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Perspective

Decarbonizing Nitrogen Fertilizer for Agriculture with Nonthermal Plasma Technology

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Abstract: Synthetic nitrogen fertilizer is the backbone of modern agriculture, helping to feed ~50% of the world's population. However, the current industrial production, distribution, and use of nitrogen fertilizers are built on an unsustainable foundation of fossil resources, and are energy-intensive, environmentally polluting, and inefficient in their usage. With the rapidly declining cost of renewable electricity, such as solar and wind, it is time to develop and implement the decentralized production and application of nitrogen fertilizer with nonthermal plasma technologies. Such locally sourced production at the farm site, using only air and water as feedstock, circumvents the need for the extensive capital investment and infrastructure required for synthetic nitrogen fertilizer production and storage, as well as the complex and costly distribution networks. It will be adaptive to the intermittency of the solar/wind electricity supply, leave no carbon footprint, and also have the advantage of being easily switched on/off, immediately responding to weather changes and local conditions, such as soil, climate, crops, and farming business models, for precision agriculture.

Keywords: decarbonization; nitrogen fertilizer; nonthermal plasma; Haber–Bosch process; nitrogen fixation; continuous process; ammonia; nitrate; sustainability

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1. Background Information

1.1. Current Unsustainable System for Nitrogen Fertilizers

The availability of nitrogen fertilizers (N-fertilizers) is crucial for achieving an optimal agricultural yield, because nitrogen is the most common limiting nutrient for plants. Ammonia and nitric acid are the primary raw materials used to produce almost all nitrogen-based synthetic fertilizers, and their demand is closely tied to global population growth and food demand. However, unless environmentally friendly alternatives are adopted, current methods established on the foundation of the Haber–Bosch process (HB process) for producing ammonia and its derivatives could lead to carbon emissions of over 1300 million tons of CO_2 per year by 2050, and significantly impact the world's energy infrastructure [1].

Industrial nitrogen fixation was first commercialized as the thermal-plasma-based Birkeland–Eyde process to produce nitrogen oxides (NO_x) and nitric acid about a century ago, which was economically outcompeted by the centralized, large-scale HB process, using an ultra-pure nitrogen and hydrogen feed (mainly from natural gas and some coal) at high temperature and pressure (>450 °C, 150–350 atm) to catalytically synthesize ammonia that dominates the production of N-fertilizers today. As the result, although nearly 50% of the nitrogen found in the human body has passed through the HB process [2], the production of ammonia is unsustainable, because making this single chemical consumes approximately 2% of the world's annual energy supply and accounts for 1.4% of the annual global carbon emissions, higher than any another chemical [1,3]; this does not include methane emitted from such facilities, which is thought to be underestimated by as much as 50 times, and the number increases further if CO_2 emissions associated with natural gas extraction are included [4,5].

Unfortunately, the production of almost all synthetic N-fertilizers relies on the HB process. Urea is produced from synthetic ammonia and carbon dioxide, and urea manufacturers are always located adjacent to the site where the ammonia is manufactured. The industrial production of ammonium nitrate, the dominant form of nitrate and ammonium fertilizer accounting for 43% of all N-fertilizers [6], entails the acid–base reaction of ammonia with nitric acid. The nitric acid is industrially produced via the Ostwald process that oxidizes ammonia, in the presence of a noble metal catalyst such as platinum with 10% rhodium (top two most expensive metals), to nitric oxide (NO), and, in a second step, NO is further oxidized to yield nitrogen dioxide (NO_2), which is absorbed by water to form nitric acid while reducing a portion of NO_2 back to NO that must be recycled. Evidently, the production of nitrate is a detour—nitrogen in N_2 (oxidation state 0) is first reduced to ammonia (oxidation state -3), and then the ammonia is oxidized to NO and NO_2 (oxidation state +2 and +4, respectively), where extensive energy and fossil fuels are consumed [7]. Furthermore, the tail gas stream in an Ostwald process contains nitrogen oxides (NO_x, mainly NO and NO_2), a gas much more harmful than CO_2 to the climate and environment. To dispose of this pollutant, the industry usually catalytically (again using a noble metal catalyst such as platinum or palladium) reduces the NO_x back to harmless nitrogen gas based on the reaction of NO_x with a fossil fuel, such as hydrogen, methane, butane, propane, or light naphtha [8].

Today, the HB process alone is responsible for the production of over 170 million tons of ammonia, and emits over 300 million tons of CO_2 per year [1,3]. However, the emission of greenhouse gases and pollutants does not just end there. Over 86% of global ammonia produced is applied as N-fertilizer in a variety of chemical forms, among which only about 50% is used by crops, and the rest is lost to the atmosphere via volatilization and denitrification or to ground water through leaching; in some cases, the loss can go up to 70% due to the excessive amount, the low plant population, poor application methods, etc. [9].

Further, global ammonia production has been exclusively established at centralized large scales to be economical, requiring massive capital and infrastructure for H_2 feedstock generation and ammonia storage, and demanding an extensive, costly, and hazardous distribution system [10]. The fossil-fuel-based transportation for the distribution system was not accounted for in the CO_2 emission stated above. Consequently, although the HB process has approached the theoretical limit after continuous development and optimization for more than a century, holding an unbeatable position in terms of energy efficiency despite having great environmental flaws, there is a large variation in the prices and inequality in the accessibility to N-fertilizers globally. For instance, in Sub-Saharan Africa, where sunshine is abundant, low crop yields are associated with low fertilizer use due to high prices [11].

