ACS Energy LETTERS

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Ammonia and Nitric Acid Demands for Fertilizer Use in 2050

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Cite This: *ACS Energy Lett.* 2021, 6, 3676–3685

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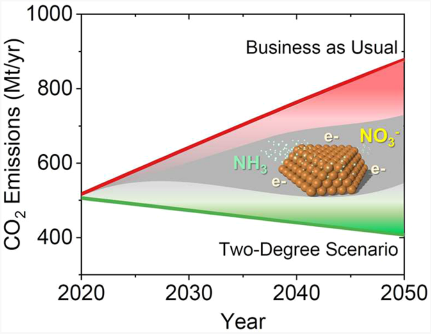
ABSTRACT: **Access to nitrogen-based fertilizers is critical to maximize agricultural yield, as nitrogen is the most common rate-limiting nutrient. Nearly all nitrogen-based fertilizers rely on ammonia and nitric acid as feedstocks, and thus the demand for these chemicals is heavily dependent on the global population and food demand. Over the next three decades, the global population will continue to dictate the market size and value for ammonia and nitric acid, which consequently will have a significant impact on our energy infrastructure. Here, we discuss the potential for carbon-free electrocatalytic nitrogen reduction, nitrogen oxidation, and nitrate reduction to meet fertilizer manufacturing demands. We also explore various growth scenarios to predict the 2050 market size and value for ammonia and nitric acid. We highlight that if the current approaches for manufacturing ammonia and nitric acid remain constant, carbon emissions from the production of fixed fertilizer feedstocks could exceed 1300 $Mt_{CO_{2eq}}$/yr, prompting a strong need for green alternatives.**



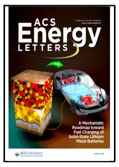
There are many types of fertilizers comprised primarily of phosphorus, potassium, and nitrogen macronutrients. However, since fixed nitrogen is most often the rate-limiting macronutrient for plant growth, the production of nitrogen-based fertilizers (ammonia, nitrate, and urea) has always been a critical global challenge. Over the next three decades, to curb global hunger, nitrogen-based fertilizer usage will only continue to rise.[1,2] This will have a substantial impact on energy and the environment as nearly all nitrogen-based fertilizers are produced using two feedstocks that have high energy and carbon footprints (ammonia and nitric acid).[3]

Ammonia is one of the largest volume chemicals produced globally, with a market size of 175 million tons and a market value of US$67 billion (~5% of chemical market value).[4,5] Fertilizer production accounts for 80% of the ammonia used by volume, and 40% of the market size in terms of revenue (Figure 1).[6] On a smaller scale, ammonia is a feedstock for explosives, pharmaceuticals, refrigerants, and textiles.[6] The production of ammonia is accomplished through the Haber–Bosch process which consumes 39 GJ of energy per ton of fixed nitrogen, and accounts for a 5.5 EJ of global energy use per year (~11% of the energy consumed in the chemical industry).[7−9]

The global market of nitric acid (HNO_3), while lower than ammonia, is also expanding largely due to the growth in synthetic fertilizers. The global market size is ~70 million tons and the market value is US$24 billion (~3% of chemical market value).[10−12] Ammonium nitrate constitutes the largest portion of the global nitrate market (80%). The production of nitric acid is accomplished through the Ostwald process, which consumes 66.6 GJ per ton of fixed nitrogen (~1.7 times the energy to produce ammonia), and 0.6 EJ of global energy use per year (~1% of the energy consumed in the chemical industry).[13]

Thus, new technological solutions for manufacturing ammonia and nitric acid, which do not rely on fossil-based fuels, are necessary. Here, we discuss the opportunities electrocatalytic nitrogen reduction, nitrogen oxidation, and nitrate reduction may aid in meeting the goal of an electrified nitrogen economy. We also explore various growth scenarios for ammonia and nitric acid and discuss the projected 2050 market size, value, and impact on the energy sector.

Received: August 2, 2021
Published: September 24, 2021



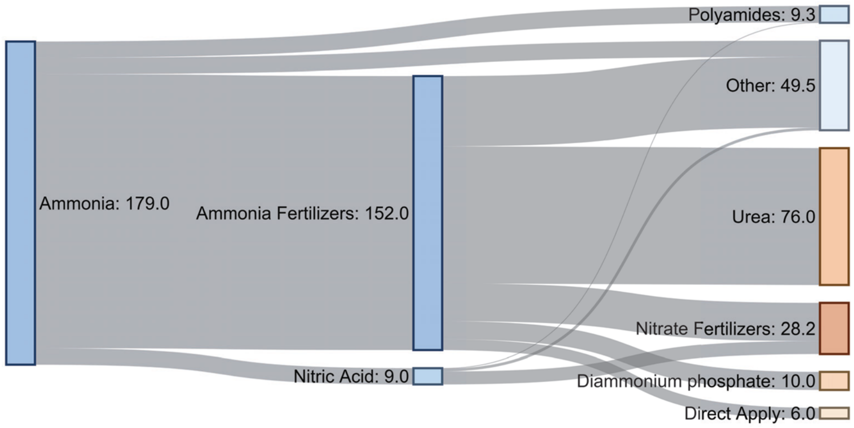


Figure 1. Mass flow of ammonia and nitric acid for the manufacture of fertilizers and other products. Values listed are million metric tons per year.

