

## **Environment and Natural Resources Trust Fund**

## 2023 Request for Proposal

## **General Information**

Proposal ID: 2023-196

Proposal Title: Produce Green Nitrogen Fertilizer from Air and Water

## **Project Manager Information**

Name: Roger Ruan Organization: U of MN - College of Food, Agricultural and Natural Resource Sciences Office Telephone: (612) 804-2270 Email: RUANX001@UMN.EDU

## **Project Basic Information**

**Project Summary:** Locally produced high-concentration nitrogen fertilizers from renewable and extremely low cost natural resources.

Funds Requested: \$499,000

Proposed Project Completion: June 30, 2026

LCCMR Funding Category: Water Resources (B)

## **Project Location**

- What is the best scale for describing where your work will take place? Statewide
- What is the best scale to describe the area impacted by your work? Statewide
- When will the work impact occur?

During the Project and In the Future

## Narrative

#### Describe the opportunity or problem your proposal seeks to address. Include any relevant background information.

The US farming and other industries use large amounts of nitrogen fertilizers such as anhydrous ammonia and ammonia nitrate. The state of Minnesota alone imports \$400 million to \$800 million retail value per year of nitrogen fertilizer from other states and countries. Current industrial technology for nitrogen fertilizer production is non-renewable, expensive, dangerous, and environmentally unfriendly. Although the Haber-Bosch process provides over 130 million tons of ammonia annually to support approximately 40% of the world's population, it is also responsible for about 2% of the global energy consumption and GHG emissions. The reaction conditions of the Haber Bosch process lie in the range of 200 to 400 atm and 400 to 600 °C, respectively. These intense temperature and pressure conditions are the main disadvantages of the Haber-Bosch process, as they prevent the possibility of lowering capital costs. Additionally, the high pressure required for the traditional Haber-Bosch Process is also a limiting factor in reducing the economies of scale of localized production facilities due to the high energy (and cost) requirements of compression. Producing fertilizers locally eliminates the need for transportation and thus reduces costs and GHG emission. Nitrogen fertilizers to be produced with the proposed technology are non-volatile.

# What is your proposed solution to the problem or opportunity discussed above? Introduce us to the work you are seeking funding to do. You will be asked to expand on this proposed solution in Activities & Milestones.

This project is intended to demonstrate a new process to fix nitrogen from water and air only to produce nitrogen-rich water using renewable electricity, e.g., from wind or solar energy, potentially eliminating the need for fossil resources and avoiding pollutant emissions all together. The nitrogen-rich water (mainly nitrate and ammonia) can be used as fertilizer directly on cropland or hydroponics systems to reduce nitrogen runoff and water needs. In the proposed process, nitrate fertilizer is produced from water and air using catalysts (N2 dissociation catalysts and photocatalysts) in the non-thermal plasma (NTP) discharge reactor and has been effectively concentrated with an electrodialysis concentration system. The objectives of the project are to (1) develop and evaluate effective and energy efficient catalysts, i.e. N2 dissociation catalysts and photocatalysts; (2) develop and construct an experimental catalytic NTP apparatus, and improve the production of nitrate fertilizer via optimizing the key processing variables and conditions, i.e. catalysts dosage, feed gas rate and ratio, electric field, NTP reactor design, increase nitrate concentration, UV intensity, wavelength; (3) evaluate the energy consumption and environmental impacts of the technology, and (4) conduct techno-economic analysis to evaluate the financial viability of the technology.

# What are the specific project outcomes as they relate to the public purpose of protection, conservation, preservation, and enhancement of the state's natural resources?

The specific project outcome will include the development of energy efficient N2 dissociation catalysts and photocatalysts, optimal processing conditions for high nitrogen fixation efficiency, efficient production of high-concentration nitrate solution in water, and a pilot-scale nitrogen fixation system for systems analysis and demonstration. These outcomes will move the technology closer to commercial implementation, which will help produce renewable nitrogen fertilizers, reduce fossil energy demand, reduce CO2 emissions, and thus reduce environmental impacts of the nitrogen production industry and agricultural activities, and conserve natural resources.

## **Activities and Milestones**

# Activity 1: Develop and evaluate effective and energy efficient catalysts for the catalytic non-thermal plasma

#### Activity Budget: \$150,000

#### **Activity Description:**

Catalysts play an important role during the plasma-based catalytic nitrogen fixation process, which involves three processes, N2/O2 dissociation process, NO oxidation and nitrite oxidation process. The catalysts not only can greatly lower the activation energy of the feedstock gas, but also oxidize the NO or nitrite into nitrate, thus improving the nitrogen fixation efficiency and reducing the energy consumption. In this activity, we will first synthesize several N2/O2 dissociation catalysts, photo-catalysts, and some multi-functional catalysts, and characterize them to understand their structure and properties, i.e. morphology, crystal structure and chemical composition. After that, we will test their performance on N2/O2 dissociation, NO oxidation and nitrite oxidation, stability and recycling, and also evaluate the economic feasibility for future large-scale application.