From a systematic engineering view, the current industrial production, distribution, and use of N-fertilizers were built on an unsustainable foundation of fossil resources, and are energy-intensive, inefficient, and environmentally polluting.

1.2. Endeavor to Decarbonize N-Fertilizer Production

The production of N-fertilizer utilizing renewable resources to decarbonize the process has received attention on a global scale driven by the fast declining cost of solar and wind electricity, and sustainability concerns were further incentivized by public policy measures such as a carbon tax [12,13]. In general, research and development endeavors for decarbonizing nitrogen fixation follow either the nitrogen reduction route to fix nitrogen in the form of ammonia (NH_3) or the oxidation path to produce nitrogen oxides (NO_x).

Current efforts in the ammonia route focus on decarbonizing the production of ammonia, not just for fertilizer, but as a platform chemical and energy vector, striving to reduce the specific energy input while increasing the ammonia production rate to achieve Haber–Bosch parity [14]. As a transitional step, the Generation 1 technology for sustainable ammonia production, referred to as “blue ammonia”, involves the use of carbon sequestration or offsets to bring the net carbon impact of the ammonia production to near-zero [4].

Recently, two major technologies were extensively researched. The Generation 2 technology still produces ammonia from the HB process, but uses “green” hydrogen from water electrolysis instead of fossil resources, requiring an enormous amount of specialized water and being limited by the energy and economic efficiency of the electrolysis equipment. Further, the HB process must run continuously, and is poorly adaptive to the day–night cycle of solar energy or the intermittency of wind energy [4]. Generation 3 technologies bypass the HB process through the electrocatalytic nitrogen reduction reaction (eNRR) of N_2 to NH_3 with a promising energy efficiency, which has recently gained increasing attention [4]. However, the low ammonia production rate and system stability, the requirement for expensive ultra-dry and oxygen-free organic solvents, or pure nitrogen and hydrogen feedstocks, and platinum and lithium metal requirements are significant drawbacks of this pathway [4,15]. Other methods include the plasma-catalysis of gaseous H_2 and N_2 to NH_3, metallocomplex nitrogen fixation, photochemical synthesis, and bio-catalysis, all of which are currently at the lab research stage, hardly to be practically applicable, scaled up, and economically competitive with the HB process [13,16,17].

In the oxidation path to fix nitrogen in the form of nitrogen oxides (NO_x), air NTP plasma technologies should be the focus, practically because the free atmospheric air is the predominant source of chemically inert N_2. It is noteworthy that the Birkeland–Eyde process to produce NO_x is the first thermal-plasma-based N_2-oxidation concept, which only utilizes around 3–4% of the applied energy in chemical reactions, the remaining applied energy being wasted as heat [18]. The theoretical energy efficiency of thermal plasma is 0.86 MJ/mol of nitrogen oxide (NO), which could be achieved under hypothetical conditions of 20–30 Bars, 3000–3500 K, and a 10^7 K/s cooling rate [19], higher than that of the HB process for N fixation into ammonia (0.48 MJ/mol ammonia produced). The renewed interest in plasma-based N fixation focuses on nonthermal or warm plasma, which has a lower theoretical energy cost than the HB process, and is projected to become a highly competitive alternative, if the actual energy cost can be significantly reduced [7]. In the case of NO_x production, nonthermal plasma (NTP) has a much lower theoretical limit of energy consumption (0.2 MJ/mol in vacuum) than the HB process [20].

However, comparing the energy efficiency of different technologies for the production of ammonia or NO_x could be misleading. Most of the studies in the oxidation path estimated the energy efficiency based on the end product of NO_x gas (mainly the mixture of NO_2 and NO, e.g., in [15,21–27]), which cannot be directly used as an N-fertilizer. NO needs to be further oxidized to NO_2, which then dissolves in water to form nitric acid, but part of the NO_2 would be reacted back to NO. Further, the nitrate fertilizer in the form of nitric acid is highly acidic, limiting its use to alkaline soil or otherwise requiring neutralization before use. For the production and application of N-fertilizers, we need to take a holistic view at the cost of practical end uses, as well as the cost to our health and environment.

1.3. Booming Renewable Electricity and Its Intermittency

The industry of renewable electricity is fast expanding and the cost of solar/wind electricity is rapidly declining (Figure 1). A U.S. Department of Energy study found that renewable electricity generation from technologies that are commercially available today, in combination with a more flexible electric system, is more than adequate to supply 80% of total U.S. electricity generation in 2050 while meeting the electricity demand on an hourly basis in every region of the country. This study explores the implications and challenges of very high renewable electricity generation levels—from 30% up to 90%, focusing on 80%, of all U.S. electricity generation—in 2050. At such high levels of renewable electricity generation, the unique characteristics of some renewable resources, specifically the geographical distribution and variability and uncertainty in output, pose challenges to the operability of the nation’s electric system [28].