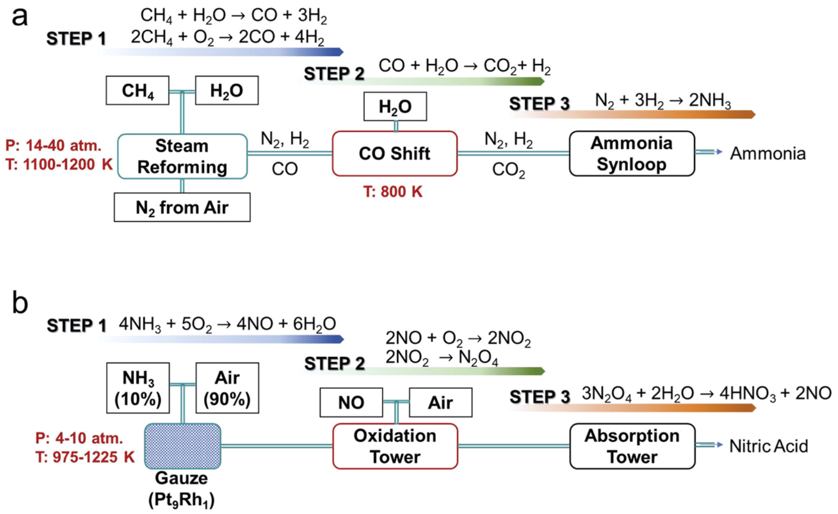


Figure 2. Production of nitrogen fertilizer feedstocks occurs through (a) the Haber–Bosch process (ammonia) and (b) the Ostwald process (nitric acid).

■ CURRENT MANUFACTURING OF AMMONIA AND NITRIC ACID

Current thermochemical approaches for ammonia synthesis (Haber–Bosch process) rely on the use of elevated temperature and pressure to drive the chemical reaction (Figure 2a). Reactant (H_2 and N_2) purification occurs in the first stage of the Haber–Bosch process. The production of high-purity hydrogen occurs by reacting steam and methane in the primary stage of a steam reformer at high temperature (1120–1170 K) and pressure (25–35 atm) with a nickel-based catalyst. The production of high-purity nitrogen occurs in the second stage of the steam reformer. The oxygen in the air reacts with methane through a combustion reaction, resulting in the formation of hydrogen, carbon monoxide, and unreacted nitrogen. Alternatively, cryogenic distillation, pressure-swing adsorption, or membrane separation can provide high-purity nitrogen. At a large scale, commercial nitrogen production occurs through fractional distillation of liquefied air, which is the most efficient method.[14,15] Steam reforming accounts for 75% of the energy used within the entire Haber–Bosch process. The cryogenic air separation has a similar energy expenditure as is required for CO_2 removal in the methane-fed Haber–Bosch process.

After steam reforming, the transformation of carbon monoxide to carbon dioxide occurs through the water–gas shift reaction. Removal of carbon dioxide then occurs using the Benfield or Selexol process, resulting in a pure mixture of hydrogen and nitrogen. Finally, ammonia synthesis occurs by reacting nitrogen and hydrogen at high temperature and pressure (723–823 K and 250–350 atm) on a Fe-based catalyst. The separation of ammonia from the reactants (H_2 and N_2) occurs through compressing and cooling the products. This results in liquefied ammonia, gaseous nitrogen, and gaseous hydrogen. This product distribution allows for easy recovery of the liquid phase ammonia, while the gaseous reactants are recycled.

Current manufacturing practices for nitric acid occur through the Ostwald process (Figure 2b). Here, ammonia vapor (10%) and compressed air (90%) react over a Pt_9Rh_1 (60–80 mesh wire gauze). The ammonia oxidation reaction results in the formation of NO gas and water at high pressure (4–10 atm) and temperature (975–1225 K). Then, the oxidation of the produced gases (10–12% NO) occurs with additional oxygen to produce NO_2 and N_2O_4 in an oxidation and absorption tower. These products then go through a hydration process to produce nitric acid. The noble Pt–Rh alloy enables high conversion (≥96%) when operated with atmospheric oxygen at 1170 K.[2] The Ostwald process requires a significant amount of precious Pt−Rh alloy catalysts, which contribute to the high system cost. Furthermore, higher catalyst loss and deactivation during the process are inevitable. Finally, a full understanding of the ammonia oxidation reaction is still lacking. Thus, the development of non-noble metal catalysts is of growing importance.

