West Hub which is the region most proportionately supplied by renewable energy sources. Variations between hubs, however, do not dramatically affect costs. When the same analysis was conducted using average prices from all ERCOT hubs, at 62% EE and Δ = \$20/MWh, for example, the minimum total per-tonne ammonia cost is \$418/mt-NH_3,[67] achieved at ca. 85% capacity, only 3.7% higher than the minimum price (\$403/mt) obtained with West Hub pricing.

Although the focus of this paper is on comparing the cost of ammonia production via H-B, E/H-B, and ENR, we note that the cost estimates projected in this study are well within the range of recent historical retail ammonia prices. For example, retail prices averaged \$540/mt-NH_3 in the US in 2019, the period used for electrical pricing (and \$493/mt-NH_3 for 2018).[76] Wholesale prices, at the Gulf of Mexico, tend to be lower by about \$250/mt-NH_3,[76] but given the opportunities in decentralization offered by ENR, the local retail prices in agricultural areas may offer a better point of comparison.

Comparison of ENR and E/H-B economics. We assume that reduction of H^+ to give H_2 in the E/H-B process will be more energy efficient than N_2 reduction to give ammonia in ENR. Nevertheless, because of the capital and energy expenses associated with the H-B component, even at the greatest economy of scale, ammonia production via E/H-B is projected to be more costly than ENR at the aspirational EE of 62%. This can be seen, for a fixed energy cost of \$50/MWh, in the data in Tables 2 and 3. Note that the total electrical power required for E/H-B (electrolysis and H-B plant operation) is approximately equal to that required for nitrogen reduction via ENR; therefore any change in electricity prices will affect production costs of E/H-B and ENR comparably in this scenario.

Like ENR, E/H-B would allow exploitation of dynamic pricing of electrical energy, but to a lesser extent. Table 5 shows estimated costs of ammonia production via E/H-B, with operation of the electrolyzer discontinued at various electricity costs using the same the approach as taken above for ENR (Table 4). The cost is calculated according to eq 12.[77] (PE_{avg} is the average price paid for electrical energy (per MWh) for 24/7 operation for the H-B plant.)

$$\text{total cost/mt-NH}_3 = (39.7\ \text{MWh})(PE_{cut} + \Delta)/(EE*5.632) + FC/OT + 1.33\ \text{MWh}(PE_{avg} + \Delta) \quad (12)$$

Selected results are shown in Table 5.[75] (Results from Table 4 for ENR at 62% energy efficiency are shown in columns 1-3 of Table 5 for comparison.) Columns 4-6 show results assuming operation at a large scale (an accompanying H-B plant with ca. 2000 mt-NH_3/day capacity) and values in columns 7-9 are obtained assuming a "medium" scale H-B reactor (545 mt-NH_3 day), which is more commensurate with the size of the electrolysis unit used to calculate these value (50 mt-H_2/day corresponding to 282 mt-NH_3/day).

Table 5. Total cost (USD, energy plus fixed costs) per mt-NH_3 produced as a function of EE, electricity cost, capital and operating expenses, with varying electricity pricing cut-offs for operation using 2019 ERCOT real-time market prices (ERCOT West Hub), shown for ENR (62% EE), and for E/H-B (80% EE) from systems that include accompanying large- or medium-scale H-B plants.

			ENR			**E/H-B** (large H-B plant)[h]			**E/H-B** (medium H-B plant)[i]		
			1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
		Energy Efficiency	**62%**	**62%**	**62%**	**80%**	**80%**	**80%**	**80%**	**80%**	**80%**
		Δ ($/MWh)[a]	10	15	20	10	15	20	10	15	20
		Fixed costs[b] ($/mT) (24/7)	**76**	**76**	**76**	**121**	**121**	**121**	**161**	**161**	**161**
energy cost cut-off ($/MWh)[c]	**% time operating[d]**	**average energy cost ($/MWh)[e]**									
			ENR			**E/H-B**			**E/H-B**		
	100	**34.60**	461	504	547	573	624	675	613	664	715
71.3	97	19.17	330	373	416	441	492	543	482	533	584
43.2	94	18.07	323	366	409	435	486	537	**478**	**529**	**579**
33.6	90	17.21	319	362	405	**434**	**484**	**535**	478	529	579
28.9	85	16.41	317	360	403	434	485	536	481	532	583
26.2	80	15.70	**317**	**360**	**403**	437	488	538	487	538	588
22.5	70	14.49	320	363	406	448	499	549	505	556	607
20.2	60	13.33	328	371	414	467	517	568	533	584	635
18.8	50	12.16	343	386	429	497	547	598	577	627	678
7.0	10	0.89	851	894	937	1365	1416	1467	1765	1816	1867
-2.8	1	-7.90	7588	7631	7675	12178	12229	12279	16178	16229	16279
		per ton cost energy only (24/7)[f]	299	299	299	351	351	351	351	351	351
		per ton cost energy + Δ (24/7)[g]	385	428	472	452	503	554	452	503	554
		per ton fixed costs (24/7)[h]	76	76	76	121	121	121	161	161	161
		per ton total costs (24/7)	461	504	547	573	624	675	613	664	715