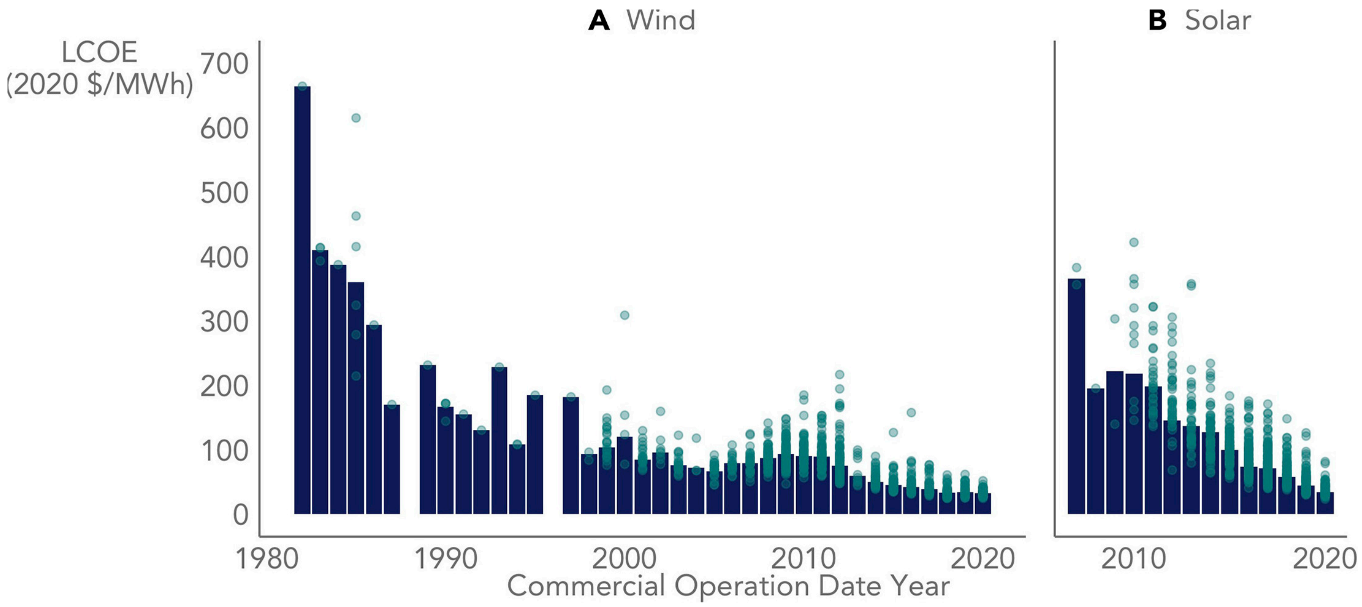

Figure 1. Historical non-normalized levelized cost of electricity (LCOE) of utility-scale wind (**A**) and solar (**B**) energy in the United States [29].

Critics of renewable energy frequently highlight that technologies such as wind and solar only generate electricity when specific natural conditions are met—wind blowing or sun shining. They argue that the widespread adoption of renewable energy is hindered until cost-effective electricity storage technologies are developed. The challenge in integrating variable electricity sources arises from the grid's historical design centered on large, controllable generators. Modern grid operators employ a three-phase planning approach to ensure power plants generate sufficient electricity precisely when needed to consistently and reliably meet demand. Due to the limited storage capacity within the grid, maintaining a continuous balance between the electricity supply and demand is critical to preventing potential blackout events or other systemic failures. Consequently, our modern power grid has been established with a significant overcapacity in order to satisfy the peak load demand in a narrow window of time [30]. Intermittent renewables are challenging because they disrupt the conventional methods for planning the daily operation of the electric grid.

In this respect, the decentralized production of N-fertilizers with NTP technologies are adaptive to the intermittency of renewable electricity and the need of the power grid by "storing" electricity into valuable chemicals, and have a high potential to change the landscape of N-fertilizers, because the production process can be easily switched on and off.

2. Perspective: Decarbonizing N-Fertilizer with NTP Technologies

2.1. Decentralized N-Fertilizer Production and Application Based on NTP

Nitrogen (N) is a critical element essential for optimal plant growth and development. Plants utilize nitrogen primarily in the forms of nitrate (NO_3^-) and ammonium (NH_4^+). Ammonium ions readily bind to negatively charged soil particles, preventing their leaching. Throughout the growing season, soil micro-organisms convert ammonium into nitrate, the primary form of nitrogen absorbed by plants [31]. However, microbial processes like denitrification also convert nitrate and nitrite (NO_2^-) into gaseous nitrogen forms, predominantly nitrogen (N_2) and nitrous oxide (N_2O) [32]. Nitrous oxide is a potent, long-lived greenhouse gas with 300 times the warming potential of CO_2 [33]. Nitrate, being negatively charged, dissolves in water and moves through the soil with the soil water movement. During rainfall, nitrate can percolate downward through the soil profile, potentially entering tiles or drainage channels and becoming lost from agricultural production. This leaching process is the primary mechanism causing nitrogen loss from coarse-textured sandy soils. Nitrite is a less common form of nitrogen in the soil, and it is typically produced by the breakdown of organic matter or the action of nitrifying bacteria. Nitrite is also absorbed by plant roots, but it is less readily available to plants than nitrate and could be toxic to plants, especially at higher concentrations [34–36]. Each form of N-fertilizers has specific properties that determine when, where, and how various fertilizer materials can be used [31].