■ FUTURE MANUFACTURING OF AMMONIA AND NITRIC ACID

The large carbon and energy footprint associated with ammonia and nitric acid production is because coal, natural gas, and petroleum are the primary energy sources utilized.[2,7] Displacing hydrocarbons directly with renewable derived electricity is one way to mitigate these issues. Yet, in most cases, the conversion of electrical energy into thermal energy (electrification of heat) to maintain current industrial processes is not possible. For instance, it is estimated that to meet thermal needs in industry, the electricity running through our distribution infrastructure would need to approximately double.[16] This would require a significant investment in our transmission and distribution infrastructure. Thus, thermochemical processes powered by electricity alone are unlikely. The only real potential would be in regions with high renewable electricity production and low electricity costs.[17]

> We highlight that current manufacturing processes for ammonia and nitric acid could produce 1300 Mt_{CO_2}/yr by 2050. This prompts a strong need for sustainable synthesis approaches such as electrochemical nitrogen/nitrate reduction for the production of ammonia and electrochemical nitrogen oxidation for the production of nitric acid.

Chemical looping (either driven by waste heat or solar energy) is another alternative approach to decarbonizing ammonia synthesis.[18] This method decouples N_2/H_2 dissociation, bond formation, and NH_3 desorption to separate thermodynamically stable reaction intermediates on oxides, nitrides, and metals.[18] However, this method has slow kinetics, still requires higher temperature, and suffers from catalyst durability issues.[19] Photocatalysis is another process capable of obtaining decarbonized ammonia. This process operates at ambient conditions, but nearly all photocatalysts suffer from low rates of production.[19−22]

Plasma-driven ammonia synthesis also operates under mild conditions and has the added benefit of fast startup and shutdown times. Two major challenges, however, remain high energy cost and low energy efficiency.[23,24] Direct electrochemical conversion systems, which manufacture ammonia and nitric acid from abundant (nitrogen) or waste (nitrate) resources, are also a desirable route to produce decarbonized ammonia. These processes occur at ambient conditions, are continuous, and easily integrate with renewable electricity. Three such reactions to achieve electrified nitrogen fertilizer feedstock production include (1) electrochemical nitrogen reduction to ammonia, (2) electrochemical nitrate reduction to ammonia, and (3) electrochemical nitrogen oxidation to nitric acid. Below we provide a brief perspective on the prospects for each of these electrosynthetic pathways, which are summarized in Figure 3.

Electrochemical Nitrogen Reduction to Ammonia. Electrochemical nitrogen reduction (NRR) is a kinetically challenging reaction,

$$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3 \tag{1}$$

as it requires six proton-coupled electron-transfer processes. While the theoretical potential is only 0.06 V under ambient conditions, most research investigations couple NRR with the oxygen evolution reaction at the anode.[25−28] Therefore, the theoretical whole cell potential is 1.17 V at ambient conditions, which resides close to the theoretical water splitting potential (1.23 V). Directly reducing nitrogen to ammonia is attractive to minimize complexity; however, competition with the hydrogen evolution reaction (HER) is the main bottleneck. This is because most catalysts preferentially adsorb hydrogen rather than nitrogen.[29] As such, typically low temperature NRR

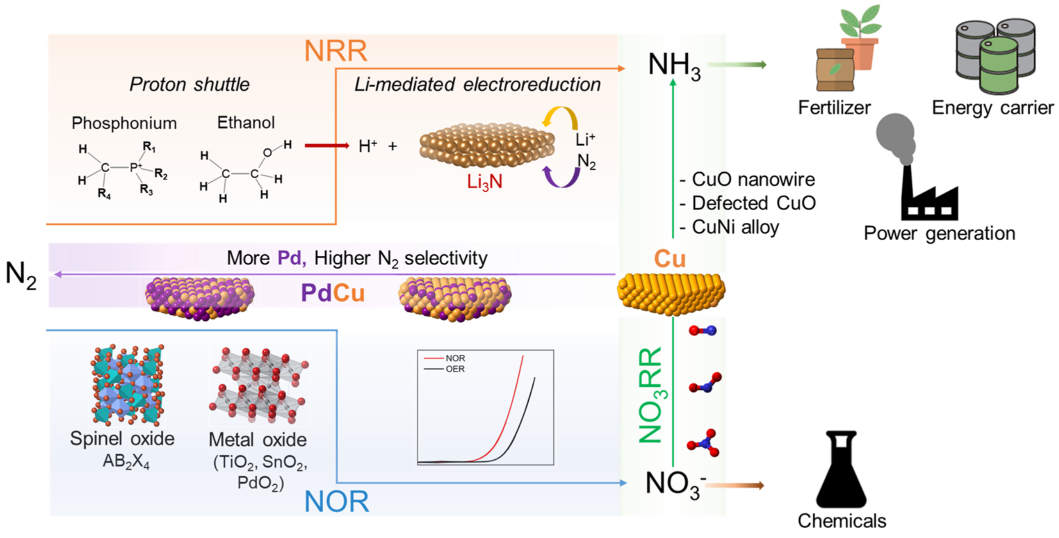


Figure 3. Overview of current status for electrochemical synthesis of ammonia and nitric acid.