#### **Activity Milestones:**

Description	Completion Date
Several catalysts will be prepared and characterized.	December 31, 2023
The performance of catalysts will be investigated.	June 30, 2024
New knowledge of catalytic mechanisms will be explored.	June 30, 2024
The economic feasibility will be evaluated.	June 30, 2024

### Activity 2: Develop an experimental catalytic NTP apparatus and optimize the synthesis process

#### Activity Budget: \$89,000

#### **Activity Description:**

The concept of synthesizing nitrogen compounds using cNTP has been proven in our preliminary studies. A new and cost effective nitrogen fixation system will be developed, and we will study processing parameters, such as the feedstock gas, catalysts, and electric field. In this activity, we will first develop a bench scale synthesis system that can house different types of NTP reactors, and allow inclusion of catalysts. Then, important parameters which greatly impact nitrogen fixation efficiency will be studied, i.e. N2/O2 ratio, feeding gas flow rate, power input, electric field, catalyst dosage, and intensity of UV or visible light. Experiments will be conducted under different conditions to understand and optimize the process in terms of nitrate yield and energy efficiency.

#### **Activity Milestones:**

Description	Completion Date
A bench scale synthesis system will be developed.	December 31, 2023
Important parameters will be optimized.	December 31, 2024
New knowledge of the process works will be obtained	December 31, 2024
Energy efficiency will be evaluated.	December 31, 2024

#### Activity 3: Develop concentration process to produce high-concentration nitrate

#### Activity Budget: \$100,000

#### **Activity Description:**

High-concentration nitrate is beneficial to storing and using the fertilizer. An efficient nitrate concentration system based on electrodialysis will be developed and the processing parameters will be investigated. In this activity, we will

fabricate several ion exchange membranes, characterize their structure, and test their performance on the selective migration of nitrate ions in the concentration system. After that, we will introduce the ion exchange membrane in an electro-osmosis system, and optimize the main parameters (such as initial nitrate concentration, pH, voltage and temperature) and develop the control strategy of this system. To confirm the level of nitrate concentration needed for practical application of nitrate solution on a typical corn crop.

#### **Activity Milestones:**

Description	Completion Date
Ion exchange membranes will be fabricated and characterized	June 30, 2025
The main parameters for the nitrate concentration system will be optimized	June 30, 2025
The control strategy of this system will be obtained	June 30, 2025

# Activity 4: Develop an integrated catalytic high-concentration nitrate production system and evaluate environmental impacts and economic performance

#### Activity Budget: \$160,000

#### **Activity Description:**

We will communicate our findings from Activity 1-3 to primary stakeholders such as fertilizer producers, farmers, and farm machine manufacturers. Based on their feedback, we will design and construct a small pilot scale integrated system for comprehensive evaluation of the technology. Rigorous tests will be conducted in the lab and then we will move the system to the field for testing and demonstration. With a small pilot system, the mass and energy balance data, together with emission data, will be used to evaluate the environmental and economic performance using a mathematical model. At this small pilot scale, the electrical energy needed to generate the non-thermal plasma, can be better evaluated, to confirm utility costs and economic analysis. This evaluation will also provide a good assessment of the environmental impact of the proposed technology. Further R&D efforts and commercialization strategies will be recommended.

#### **Activity Milestones:**

Description	Completion Date
An integrated catalytic high-concentration nitrate production system will be developed.	June 30, 2026
The energy efficiency, cost, and emission will be evaluated	June 30, 2026
Environmental impacts will be assessed	June 30, 2026
Further R&D and commercialization strategy will be recommended	June 30, 2026

## **Project Partners and Collaborators**

Name	Organization	Role	Receiving Funds
Paul Chen	University of Minnesota	Co-PI	No

## Long-Term Implementation and Funding

Describe how the results will be implemented and how any ongoing effort will be funded. If not already addressed as part of the project, how will findings, results, and products developed be implemented after project completion? If additional work is needed, how will this work be funded?

New scientific knowledge on feedstock breakdown and product synthesis during the plasma-based catalytic nitrogen fixation process will be acquired through this research, techno-economic analysis will be conducted to evaluate the financial viability of the technology, and the demonstration will help raise significant interests from the public. We will seek industry partners and private, state, and federal funding to further develop, and eventually commercialize the technology. Our lab work has already shown that 200 mg/Liter nitrate solution can be concentrated to over 2,000 mg/Liter, which is needed for practical application on corn crops.