We need to re-examine our current system for N-fertilizer production and distribution established on the foundation of the HB process. A recent spike in the prices of N-fertilizers (in U.S., the farmer-paid price for anhydrous ammonia increased from $487/ton in 2020 to $1516/ton as of March 2022), due to the disruption of the natural gas supply chain, intensifies the alarm on this fragile and unsustainable system [37].

Given that over 86% of the global ammonia production involves either the direct application to soil as ammonia fertilizer or conversion into other forms such as ammonium, nitrate, and urea, it results in a complex distribution network, uneven access to nitrogen fertilizers, and significant application losses [9]. Therefore, there is an urgent and practical need to develop an N-fertilizer production system that utilizes renewable electricity (solar or wind) and NTP technologies for a sustainable decentralized production and application in the future. Such a system would utilize water, air, and electricity as the primary inputs to synthesize an aqueous mixture of nitrate and ammonium suitable for the direct application to crops. This approach facilitates local production at the farm level, allowing installation either independently or integrated with existing irrigation systems. It can operate effectively with an intermittent solar or wind electricity supply, resulting in zero carbon emissions. Furthermore, it can enable rapid startup and shutdown, promptly responding to weather fluctuations and local agricultural conditions such as the soil type, climate, crop varieties, and farming practices, for precision agriculture.

Prospectively, the implementation of such an N-fertilizer system will require the demonstration of the following: (1) a scalable modular system that can deliver sufficient aqueous N-fertilizer according to the demand of an agricultural land, small or large, (2) a sufficiently low electric energy cost to be economically competitive, and (3) evidence that the N-fertilizer product can be directly applied to grow crops/vegetables and totally replace synthetic N-fertilizers.

2.2. Plasma-Activated Water and the Applications in Agriculture

Plasma-activated water (PAW), commonly derived from the interaction of atmospheric plasma with water in a batch mode, has attracted widespread attention, with applications ranging from microbial decontamination in the food industry to medical wound healing. Importantly, it is considered a supplement to chemical fertilizers in agriculture because it is rich in fixed nitrogen in the forms of nitrate and nitrite. Other reported benefits of PAW in agriculture include enhancing seed germination, increasing rooting speed, promoting plant growth, enhancing drought tolerance and resistance to abiotic stresses, and controlling plant diseases and pests, due to the presence of reactive oxygen and nitrogen species (RONS), such as hydroxyl radicals ($\cdot OH$), hydrogen peroxide (H_2O_2), ozone (O_3), and nitrate/nitrite (NO_3^- and NO_2^-) [38–41]. Although there are reported negative effects of high-concentration PAW on plants [39,42], a recent study concluded that PAW application, even at high amounts, has no negative influence on the physicochemical properties of soil and it can be safely applied in sustainable, environmentally friendly agriculture [43].

Although the benefits of PAW for agriculture production deserve further research, PAW is not a well-defined product; different methods of generating PAW lead to different contents of reactive chemical species, and most of them are transient, which will ultimately affect the activity of the resulting PAW for different applications. To the prospect of this article, the fixed N content in PAW is insufficient to replace synthetic N-fertilizers.

2.3. On-Site Production of Liquid N-Fertilizer

As discussed in Section 2.1, the decentralized N-fertilizer production utilizing air, water, and renewable electricity holds significant promise for the on-site production of liquid N-fertilizer. This approach circumvents the need for the extensive capital investment and infrastructure required for ammonia production and storage, as well as the complex and costly distribution networks associated with synthetic N-fertilizers. Moreover, it eliminates the necessity for downstream separations or additional processes to obtain nitrate, ammonium, or urea, as the desired product would be a blend of nitrate and ammonium directly suitable for application to crops and vegetables.

The key to achieving such production capabilities lies in the development of nitrogen fixation technologies based on NTP in continuous reactors that can achieve a high productivity of nitrate and ammonium at sufficiently low electricity costs to be economically viable for agriculture. Recent research has increasingly focused on understanding the interaction between plasma and water, aiming to advance the fundamental knowledge at the largely unexplored interface of NTP and water for engineering development [44–46]. Despite advancements in energy efficiency in nitrogen fixation using NTP technologies, few reported developments have successfully balanced a high productivity with the low electricity costs required for continuous operation and practical applicability in agricultural settings.

2.3.1. Recent Development of a Continuous NTP Reaction System for N-Fertilizer

The author has recently developed a continuous NTP reaction system (denoted as cNTP-H_2O hereafter) for the distributed on-site production and delivery of N-fertilizer [47], as presented in Figure 2. This design enables a high rate of water-flow-through operation, continuously delivering an aqueous N-fertilizer, mainly in the forms of nitrate and ammonium with a trace of nitrite.