Table 1. Summary of Various Lithium-Mediated Routes of NRR with Different Proton Sources in Non-aqueous Electrolytes

catalyst	operating condition	electrolyte	proton source	FE (%)	NH_3 production rate (mol cm^{-2} s^{-1})	ref
Cu electrode	3 mA cm^{-2} ambient N_2	1 M $LiBF_4$ THF	EtOH	18.5	7.9×10^{-9}	45
Ag–Au@ZIF	−2.9 V for 6 h ambient N_2	0.2 M $Li(CF_3SO_3)$ THF	EtOH	18	1.0×10^{-11}	54
Cu	2 mA cm^{-2} 50 bar of N_2	0.2 M $Li(CF_3SO_3)$ THF	EtOH	59.8	4.0×10^{-9}	55
Cu electrode	−22.5 mA cm^{-2} 19.5 bar of N_2	0.2 M $LiBF_4$ phosphonium	0.5 bar H_2	69	53×10^{-9}	50
Au/carbon paper	−4 V ambient N_2	0.2 M $LiClO_4$ THF	EtOH	34	7.7×10^{-10}	46
Ni	1.8 V ambient N_2	0.1 M LiCl EDA	H_2O	17.2	3.6×10^{-11}	56
Li on Mo	−3.1 V ambient N_2	0.2 M $LiClO_4$ THF	EtOH	7.5	2.2×10^{-10}	42
Li on Mo	3.3 mA cm^{-2} ambient N_2	0.5 M $LiClO_4$ THF	EtOH	10	N/A	57

experiments result in low rate of production (10^{-11} mol cm^{-2} s^{-1}), faradaic efficiency (10^{-2}–10%), and energy efficiencies (1–2%).

Strategies for achieving highly active and selective NRR electrocatalysts focus on single atom construction,[30] crystal engineering,[31,32] metal doping,[33,34] vacancy engineering,[35,36] and surface/interface engineering.[26,37] However, the feasibility for large-scale commercialization is not clear as reproducibility remains a critical challenge.[38] This is in part due to documented challenges with contamination.[39−41] In addition, catalyst decomposition can also lead to false positives. This was demonstrated with N-containing catalysts (tetragonal Mo_2N), where chemical decomposition rather than catalysis resulted in an overestimation of NH_3 selectivity.[39] Thus, care is needed in performing these experiments, and validation is necessary using isotope-labeled gases and quantitative NMR spectroscopy.[42]

NRR can also occur through a lithium-mediated reaction in a non-aqueous medium (see Table 1). To date, this approach has achieved the most promising ammonia production rates and yields.[41,43−45] The reduction of Li^+ under a N_2 environment forms lithium nitride. If this lithium nitride is exposed to a proton source, the formation of ammonia is feasible. The lithium nitridation reaction is sensitive to the concentration of Li^+ and nitrogen in a given solvent.[45−47] One challenge is that lithium deposition during the cyclic process can reduce the overall energy efficiency.[45,48] This can also degrade the electrode/electrolyte interface under strong reducing potentials causing performance decline.[41,49] A number of promising proton sources have been investigated to improve the system performance. Currently, phosphonium is emerging as an ideal candidate to enhance system performance. Phosphonium provides a source of protons and additional ionic conductivity that allows for high FE (69 ± 1%) and production rates of (53 ± 1 nmol s^{-1} cm^{-2}).[50] In addition, the potassium ions in the electrolyte stabilize the reaction intermediates and increase the selectivity.[51]

System design is also critical to enable realistic production. Gas diffusion-based electrochemical cells have emerged as an ideal platform to enhance mass transport and production yield.[48,52] However, more work is needed to understand how each system component contributes to the overall system cost. To date, there have only been a few investigations into the technoeconomics of electrochemical nitrogen reduction.[53] Finally, addressing the low energy efficiency, poor stability, and the need to continuously replenish the electrolyte is critical for lithium-mediated approaches to reach commercialization.

Electrochemical Nitrate Reduction to Ammonia. The electrochemical nitrate reduction (NO_3RR),

$$NO_3^- + 9H^+ + 8e^- \rightarrow NH_3 + 3H_2O \qquad (2)$$

is another potential pathway to produce ammonia. The theoretical potential is 0.88 V at standard conditions. The conversion of nitrate to ammonia (eq 2) not only produces a valuable product (ammonia) but also remediates a prominent groundwater contaminant, and therefore is a form of water treatment. Like NRR, the NO_3RR requires multiple proton and electron transfer processes. Unlike NRR, ammonia production from NO_3RR is catalytic easier than NRR because the adsorbed/activated ion reactants (NO_3^-, NO_2^-) have an advantage of a lower dissociation energy for the N—O and N═O bonds (204 and 607 kJ mol^{-1}) than that of N≡N bond (941 kJ mol^{-1}).[58−64] In addition, nitrate adsorbs more easily than nitrogen to surfaces at ambient conditions.