## Other ENRTF Appropriations Awarded in the Last Six Years

Name	Appropriation	Amount Awarded
Demonstrating Innovative Technologies to Fully Utilize Wastewater Resources	M.L. 2014, Chp. 226, Sec. 2, Subd. 08c	\$1,000,000
Development of Innovative Sensor Technologies for Water Monitoring	M.L. 2016, Chp. 186, Sec. 2, Subd. 04j	\$509,000

## Project Manager and Organization Qualifications

#### Project Manager Name: Roger Ruan

#### Job Title: Professor and Director

#### Provide description of the project manager's qualifications to manage the proposed project.

Dr. Ruan, Professor and Director of Graduate Studies of Bioproducts and Biosystems Engineering Department, and Director of Center for Biorefining at University of Minnesota, is a Fellow of ASABE, IFT, Vebleo, and IAAM, and has received many other awards, including CAFS Professional Achievement and Scientist of IAAM, etc. He is a top cited author in engineering and technology with an h-index of 80, i10-index of 392, and has over 25,000 citations. Dr. Ruan's research include renewable energy and environment technologies for sustainable development. He has published over 500 referred journal articles, two books, 24 book chapters, and holds 20 US patents in the areas of municipal, agricultural, and industrial liquid and solid waste including biomass and waste plastics treatment and utilization through novel anaerobic digestion, microalgae and hydroponic cultivation, pyrolysis and gasification, airborne and other pathogen disinfection and pollutant control, catalysis, non-thermal plasma, and nitrogen fixation, etc. He has received over 200 grants totaling over \$45 million in various funding for research, including major grants from USDA, DOE, DOT, DOD, LCCMR, and industries. He has served as guest editor or editorial board member of Bioresource Technology, Renewable Energy, Engineering, Applied Catalysis and Chemical Engineering, Journal of Food Process Engineering, The Open Plasma Physics Journal, and Associate Editor of Transactions of ASABE, Engineering Applications in Agriculture, and Transactions of CSAE, and Chairman of Editorial Board and Editor-in-Chief of International Journal of Agricultural and Biological Engineering, etc. He has supervised over 75 graduate students, 140 post-doctors, research fellows, and other engineers and scientists. He has given over 300 keynote lectures, invited symposium presentations, and short courses. His earlier LCCMR funded projects have resulted in several patented technologies which have been successfully licensed

to the industry. He has the technical expertise and project management experience to ensure the execution of proposed projects.

Organization: U of MN - College of Food, Agricultural and Natural Resource Sciences

#### **Organization Description:**

The Center for Biorefining is a University of Minnesota research center affiliated with the College of Food, Agricultural and Natural Sciences and help coordinate the University efforts and resources to conduct exploratory fundamental and applied research and provide education on science and technology for environment protection and circular economy; stimulate collaboration among the University researchers, other public sector investigators, and private investigators involved in biobased production technology development; promote technology transfer to industries; and foster economic development in rural areas. The Center's research programs are founded by DOE, USDA, DOT, DOD, LCCMR, IREE, Xcel Energy, and other federal and state agencies, NGOs, and private companies. The Center is equipped with state of the arts analytical instruments, and processing facilities ranging from bench to pilot scale.

## Budget Summary

Category / Name	Subcategory or Type	Description	Purpose	Gen. Ineli gible	% Bene fits	# FTE	Class ified Staff?	\$ Amount
Personnel								
Professor/faculty		Primary Investigator - project lead, advises researchers, plans and directs research, oversees budget, monitors and reports progress			33.5%	0.06		\$15,940
Professor/faculty		Co-Primary Investigator - advises researchers, designs and directs experiments, conducts data analysis, writes reports and publications			33.5%	0.15		\$69,062
1 Graduate Research Assistant		carries out experiments, collects and analyzes data, prepares reports and manuscripts			45%	1.5		\$160,139
Post Doctoral Reseracher		designs and carries out experiments, collects and analyzes data, prepares reports and manuscripts			20.9%	3		\$185,001
							Sub Total	\$430,142
Contracts and Services								
equipment manufacturer	Professional or Technical Service Contract	Maintenance and repair, including callibration				0		\$9,000
							Sub Total	\$9,000
Equipment, Tools, and Supplies								
	Equipment	Components for fabrication of a small pilot system including reactor vessel, high voltage power supply, catalysts, pumps, membrane separator	To fabricate a small pilot system for extensive testing, cost analysis, and demonstration					\$25,000
	Tools and Supplies	Purchase of lab and miscellaneous supplies, including feed gases, catalysts, chemicals, consumable supplies for analytical instruments	For running experiments and operating conversion systems					\$31,858
							Sub Total	\$56,858
Capital Expenditures								
							Sub Total	-