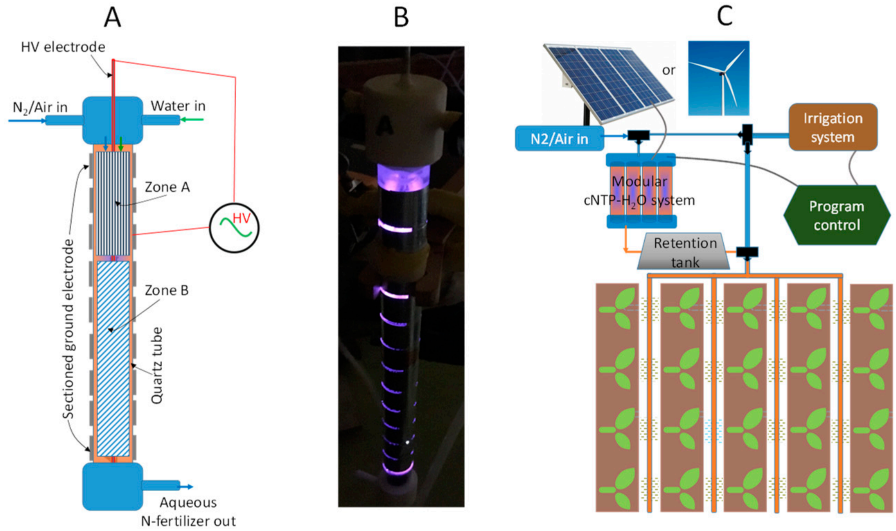

Figure 2. (**A**) Schematic unit-cell design of the cNTP-H_2O system; (**B**) photo image showing a discharging unit-cell against dark background; and (**C**) vision of integrating modular cNTP-H_2O system with irrigation.

The modular cNTP-H_2O system consists of uniquely designed unit-cells, featuring a two-zone, configurable high-voltage (HV) electrode and ground electrode to generate dielectric barrier discharge (DBD) plasma, as schematically presented in Figure 2A. Figure 2B shows the photo image of a discharging unit-cell against a dark background during operation. It is envisaged that the system can be scaled up by the parallel connection of a number of unit-cells and coupled to an irrigation line as illustrated in Figure 2C. Importantly, this invention establishes an innovative platform for research and development, which will allow us to configure the reactor (e.g., the shape, geometry, and metal materials for the two zones of HV electrode) and tune the product composition of nitrate/nitrite and ammonium, aiming to maximize the productivity of the N-fertilizer while minimizing the energy cost.

Interest in exploring the interaction between plasma and water has grown due to its potential to enhance the efficiency of nitrogen fixation, producing an aqueous N-fertilizer.

Redox reactions induced by NTP occur not only at the plasma/air and plasma/water interfaces, but also in the volume of the aqueous phase [48]. Both the oxidation and reduction of nitrogen can be achieved using NTP with water, despite thermodynamic or kinetic limitations at ambient conditions, leading to the production of both NO_x and ammonium [49]. Although this is still a largely unexplored area, good discussions on the mechanisms and pathways for the formation of reactive oxygen and nitrogen species (RONS) leading to the production of NO_x and ammonium can be found in recent publications [44–46]. However, most highly reactive plasma species have a very short half-life in the order of a few nanoseconds to a few milliseconds. Therefore, it is important to consider not only the generation of these reactive species, but also their efficient delivery into liquid products when designing an NTP reaction system.

In the design of the cNTP-H_2O system, both water and air simultaneously flow through plasma discharge zones, intensifying the interfacial reactions to enhance mass transfer and tune the production of fixed nitrogen continuously. In addition to common RONS generated in air plasma, the presence of water in the plasma also generates solvated electrons, hydrogen radicals ($H^{\bullet}$), hydroxyl radicals ($^{\bullet}OH$), perhydroxyl radicals ($HOO^{\bullet}$), and hydrogen peroxide (H_2O_2), which are among the strongest reduction or oxidation agents for nitrogen fixation [48,50,51]. The presence of water helps quench the RONS produced by NTP, rapidly converting them into more stable N-containing compounds. This quenching effect helps prevent the back reactions of RONS. Water also acts as an absorption medium in situ for the fixed N, effectively removing it from the gas phase where back reactions are more likely to occur, shifting the equilibrium towards product formation.

For the cNTP-H_2O system, we designed multiple plasma discharge regimes within one unit-cell, which make efficient utilization of the applied power and reduce energy consumption. As an example, the generation of RONS and reactive hydrogen species can be greatly enhanced as the glow discharge acts as an excitation pre-treatment in Zone A prior to the filament discharge in Zone B. The designed turbulent flows of air and water transiently pass through the multiple plasma discharge regimes, undergoing intensified contact and mixing, while the produced NO_x and ammonium are absorbed by water in situ, further driving reactions toward a higher yield of fixed nitrogen.

Different configurations of the cNTP-H_2O system were tested and key results are summarized in Table 1, which also includes preliminary economic estimations. Table 1 shows the significant progress of improving the energy efficiency and production rate of fixed nitrogen by configuring the cNTP-H_2O system and operation parameters.