a) Δ = difference between wholesale electricity price and price paid
b) Fixed costs (capital and operating expenses) per ton assuming full-time operation at capacity
c) Greatest wholesale electricity price at percent operating time indicated (i.e. pricing at percentile indicated)
d) Percent time operating, assuming full operation at indicated pricing level or lower
e) Average cost of energy during time operating
f) Energy cost (not including Δ) per mt, full-time operation at capacity (including energy to run H-B plant for E/H-B)
g) Energy cost (including Δ) per mt, full-time operation at capacity (including energy to run H-B plant for E/H-B)
h) Associated H-B plant with capacity of ca. 2000 mt-NH_3/day (see Table 2)
i) Associated H-B plant with capacity of 545 mt-NH_3/day (see Table 2)

These calculations show that E/H-B is not only intrinsically more costly than an efficient ENR process, but also does not benefit as greatly as ENR from pricing fluctuations because of higher (fixed) capital costs and, to a lesser extent, because H-B (electrically powered in this case) must run continuously, regardless of electricity prices. Moreover, we note that this conclusion is reached in spite of two simplifying assumptions we have made that favor the projected economics of E/H-B: (i) a 100% yield of NH_3 from the synthesis process and (ii) the assumption that the smaller H-B plants operate with the same energy efficiency as the largest plants.

Additionally, because of the requirement that H-B must run continuously, E/H-B would require associated hydrogen storage capacity to provide hydrogen when none is being produced. We can calculate the storage capacity required for any given energy cost cut-off and its corresponding percent electrolyzer operating time (OT), for a given set of electricity pricing data, by assuming that H_2 is produced during operating time in excess of the average need by a factor of 1/OT, to contribute to a reserve which is depleted during periods when the electrolyzer is not operating. Using the same data set as was used for Table 5, the storage capacity (SC) required to allow for continuous H-B ammonia production under these conditions was calculated[67] for the following selected values of electrolyzer operating time (OT, SC expressed as a percent of annual output): 80%, 3.05%; 90%, 1.56%; 94%, 1.32%; 97%, 1.02%; 99%, 0.49%.

Based on the mid-range capital cost of large-scale hydrogen storage estimated by Schoenung[78], (\$15/kWh or \$495/kg[78]), the cost of SC required to hold 1% of annual production, for example, would be \$320,800 per mt-NH_3/day production capacity (177.6 kg-H_2/day or 64,800 kg-H_2/year production capacity). Using costs of capital discussed above this corresponds to an annualized cost of \$16,040 or \$43.9/mt-NH_3 produced for a 1% annual-production storage capacity. At the 90% level of OT, which requires SC of 1.56% of annual production, this corresponds to \$68.5/mt-NH_3 produced, while at 97% OT (1.02% SC) the corresponding cost is \$44.8/mt-NH_3. Thus the need for hydrogen storage capacity in an E/H-B system obviously disfavors lower OT and therefore reduces the ability to take advantage of volatility in electricity pricing. For example, using Schoenung's estimated values[78], a 97% OT would be preferred for all E/H-B scenarios considered in Table 5. However, estimates of SC cost vary very widely;[79] for example Schoenung estimates the cost of underground storage of hydrogen as only \$0.3/kWh.[78] We therefore do not include SC in Table 5, but we note that H_2 storage costs could potentially make a significant additional contribution to the cost of ammonia produced via E/H-B, and the opportunity cost would increase with increasing volatility of electricity pricing.

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Lastly, we note that the presumed higher efficiency of the electrolysis of water compared with reduction of N_2 is in part due to the presumed lower Faradaic efficiency (FE) of ENR. However, as the primary competitive process for ENR is the reduction of H^+ to H_2, an FE less than unity does not actually represent "lost" energy. Since the value of H_2 is very dependent on the circumstances and location where it is produced, it is beyond the scope of this study to estimate the economic value of the H_2. But even in the absence of a suitable market, one could envision several internal uses of H_2 byproduct including (1) generating electricity that could be "recycled" to further increase the yield of NH_3, (2) mixing the H_2 into the feed at the anode of the ENR cell, thereby lowering the oxidation potential, or (3) as a scavenger for O_2, for use in the air separation process required to generate O_2-free N_2 for the electrocatalytic reaction.