Acquisitions and Stewardship					
				Sub Total	-
Travel In Minnesota					
	Miles/ Meals/ Lodging	12 one-day 3-person trips, ~100 miles each round trip (\$0.585/mile), meals @\$49/person	Visits to farms, conduct experiments on farms and industry collaborators sites		\$3,000
				Sub Total	\$3,000
Travel Outside Minnesota					
				Sub Total	-
Printing and Publication					
				Sub Total	-
Other Expenses					
				Sub Total	-
				Grand Total	\$499,000

## Classified Staff or Generally Ineligible Expenses

Category/Name	Subcategory or Type	Description	Justification Ineligible Expense or Classified Staff Request
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## Non ENRTF Funds

Category	Specific Source	Use	Status	Amount
State				
			State Sub	-
			Total	
Non-State				
			Non State	-
			Sub Total	
			Funds	-
			Total	

## Attachments

### **Required Attachments**

*Visual Component* File: <u>f0156bdb-a15.pdf</u>

#### Alternate Text for Visual Component

Figure 1 and 2 show how nitrate fertilizer generates and concentrates and the preliminary results. Catalytic non-thermal plasma (cNTP) provides an alternative way to ensure green synthesis of nitrate fertilizers efficiently. Nitrate is produced from water and air in an NTP reactor and then concentrated by an effective electrodialysis system....

### **Optional Attachments**

#### Support Letter or Other

Title	File
Financial audit	c0bec3bb-235.pdf
Institutional Approval to Submit	bb17e55d-c1f.pdf

### **Administrative Use**

Does your project include restoration or acquisition of land rights?

No

- Does your project have potential for royalties, copyrights, patents, or sale of products and assets? Yes
- Do you understand and acknowledge IP and revenue-return and sharing requirements in 116P.10? Yes
- Do you wish to request reinvestment of any revenues into your project instead of returning revenue to the ENRTF? No
- Does your project include original, hypothesis-driven research?

Yes

Does the organization have a fiscal agent for this project?

No

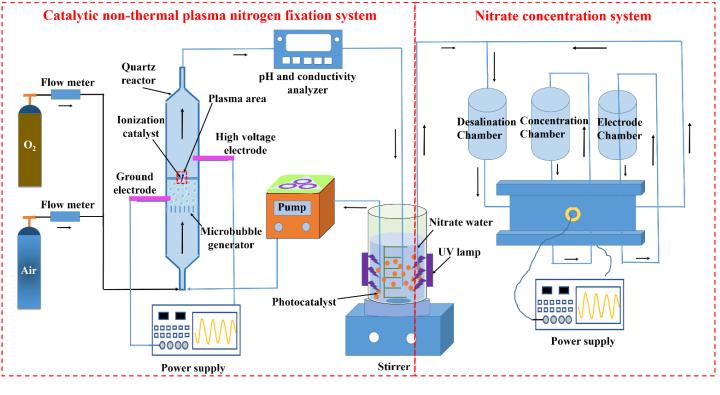


Figure 1 Schematic diagram of the integrated catalytic high-concentration nitrate production system

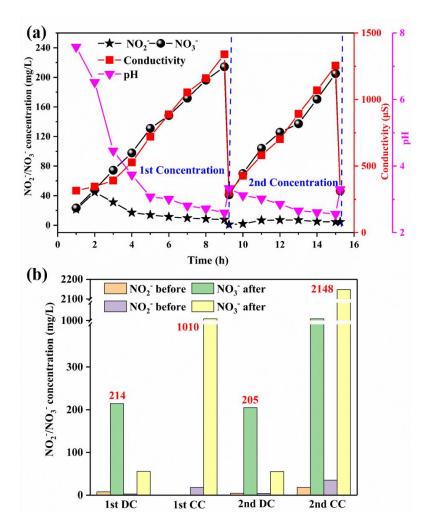


Figure 2 shows the preliminary results of integrated catalytic high-concentration nitrate production system. The catalytic non-thermal plasma system can effectively produce nitrate water, with over 200 mg/L in 6 h. And then the concentration system can rapidly enrich the nitrate concentration (from 205 mg/L to 2148 mg/L) in 15 min. After optimizing the processing parameters, we firmly believe that the technology can be a good alternative to produce the nitrogen fertilizer in a green and sustainable way.