There is potential to significantly improve the performance of the cNTP-H_2O system through systematic optimization. A major challenge arises from balancing minimizing the energy cost and maximizing the production rate, which is a complex function of a multitude of factors including the plasma discharge type, the reactor geometry/configuration, the discharge operating parameters, and the presence of catalysts. Two targets that could be potentially achieved after the optimization for practical implementation are also listed in Table 1. Target 1 has a high optimized production rate, and Target 2 has a high optimized energy efficiency. If one of the targets is achieved, solar panels with a surface area of only about 1% of a land area will produce sufficient N-fertilizer for the land. Although the specific energy cost is still higher than that of the HB process, they are potentially viable at the farm site without the emissions and distribution costs associated with the HB process.

Table 1. Test results of the cNTP-H_2O system with preliminary economic estimations.

Unit-Cell Configuration	Unit Feed Gas and Flow Rate (mL/min) [1]	Unit Feed Water Content and Flow Rate (mL/min) [2]	Total N Production Rate per Unit-Cell (mg-N/min) [3]	NH_4^--N Production Rate per Unit-Cell (mg-N/min)	Energy Efficiency (kWh/mol-N) [4]	Number of Unit-Cells for 115 lb N per Acre [5]	Electricity Cost for 115 lb N ($/Season) [6]	% Surface Area of Solar Panel [7]
A	N_2/400	DW/48	834.2	15.4	42.5	1737	4752	36.3
B	N_2/500	DW (2% ethanol)/47	808.4	503.6	42.4	1792	4743	36.2
C	N_2/400	DW/48	1629.1	129.0	25.5	889	2850	21.8
D	N_2/580 + H_2/80	DW/50	1095.0	865.2	42.4	1323	4740	36.2
E	Air/2302	DW/48	4094.4	94.0	10.4	354	1159	8.8
F	Air/2302 + H_2/80	DW/50	3800.0	257.1	12.3	381	1380	10.5
G	Air/3800	TW/95	8265.0	14.3	5.3	175	587	4.5
Target 1	**Air**	**TW/100**	**30,000**	**3000.0**	**1.6**	**48**	**174**	**1.3**
Target 2	**Air**	**TW/100**	**11,000**	**1100.0**	**1.1**	**132**	**119**	**0.9**

[1] The feed gas was either pure nitrogen, air (79% nitrogen, 21% oxygen), or air/nitrogen plus (+) hydrogen gas with flow rate indicated. [2] The feed water was either distilled water (DW), tap water (TW), or DW added with 2% ethanol. [3] The number indicates the summation of measured NO_3^-, NO_2^- and NH_4^+ in the aqueous N-fertilizer. [4] This is based on the production of total fixed nitrogen, including NO_3^-, NO_2^-, and NH_4^+, and the measurement of NTP power consumption using Lissajous parallelogram method [52]. [5] This is calculated practically assuming that the reaction system is powered by intermittent solar or wind electricity for a typical crop growing season of 600 h (6 h per day for 100 days). We aim to demonstrate the economic feasibility of replacing the use of synthetic N-fertilizer at an ideal rate of 115 lb-N per acre per season for corn production, which is arguably the most demanding agricultural practice for N-fertilizer. Nationally, the weighted average of corn N inputs (188 kg-N per hectare) based on corn-planted area exceeded N needs (115 lb-N per acre) by 60 kg-N per hectare, with N surplus found in 80% of all U.S. corn-producing counties [53]. [6] This is calculated assuming that levelized cost of renewable electricity is $0.03/KWh. The levelized cost of electricity (LCOE) is a measure of the average net present cost of electricity generation for a generator over its lifetime. It is used for investment planning and to compare different methods of electricity generation on a consistent basis. It can include the cost of capital, decommissioning, fuel costs, fixed and variable operations and maintenance costs, financing costs, and an assumed utilization rate. In 2020, the LCOE of utility-scale solar and wind reached down to $0.03/KWh, and further decline in the future is forecasted [54]. [7] Using installed solar panels as example, the number gives a visual estimation of the panel surface area for providing 115 lb-N/acre. The footprint of the corresponding cNTP-H_2O system is much smaller and can easily fit under the solar panels. The area occupied by solar panels is estimated based on the total wattage required to power the calculated number of cNTP-H_2O unit-cells and that the area of a 1 KW panel is 5.56 m^2 [55]. It is noteworthy that, in the case of installed solar panel operation, only 600 h are dedicated to power the cNTP-H_2O modules for a crop-growing season; the electricity generated in the rest of time can be sold to the grid.

2.3.2. Implications and Significance of the cNTP-H_2O System

The implications for further development are listed below:

- Hydrogen is the limiting reactant in the reduction pathway to make ammonium. This limiting reactant could be supplemented by H_2 gas or ethanol, and potentially by methane, which can be generated at the farm site via anaerobic digestion; however, the use of an extra hydrogen source or enriched N_2 or O_2 input will inevitably increase the cost for the production of the N-fertilizer.
- Compared to the reduction pathway for making ammonium, the oxidation pathway to produce an aqueous N-fertilizer rich in nitrate from air and water is advantageous; the key is to minimize the energy cost, and the content of nitrite to avoid toxicity to plants.
- Using air as a feed gas to the cNTP-H_2O system, the fixed N in the product is dominantly in the form of nitrate, with less than 10 ppm of nitrite in all the cases listed in Table 1, which can be directly utilized by plants. Importantly, the nitrate concentration reached an unprecedented 380 ppm (Entry G in Table 1), ideal for fertigation.
- It appeared that the metal material of the electrode that was in contact with reactants affected the performance. Therefore, catalysts can be added onto the electrode (e.g., coating/embedding catalysts onto the electrode), which may potentially improve the reaction kinetics and product yield significantly.
- With the non-equilibrium DBD plasma, the cNTP-H_2O system runs at non-equilibrium steady states; thus, the NTP thermodynamics and kinetics, transport processes, and chemical reaction kinetics all influence the production rate and product composition. Therefore, it is possible, based on the cNTP-H_2O platform, to further improve the production rate and specific electric energy consumption through the optimization of the process parameters and configurations.