COMPARISON OF ECONOMICS OF ENR WITH FOSSIL-FUEL-BASED H-B

Under current market conditions, the private cost of ammonia production from fossil-fuel based H-B is substantially less than from even an ENR system of aspirational efficiency. The low cost to the producer notwithstanding, fossil-fuel based H-B has major implications for global greenhouse gas (GHG) emissions.[80] Production based on natural gas feedstock results in at least 1.33 mt-CO_2 produced per mt-NH_3.[9, 11, 13, 81] Including the cost of this externality yields a significant increase in the *total* (social and private) cost of ammonia produced via a natural-gas-based H-B process relative to production via ENR based on carbon-free electricity. The magnitude of this effect of course depends on the social cost of carbon, estimates of which vary greatly. A detailed survey by Pindyck yields a mean value of \$174/mt-CO_2 based on responses from economists, and \$316/mt-CO_2 based on responses from climate scientists (corresponding to \$231/mt-NH_3 and \$421/mt-NH_3, respectively) with an overall value of \$291/mt-CO_2 (\$387/mt-NH_3) based on responses from all experts surveyed.[82] Ricke *et al.* in a recent extensive study determined the median estimated social cost to be \$417/mt-CO_2 (\$555/mt-NH_3), with \$177-\$805 (\$235-\$1070/mt-NH_3) representing 66% confidence intervals.[83] Additionally, methane emissions associated with natural gas use (primarily from natural gas extraction) may be considered to have an additional social cost approximately equal to 10% that of the CO_2 emissions.[84]

ENR would therefore become increasingly cost competitive with H-B as the externalities of CO_2 emissions are incorporated (directly or indirectly) into the cost of ammonia produced from natural gas. This may occur in the form of a carbon tax or a cap-and-trade system, or renewably produced ammonia could be favored by subsidies or other measures commensurate with the value of avoided CO_2 emissions. More extreme measures are also possible such as legislation requiring a carbon-free economy; for example, the state of New York recently passed a resolution to achieve this goal by 2050.[85]

Projected decreases in the cost of renewable energy[86-88] will also favor ENR. Levelized costs of electricity from both onshore wind and solar photovoltaic are projected to be ca. \$50/MWh for sources scheduled to go online in 2023,[89] with large scale solar photovoltaic power costing as little as \$20/MWh.[90] Conversely, natural gas prices are unlikely to remain at the current historically low levels of ca. \$3/MBTU. In the AEO2019 reference case of the U.S. EIA, natural gas is projected to rise to \$5 per MBTU by 2050 with scenarios at two extremes giving respective prices of slightly over \$3 and slightly over \$8 per MBTU (all prices in 2018 dollars).[86]

In sum, even if only the low end of the estimated ranges of social costs of CO_2 emissions is incorporated into the cost of fossil-fuel-based H-B, then renewable-power-based ENR at ca. 60% energy efficiency would already be competitive. Alternatively or in parallel, limitations on GHG-emissions could favor ENR over H-B. The economic advantage of ENR will increase as renewable energy costs decrease,[86-88] and natural gas prices increase.[86] Moreover, as the market penetration of renewables continues to grow,[88-89, 91-93] its value to the electric grid decreases[94] due to issues of intermittency; therefore, consumers of electricity with flexible demand will have increasing opportunities to purchase power at a price below the 24/7 average. As noted above, the cost Faradaic inefficiency in a ENR process can be partly offset by the value of the hydrogen byproduct.

Although there is too much uncertainty (particularly in the social cost of carbon) to allow an accurate comparison of the economics of H-B with ENR or E/H-B, a crude estimate may be useful. For this purpose we employ values projected for 2040 (in present dollars) for the total-system levelized cost of electricity (including transmission) from onshore wind (\$40.2/MWh),[95] the mid-range 2040 projected price of natural gas (\$4.1/MBTU),[86] and Pindyck's mean value for the social cost of carbon (\$291/mt-CO_2 corresponding to \$387/mt-NH_3). For the purposes of this crude comparison we neglect the ability to exploit dynamic pricing in the case of ENR or E/H-B. The results (Table 6) highlight that the economic competitiveness of ammonia production via ENR relative to H-B is very strongly dependent on whether (and to what extent) the social cost of carbon emissions is incorporated into the cost of production via H-B.

Table 6. Estimated costs, projected for 2040, of ammonia production (\$/mt-NH_3) via gas-based H-B (full-scale plant), ENR, and E/H-B with accompanying H-B plants of varying capacity. Projected prices for electricity and natural gas are \$40.2/MWh[95] (fixed) and \$4.1/MBTU[86] respectively. Social cost of carbon emissions (SCC) is the mean value reported in reference [82].