Nitrate can be electrochemically converted into urea,[64] ammonia,[58,60−62,65,66] and nitrogen[67,68] depending on a preferred pathway from nitrate. Indium hydroxide (with single {100} facets) ($In(OH)_3$-S) generated urea with a yield of 533.1 μg h^{-1} $mg_{cat.}^{-1}$, high FE of 53.4%, and nitrogen selectivity of 82.9%.[64] It was shown that CO_2 suppresses HER and boosts urea production, inducing a n-p transform in the semiconductor surface. Copper (Cu) is a promising catalyst to promote ammonia production through a direct eight-electron transfer pathway. Engineering Cu electrocatalysts have shown a variety of results. For example, the incorporation of Cu in a PTCDA achieved a FE of 85.9%, and ammonia production rate of 436 ± 85 μg h^{-1} cm^{-2}.[60] CuO nanowire arrays achieved a FE of 95.8% and ammonia production rate of 0.2449 mmol h^{-1} cm^{-2},[61] and $Cu_{50}Ni_{50}$ achieved a FE of ~95%.[62] Finally, defected CuO achieved a FE of 89% and ammonia production rate of 520 μmol h^{-1} cm^{-2}.[65] The Cu aids in regulating the proton transfer and suppressing hydrogen production. Furthermore, modulation of Cu electronic structure and the oxygen vacancy (defects), aid in improving NO_3^- and relevant intermediate adsorption.

Strained ruthenium nanoclusters exhibited nearly 100% ammonia selectivity and high ammonia production rate (5.56 mol $g_{cat.}^{-1}$ h^{-1}). Performance was attributed to the production of hydrogen radicals which suppressed hydrogen−hydrogen dimerization.[58] For denitrification (nitrate conversion to nitrogen gas), pure metals have yielded low selectivity to nitrogen. Thus, introducing secondary materials consisting of a bimetal system is necessary to achieve high nitrogen selectivity. Pd−Cu bimetal electrocatalysts exhibit high N_2 selectivity (99% by CuPd on Ni foam,[69] 97% by Cu−Pd@N-doped ordered mesoporous carbon,[70] and 85.5% by CuPd/rGO[71]). This is due to Cu capturing and reducing nitrate and Pd promoting nitrite reduction to N_2.

As we discussed above, the electrochemical nitrate reduction is an efficient and attractive method to produce various final products relevant to the fertilizer industry (ammonia, urea, nitrogen).[68] However, when compared to NRR, very few investigations have probed the impact of nanocatalyst engineering and catalytic modification (e.g., single atom catalysts, metal doping, surface and interface engineering). Thus, there is significant room for catalyst engineering. There is also a growing interest in gaining a mechanistic understanding about the nitrate and nitrite reduction reactions on model systems, since there are a number of different pathways to ammonia, urea, and nitrogen. There is also a strong need to evaluate the durability of these systems with long-term cycling, and in complex and real solutions.[72] Furthermore, unifying testing protocols are important to avoid contamination, especially when measuring ammonia.

Electrochemical Nitrogen Oxidation to Nitric Acid. Electrochemical nitrogen oxidation to HNO_3 is theoretically possible through the following reaction,

$$N_2 + 6H_2O \rightarrow 12H^+ + 10e^- + 2NO_3^- \quad (3)$$

but still requires a 10-electron transfer process. The reaction is a more thermodynamically favorable reaction than the parasitic oxygen evolution reaction for a wide potential range at pH above 1.3.[73] Thus, nitrogen can be converted to nitrate that could be the only product of nitrogen oxidation reaction (NOR), theoretically. Despite this, there have been very few reports for NOR electrocatalysts. Discovering highly efficient and selective electrocatalysts will require excellent selectivity (poor water oxidation selectivity), and high stability under high pH conditions. Selectivity can be overcome through designing catalysts which prevent water adsorption and promote OH^- and N_2 adsorption to prevent oxygen evolution reaction (OER).

Electrochemical NOR has been demonstrated to occur on $ZnFe_xCo_{2-x}O_4$ spinel oxides.[74] Here, the highest nitrate production rate 130 ± 12 μmol h^{-1} g_{MO}^{-1} and FE of ~10% at 1.6 V_{RHE}. Tensile-strained palladium (Pd) porous nanosheets showed high nitrate yield (18.56 μg h^{-1} $mg_{cat.}^{-1}$), but still low FE of 2.5%. Electrochemical in situ Raman and FTIR demonstrated that PdO_2 is the active site.[75] Transition metal oxide materials may be able to promote nitrogen oxidation as they have been shown to mitigate the water oxidation reaction. In addition, the synergistic effect of Pt and transition metal oxide hetero-nanostructures can offer a plausible new approach to achieve high activity and selectivity for synthesizing nitric acid.[76] Some potential catalyst candidates include Pt or Pd-based alloy nanoparticles on titanium dioxide or antimony trioxides.[77] However, NOR electrocatalysts are not largely explored yet. Furthermore, the use of inert nonpolar nitrogen gas for the direct NOR under ambient operating conditions and OER in aqueous electrolyte limit the high production of nitric acid. Therefore, with highly active and selective NOR electrocatalysts, testing in non-aqueous media with various additives/mediates should be investigated. Like NRR, contamination and false positives will also be critical to rule out in all experiments. Nitrate-based salts are commonly used in most catalyst syntheses, and therefore care in cleaning the synthesized or purchased catalyst is critical. Adventitious ammonia known to arise in NRR experiments may also promote false production of nitrate, as oxidation of ammonia can form nitrite.