The significance of the results can be revealed by benchmarking against published data, as shown in Figure 3. Because there are different technologies using different feedstocks for nitrogen fixation (e.g., air, N_2, or artificially mixed N_2/O_2 with various ratios as the nitrogen source; and pure H_2 or water as the hydrogen source), preventing straightforward and fair comparisons, we benchmark against four categories of promising technologies: (1) the electrocatalytic nitrogen reduction of N_2 to NH_3 (eNRR-NH_3) [15,56–67], (2) the lithium-mediated electrocatalytic nitrogen reduction of N_2 to NH_3 (Li-eNRR-NH_3) [68–74], (3) the plasma-driven NO_x production (NTP-NO_x) [15,21–26], and (4) the plasma-driven NH_3 production from N_2 and water (NTP/H_2O-NH_3) [75–79].

It should be pointed out that: (1) although the research effort worldwide focuses on reducing the specific energy consumption to achieve Haber–Bosch parity, both a high production rate and low specific energy consumption are required for practical implementation; (2) we had to use the logarithmic scale for the plot in Figure 3 in order to capture the large variation in both the production rate and specific energy consumption reported in the literature; (3) except for the NTP-NO_x category, most other technologies require N_2 gas instead of air as feedstock, potentially increasing the production cost; and, (4) even in the NTP-NO_x category, the artificial mixture of N_2/O_2 with various ratios, instead of air, were commonly used to improve the NO_x yield, and the reported yields were based on the measurement of the produced NO_x gas, not ready to be used as N-fertilizer. Nonetheless, Figure 3 provides an overview of the significant status of the cNTP-H_2O system.

For the eNRR-NH_3 and Li-eNRR-NH_3 technologies to make ammonia, although some achieved a very low specific energy consumption, the production rates were too low for practical applications; the only promising one in the eNRR-NH_3 category used a hybrid method, in which NTP was first used to produce NO_x, then the NO_x was fed to an eNRR cell to make ammonia [15]. Furthermore, a low system stability, the requirement for expensive ultra-dry and oxygen-free organic solvents, or the demand for pure nitrogen and hydrogen feedstocks, and platinum and lithium metal, result in low levels of technology readiness [4,15].

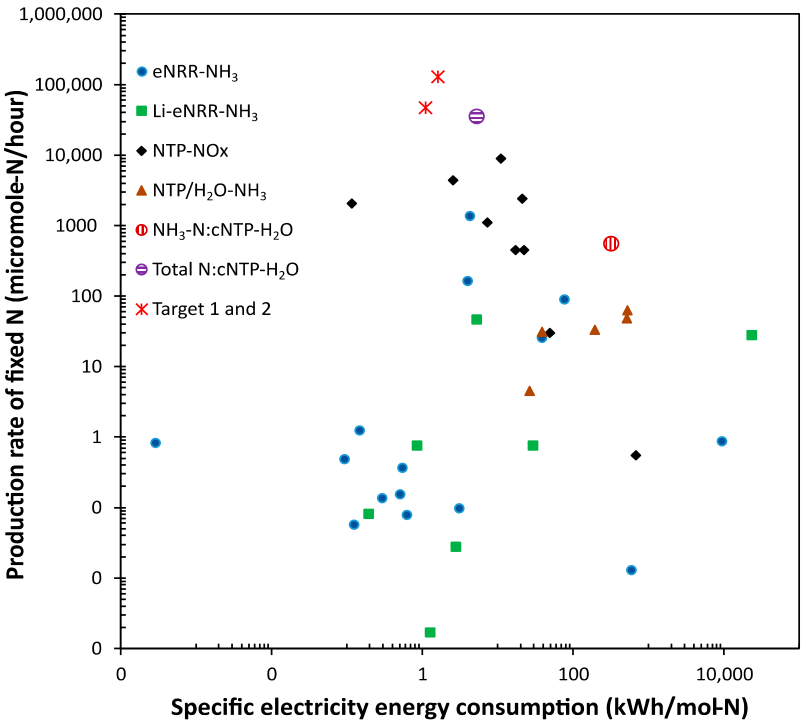

Figure 3. Benchmarking the performance of the cNTP-H_2O system against literature data.

Generally, the NTP-NO_x technologies have a higher production rate and moderate specific energy consumption, but most of these studies reported NO as the major product. Although a recent study in this category [26] claimed a record-low specific energy consumption of 0.42 MJ per mol of fixed N (mainly NO) by using a pulsed plasma jet, the production rate is very low (~480 µg-N/min).