	H-B Large H-B plant (2000 mt/day)		**ENR**	**E/H-B**	
	not including SCC	**including SCC**		**Large H-B plant (2000 mt/day)[a]**	**Small H-B plant (91 mt/day)[a]**
Electricity to produce H_2 or NH_3[b]	0	0	\$347	\$354	\$354
Capital cost (electrochemical stacks)	0	0	\$35	\$33	\$33
O&M expenses (electrolysis unit only)	0	0	\$41	\$41	\$41
Electricity to run accompanying H-B plant	0	0	0	\$42	\$42
Capital cost for H-B plant	\$55	\$55	0	\$32	\$66
O&M expenses for H-B plant	\$22	\$22	0	\$13	\$77
Natural gas	\$124	\$124	0	0	0
Social cost of carbon emissions	-	\$387	0	0	0
Total	**\$201**	**\$588**	**\$423**[c]	**\$515**[c]	**\$613**[c]

a) Cost for H-B plant for E/H-B assumed to equal 58% of costs of full gas-based H-B plant (large or small).
b) 62% EE and 80% EE assumed for ENR and E/H-B respectively.
c) Costs would presumably be lowered somewhat by taking advantage of dynamic electricity pricing.

CONCLUDING REMARKS

In this paper, we break down the ENR cost structure to allow comparison with conventional H-B and with E/H-B alternatives. Unsurprisingly, the cost of electricity is predicted to be the major determinant of the cost of ammonia production via ENR. Substantial decreases of the levelized cost of ammonia production may be obtained by operating the ENR plant only when the price of electric power is low. We quantify the influences of various cutoff prices, and of various levels of electrical efficiency and fixed (capital and operating) costs.

An ENR process operating at our aspirational levels of FE and overpotential is intrinsically more economical than the electrolysis of water followed by the Haber-Bosch process (E-H/B), which is also carbon-free. This is because ENR does not require the energy consumption and high capital costs of the H-B component of E/H-B. Thus, even at our benchmarked 62% level of energy efficiency, the ENR process would be significantly more economical than E/H-B with electrolysis of water at 80% energy efficiency. Moreover, the less capital-intensive cost structure of ENR can better take advantage of volatility in electrical pricing. Likewise, ENR provides more opportunity to discontinue and resume production according to fluctuations in ammonia pricing or demand. As the cost of carbon-free electricity continues to decline, ENR becomes relatively even more economically attractive. In addition, removing the need for a H-B plant also allows decentralization which provides benefits for farming, particularly in geographical areas that are less connected to infrastructure.

Nitrogen fixation is critical to the agricultural production necessary to feed humanity and is potentially of tremendous value for the storage, transportation, and consumption of renewable energy. But while conventional natural-gas-based H-B production provides a low cost to the producer, its combined social and private cost is high if even conservative estimates of the social costs of GHG emission are included. In addition, the reliance of conventional H-B on fossil fuels leads to vulnerability to volatile global market prices and a complex intersection with the geopolitical landscape.[96]

At the current time, E/H-B is the only technology that is efficient enough to feasibly replace H-B on the scale necessary for fertilizer production. The results of this study indicate, however, that the development of a feasibly efficient ENR process is a more attractive ultimate solution. Though the current state of ENR technology is still far from economically feasible for this scale, the fundamental considerations illuminated in this work indicate that development of an efficient ENR technology has enormous potential for reward.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.XXXXXX.

> Detailed explanation of pricing data presented in Tables 1 and 2. Fuller data set (higher resolution) corresponding to data in Tables 4 and 5 (2019 ERCOT West Hub pricing), and corresponding data set based on average of electricity prices for all ERCOT hubs. Excel worksheet used to calculate required hydrogen storage capacity for various electrolyzer percent operating times.

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Notes

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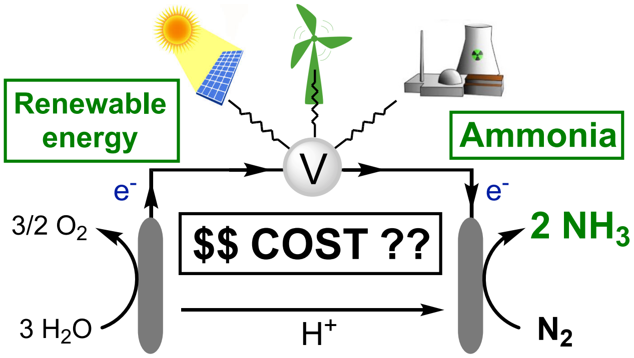

Synopsis. The economics of electrochemical nitrogen reduction are compared with Haber-Bosch-based ammonia production and found to be potentially advantageous at feasible levels of energy efficiency.