Finally, most protocols used for measuring nitrate use standard spectroscopy (UV/Vis) or chromatography (ion chromatography). Both instruments and protocols are standardized by the EPA for water treatment purposes (wastewater, groundwater, etc.). Therefore, many constituents common in electrochemical media (supporting electrolytes) may interfere with these established nitrate measurement techniques and protocols. Electrochemically generated products (peroxides) may also interfere with common measurements, and the residual NO_X found in gas cylinders may produce false positives. For these reasons, care must be taken to ensure all measurements are accurate. Like electrochemical NRR studies, the use of isotope-labeled gases and quantitative NMR may prevent false positives. Proper control should include (1) argon with applied potential control and (2) no applied potential with feedstock gases (N_2/O_2) supplied.

■ CURRENT AND FUTURE MARKET AND ENERGY DEMANDS FOR AMMONIA AND NITRIC ACID

Since fertilizers dominate both the nitrate and ammonia market, it is not surprising that the main market driver for ammonia and nitric acid is the global population. Thus, here we project the ammonia and nitric acid market using population models and current per capita global nitrogen inputs for food production.[78,79] Due to the uncertainty in population models, we have developed low, moderate, and high market projections. The low projection assumes a fertility rate (number of children per woman), which is 0.5 birth below the total fertility in the medium variant. The moderate projection assumes that the fertility rate (number of children per woman) is 2.42 between 2020 and 2025, and decreases to 2.21 between 2045 and 2050. Finally, the high projection assumes that the population growth rate is high (0.5 birth above the total fertility in the medium variant).[78] The low projection also assumes that per capita nitrogen fertilizer usage remains unchanged (24 kg cap^{-1} yr^{-1}). The moderate projection assumes that the per capita nitrogen fertilizer usage increases to 28 kg cap^{-1} yr^{-1} by 2050. Finally, the high projection assumes that per capita nitrogen fertilizer usage

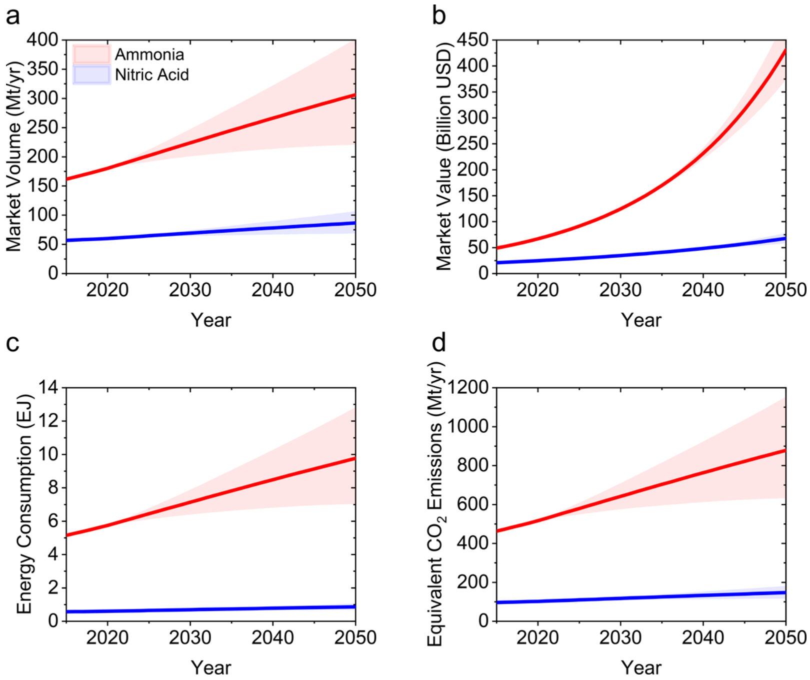


Figure 4. Business as usual projections for the ammonia and nitric acid market size (a), market value (b), energy consumption (c), and equivalent CO_2 emissions (d). The solid line represents the moderate projection for ammonia (red) and nitric acid (blue). The shaded area represents all the possible scenarios bounded by the low projection at the bottom and the high projection at the top.

increases to 32 kg cap^{-1} yr^{-1} by 2050.[79] The low projections represent conditions where there is no change in the global nitrogen fertilizer input to croplands. Nitrogen stress is defined as a country having a per capita nitrogen fertilizer input below 15 kg cap^{-1} yr^{-1}.[79] While the moderate conditions allow for a near elimination of global nitrogen stress, and the high projection allows for the complete elimination of global nitrogen stress.