Comparing the cNTP-H_2O result (Entry C in Table 1) with those reported using NTP/H_2O-NH_3 technologies and N_2 gas as the feed for ammonia production, a much higher production rate was achieved using the cNTP-H_2O system, although the specific energy consumption is at the higher end of this category (but it is at the lower end considering the total fixed N). In terms of the total fixed N using air as the feed, we achieved the highest production rate compared with others in the category of NTP-NO_x, and the specific energy consumption is at the lower end (Entry G in Table 1). Importantly, the product of the cNTP-H_2O system is an aqueous mixture of nitrate and ammonium, which can be directly applied to plants.

Another important consideration in the development of the cNTP-H_2O system is practicality. Although the concentration of the fixed N in the aqueous N-fertilizer product (Entry G in Table 1) is about 87 mg-N/L, mainly in the form of NO_3^-, the pH is nearly neutral, which can be directly applied to plants without neutralization. This is because tap water has a buffering effect due to its carbonate hardness (KH) and general hardness (GH). Especially, the GH measures the concentration of calcium, magnesium, and other mineral ions present in the water, ranging from 10 to over 300 mg/L depending on the locations. In fact, nitric acid is used to dissolve the mineral deposition in irrigation systems [80], and calcium/magnesium nitrates are excellent fertilizers. Further, the pH of the aqueous N-fertilizer could be tuned by adjusting the process parameters of the cNTP-H_2O system according to specific applications, e.g., for citrus trees that prefer slightly acidic soil, or for alkaline soil.

3. Conclusions and Prospects

With the advancement in the fundamental sciences of nonthermal plasma and engineering development in recent years, the implementation of the decentralized on-site production of N-fertilizer is urgently needed and practically feasible. It has taken more than a century of continuous development and optimization for the HB process to achieve its current level of energy efficiency of approximately 0.5 MJ/mol, which is near its theoretical limit. However, we must point out that the HB process is just one step in the extensive chain of the synthetic N-fertilizer production and distribution entailing heavy emissions and pollutions, which could be largely bypassed by implementing the on-site production of the N-fertilizer using NTP technologies.

We would like to point out the following for accelerating the implementation:

(1) Minimizing the electric energy cost with NTP technologies without sacrificing productivity should be the priority, because this is directly related to the economic competitiveness. This requires the fundamental research of plasma physics and chemistry, and the reaction kinetics and engineering, especially at the NTP/water interface. Further, the design of the electric power supply directly converting solar or wind electricity to high voltage for better efficiency, although it is out of the scope of this article, is an important aspect for the on-site N-fertilizer production that will certainly improve the performance and energy efficiency. For example, nanosecond-pulsed high voltage has the potential to significantly reduce plasma energy consumption [81], but this type of power supply is expensive. We call on the development of efficient and inexpensive power supplies dedicated to N-fertilizer production with NTP technologies.

(2) The involvement of agronomists, plant scientists, and soil scientists is crucial for the implementation of the on-site N-fertilizer production and application. As for any disruptive technologies, the new technologies and N-fertilizer products require testing and validation, involving field tests, nutrient uptake studies, soil health monitoring, crop management and improvement, the optimization of fertilizer application, farmer education and training, and an economic and environmental impact assessment. In some cases, the implementation may require the adjustment of current agricultural practices.

(3) In the early stage of a new technology, process modeling and techno-economic analysis (TEA) can help to assess potential economic feasibilities, bottlenecks, and operation targets for process improvement, and identify further research and development effort requirements. Life cycle analysis (LCA) will evaluate the reduction of greenhouse gas emissions and the environmental impact, resource efficiency, the impact on the ecosystem and human health, and long-term sustainability. Results from the TEA and LCA will also help mitigate socioeconomic and behavioral challenges in adopting new technologies, facilitating the effort of technology transfer for real-world applications.

Opportunities for the on-site N-fertilizer production with NTP technologies are already here.

Agrivoltaics is an innovative approach that combines solar energy production with agriculture on the same land, offering dual land use, a symbiotic relationship, and resource efficiency. Agrivoltaics is wide-spreading globally, and there are more than 300 identified agrivoltaic projects in the United States, representing over 2.8 GW of solar capacity [82]. Assuming only 600 h of usage of the solar capacity for a crop-growing season and that the energy cost of the on-site N-fertilizer production reaches 0.5 MJ/mol-N of Haber–Bosch parity, the 2.8 GW solar capacity would produce 0.17 million tons of fixed N, equivalent to 0.5 million tons of ammonium nitrate fertilizer on site, cutting down the CO_2 emission from the production alone by 0.8 million tons [83].

The NTP-produced N-fertilizer can be combined with animal waste management to treat animal manure, resulting in antimicrobial effects and a higher N content compared to untreated manure, and reducing ammonia and methane emissions [84,85].

Controlled Environment Agriculture (CEA) is an advanced approach to food production that uses technology to create optimal growing conditions for crops. We expect that CEA is ideal for starting the implementation of NTP-produced N-fertilizer, because of its investment in emerging technologies and the need to use nitrate N-fertilizer [86]. A current trend in new CEA facilities is to implement micro-grids of renewable electricity [87], thus enabling local N-fertilizer production with NTP technologies.

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