The most likely scenario is the moderate projection as this scenario is based on median probabilistic fertility. The projections indicate a realistic market size for ammonia in 2050 may be between 220 million and 402 million tons. To put this into perspective, this is equivalent to ∼10% of the current global oil production (Figure 4a). According to our projections, the compound annual growth rate (CAGR) for the production volume of ammonia is 2.1% between 2020 and 2026. Our projections match the market report analysis that predicts a CAGR of 2.03% for the same forecast period.[5] Our predictions show that the CAGR for the market volume in the forecast period between 2021 and 2030 is 2.2%, between 2031 and 2040 is 1.8%, and between 2041 and 2050 is 1.4%.

> Our predictions demonstrate that the 2050 market size and value for ammonia and nitric acid will significantly impact on our energy infrastructure.

The value of the ammonia market is expected to grow with a compound annual growth rate (CAGR) of 6.4% yearly in the next decade.[4] If this growth rate is preserved through 2050, the market value will increase from US$67 billion in 2020 to US $430 billion in 2050 (Figure 4b). However, assuming accelerated market growth, with a CAGR of 6.4% between 2021 and 2030, a CAGR of 6.9% between 2030 and 2040, and a CAGR of 7.4% between 2041 and 2050, a projected market value of US$495 billion is possible in 2050. Similarly, assuming decelerating market growth over the next few decades, with a CAGR of 6.4% between 2020 and 2030, a CAGR of 5.9% between 2030 and 2040, and a CAGR of 5.4% between 2040 and 2050 could result in a projected market value of US$374 billion in 2050. Thus, even with a decelerating market growth, the ammonia market is expected to grow by over US$300 billion over three decades. This market growth promotes opportunities to invest in innovations, which maximize both industrial and environmental considerations. This innovation can occur through companies reinvesting a portion of their profits into R&D or through government and like agencies investing in new startups.

The value of the nitric acid market is expected to grow with CAGR of 3.4% yearly in the next decade.[12] If the growth rate is preserved through 2050, the market value will increase from US$24 billion in 2019 to US$68 billion in 2050. If there is accelerated market growth, with a CAGR of 3.4% between 2020 and 2030, a CAGR of 3.9% between 2030 and 2040, and a CAGR of 4.4% between 2040 and 2050, the projected market value may reach US$78 billion in 2050. Similarly, assuming decelerating market growth over the next few decades, with a CAGR of 3.4% between 2020 and 2030, a CAGR of 2.9% between 2030 and 2040, and a CAGR of 2.4% between 2040 and 2050 could result in a projected market value of US$58 billion in 2050 (Figure 4b). The nitric acid market value and size are substantially smaller than ammonia (Figure 4a,b), and this is in part due to the complexity of the Ostwald process which has higher operational costs (increased energy demand). Despite this fact, there is a growing interest in expanding the use of nitrate-based fertilizers. These are fertilizers where the primary nitrogen compound is nitrate rather than ammonia. Nitrate-based fertilizers have some environmental benefits, namely, less ammonia volatilization and reduced nitrate

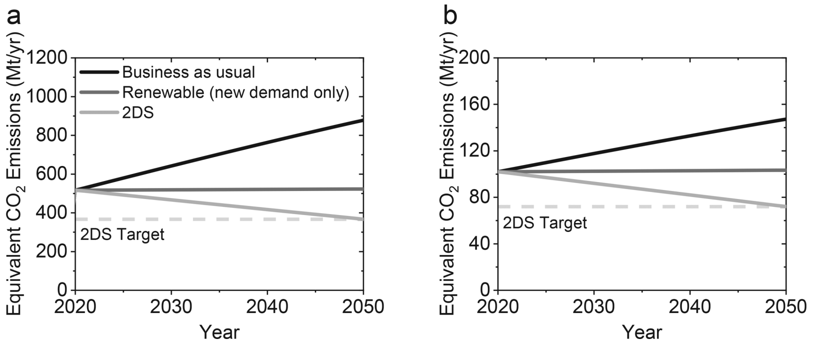


Figure 5. Equivalent CO_2 emissions for ammonia (a) and nitric acid (b). Dashed line in is a two-degree scenario that must be achieved in order to limit a global mean temperature rise to 2 °C.[2]

contamination. However, exploration of new technologies which can produce nitric acid without ammonia as a feedstock may be necessary to decrease the interdependency between the two chemicals.

The current method to produce ammonia at industrial scales is the Haber–Bosch process. This process consumes 5.5 EJ of energy every year (~38 $\mathrm{GJ/t_{NH_3}}$) and emits over 450 million metric tons of carbon dioxide (~2.9 $\mathrm{t_{CO_2}/t_{NH_3}}$).[7,80,81] Using the market trends outlined above, by 2050, the expected global energy consumption for the production of ammonia may approach 10 EJ, and the yearly carbon dioxide emissions may approach 1 billion tons (Figure 4c,d).

The production of nitric acid currently is primarily accomplished through the Ostwald process, and consumes 66.6 GJ per ton of fixed nitrogen, ~10 GJ of energy per ton of nitric acid produced.[13] This equates to a yearly energy demand of 0.6 EJ. Nitric acid production practice also emits 1.7 equivalent tons of carbon dioxide per ton of nitric acid, resulting in yearly carbon dioxide emissions of 60 million tons.[82] Using our market projections by 2050, the expected energy consumption for nitric acid production may increase to ~1 EJ (Figure 4c), and the expected emissions will approach 150 tons of equivalent carbon dioxide (Figure 4d).

■ PATHWAYS TOWARD CARBON-NEUTRAL FERTILIZERS

As shown above, it is unlikely that fertilizer feedstock (ammonia and nitric acid) production will decrease within the next three decades. This is because without fertilizers, the global population can not be sustained. In addition, with the growing interest in using ammonia in non-agriculture sectors (energy) as an alternative fuel or hydrogen storage media, the production of ammonia is likely to increase. Thus, redesigning the catalytic manufacturing processes responsible for producing ammonia and nitric acid is essential to meet the COP21 two-degree scenario (2DS) targets. Specifically, to meet the COP 21 2DS targets, the emissions tied to chemical processes must decrease by 20% from the 2013 levels.[2] The 2050 target for the ammonia-related carbon dioxide emissions is 367 $\mathrm{Mt_{CO_2}/yr}$ (Figure 5a) and the target for nitric acid-related emissions is 72 $\mathrm{Mt_{CO_2}/yr}$ (Figure 5b). If we continue our current reliance on the Haber–Bosch and Ostwald processes for ammonia and nitric acid production, the ammonia-related emissions will reach 900 $\mathrm{Mt_{CO_2}/yr}$ (Figure 5a, Business as usual) and the nitric acid-related emissions will reach 150 $\mathrm{Mt_{CO_2}/yr}$ (Figure 5b, Business as usual). This is 245% over the 2DS target for ammonia and 208% over the 2DS target for nitric acid. Replacing all new demands for ammonia and nitric acid with renewable approaches such as electrochemical synthesis or a green Haber–Bosch process coupled with water electrolysis will not be enough to reach the 2DS target. If we replace all new demands with renewable approaches, which have emissions equivalent to approximately 0.05 $\mathrm{t_{CO_2}/t_{NH_3}}$, ammonia-related emissions are projected to be 523 $\mathrm{Mt_{CO_2}/yr}$ and nitric acid-related emissions are projected to be 103 $\mathrm{Mt_{CO_2}/yr}$.[53] Thus, to meet the 2DS target for ammonia, we have to reduce existing ammonia-related emissions by 5 $\mathrm{Mt_{CO2}/yr}$. This is equivalent to converting 1.7 $\mathrm{Mt_{NH_3}/yr}$ produced through the Haber–Bosch process (0.95% of the current ammonia production capacity) to a renewable driven synthesis process. Similarly, to meet the 2DS target for nitric acid, we have to reduce existing nitric acid-related emissions by 1 $\mathrm{Mt_{CO2}/yr}$. This is equivalent to replacing 0.6 $\mathrm{Mt_{HNO_3}/yr}$ of nitric acid capacity from the Ostwald process to a renewable synthesis process (1% of the current nitric acid production capacity). This means that to meet the 2DS targets, all new demand for ammonia and nitric acid, and 29% of the current ammonia and nitric acid production capacity must be produced with renewable energy.

> Electrochemical synthesis of ammonia and nitric acid could aid the chemical industry in meeting the COP21 two-degree scenario targets to alleviate carbon emissions.

Transitioning the current infrastructure to renewable-driven approaches will be challenging, and solutions that utilize the existing infrastructure will be essential to avoid financial losses. A possible solution is to replace steam–methane reforming (SMR) and coal gasification in the current infrastructure with green hydrogen. This solution would take advantage of existing infrastructure (Haber–Bosch loop, air separation, product purification loop, etc.) to alleviate capital investment. We recommend targeting Haber–Bosch facilities that use coal gasification instead of SMR. These facilities already use cryogenic air separation to purify nitrogen. In contrast, the methane-fed Haber–Bosch process relies on SMR to produce both hydrogen and nitrogen. Therefore, the coal gasification process can be replaced by a water electrolysis facility. However, the SMR process requires the same water electrolysis facility and an additional air separation unit. Additionally, it is essential that all new infrastructure is built, paying close attention to sustainability based best practices. The best renewable approaches to replace the Haber−Bosch and Ostwald processes are unclear. In some scenarios, electrochemical approaches will be more economical, while in other scenarios, coupling Haber−Bosch with green hydrogen might be more affordable. However, for electrochemical ammonia or nitric acid production to become feasible, electricity prices will need to be below \$0.03/kWh.[53] Thus, this may only be viable in areas with high levels of renewable electricity and low electricity prices.

■ CONCLUSIONS

Ammonia and nitric acid have a large impact on both global economic markets and food production. For all growth models, these demands are only going to increase over the next three decades. Thus, to meet the COP21 two-degree scenario targets, game-changing approaches are needed to achieve green catalysis. Long-term electrochemical conversion of nitrogen to ammonia and nitric acid, and nitrate to ammonia may enable widespread production of fertilizer feedstocks with only renewable-based electricity.

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■ ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation under Grant Nos. 1846611 and 1933646.

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