



Environment and Natural Resources Trust Fund

2022 Request for Proposal

General Information

Proposal ID: 2022-054

Proposal Title: Nitrogen fixation and nitrate concentration for land crops

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: Develop a novel technology to produce high-concentration nitrogen fertilizers from water and air using catalytic non-thermal plasma coupled with a nitrate concentration system

Funds Requested: \$802,000

Proposed Project Completion: June 30 2025

LCCMR Funding Category: Air Quality, Climate Change, and Renewable Energy (E)

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 a large amount 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 is responsible for providing 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. 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. Therefore, it is highly sought to develop a green technology to produce high-concentration nitrate fertilizer.

What is your proposed solution to the problem or opportunity discussed above? i.e. What are you seeking funding to do? You will be asked to expand on this in Activities and 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 is concentrated with an electro dialysis 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 experimental catalytic NTP apparatuses 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, UV intensity, wavelength, etc., (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 and efficient production of high-concentration nitrate, 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, and reduce CO₂ emission, 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: \$223,124

Activity Description:

Catalysts play an important role during the plasma-based catalytic nitrogen fixation process, which involves three processes, namely nitrogen and oxygen dissociation, nitroxide oxidation and nitrite oxidation process. The catalysts not only can greatly lower the activation energy of the feedstock gas, but also oxidize the nitroxide or nitrite into nitrate, thus improving the nitrogen fixation efficiency and reducing the energy consumption. In this activity, we will first synthesize several nitrogen and oxygen dissociation catalysts, photocatalysts 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 nitrogen and oxygen dissociation, nitroxide 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 2022
The performance of catalysts will be investigated.	June 30 2023
New knowledge of catalytic mechanisms will be explored.	June 30 2023
The economic feasibility will be evaluated.	June 30 2023

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

Activity Budget: \$200,000

Activity Description:

The concept of synthesizing nitrogen compounds using cNPT has been proven in our preliminary studies. A new and cost effective nitrogen fixation system will be developed and we will study the processing parameters including feedstock gas, catalysts, electric field, and so on. In this activity, we will first develop a bench scale synthesis system that can house different types of NPT reactors and allow inclusion of catalysts. And then, the important parameters which greatly impacts nitrogen fixation efficiency will be studied, i.e. N₂/O₂ ratio, feeding gas flow rate, power input type, 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.	June 30 2024
New knowledge of the process works will be obtained	June 30 2024
Energy efficiency will be evaluated.	June 30 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 the 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 electroosmosis system, and optimize the main parameters (such as initial nitrate concentration, pH, voltage and temperature) and develop the control strategy of this system.

Activity Milestones:

Description	Completion Date
Some ion exchange membranes will be fabricated and characterized.	December 31 2024
The main parameters for the nitrate concentration system will be optimized.	December 31 2024
The control strategy of this system will be obtained.	December 31 2024

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

Activity Budget: \$278,876

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. After that, the mass and energy balance data together with emission data will be used to evaluate the environmental and economic performance using mathematics models. This evaluation will provide good assessment of the environmental impact of the proposed technology. Further R&D efforts and commercialization strategy will be recommended.

Activity Milestones:

Description	Completion Date
An integrated catalytic high-concentration nitrate production system will be developed.	June 30 2025
The energy efficiency, cost, and emission will be evaluated	June 30 2025
Environmental impacts will be assessed	June 30 2025
Further R&D and commercialization strategy will be recommended	June 30 2025

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 be funded?

New scientific knowledge on the feedstock breakdown and product synthesis during plasma-based catalytic nitrogen fixation process will be acquired through research, and the 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.

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. Roger Ruan, Professor and Director of Graduate Studies, Department of Bioproducts and Biosystems Engineering, and Director of Center for Biorefining at University of Minnesota, is a Fellow of ASABE and a Fellow of IFT. Dr. Ruan's research focuses on renewable energy and environment technologies for sustainable development and circular economy. Specifically, he has conducted research and published his findings in the areas of municipal, agricultural, and industrial wastewater treatment and utilization through novel anaerobic digestion, microalgae cultivation, and hydroponic cultivation, biomass and solid wastes (including plastics) pyrolysis and gasification, airborne and other pathogen disinfection and pollutant control, catalysis, non-thermal plasma, and nitrogen fixation, etc. He is a top-cited author with an h-index of 69, i10-index of 301, and over 19,000 citations. He has supervised over 75 graduate students, 140 post-doctors, research fellows, and other engineers and scientists, and 21 of his Ph.D. students and post-doctors hold university faculty positions. He has also been invited to give over 300 keynote lectures, invited symposium presentations, company seminars, and short courses. Professor Ruan has received and managed over 200 projects totaling over \$45 million in various funding for research, including major funding 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. His earlier LCCMR funded projects have resulted in several patented technologies which have been

successfully licensed to the industry. Therefore, 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. Ineligible	% Benefits	# FTE	Classified Staff?	\$ Amount
Personnel								
Professor/faculty		PI - 2 weeks summer salary			36.5%	0.12		\$30,285
Professor/faculty		Co-PI - contract faculty			36.5%	0.24		\$66,920
Two Graduate Research Assistants		Researchers			45%	3		\$301,902
Post Doctoral Reseracher		Research			25.4%	3		\$191,887
							Sub Total	\$590,994
Contracts and Services								
University of Minnesota	Internal services or fees (uncommon)	Lab services				0		\$15,000
equipment manufacturer	Professional or Technical Service Contract	Maintenance and repair				-		\$6,000
							Sub Total	\$21,000
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					\$150,000
	Tools and Supplies	Purchase of lab and miscellaneous supplies, including feedstock, catalysts, chemicals, consumable supplies for analytical instruments	For running experiments and operating conversion systems					\$37,570
							Sub Total	\$187,570
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 (\$0.56/mile), meals @\$49/person	Visits to farms, conduct experiments on farms and industry collaborators sites					\$2,436
							Sub Total	\$2,436
Travel Outside Minnesota								
							Sub Total	-
Printing and Publication								
							Sub Total	-
Other Expenses								
							Sub Total	-
							Grand Total	\$802,000

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

Optional Attachments

Support Letter or Other

Title	File
Institutional Authorization to Submit	09d105b0-de6.pdf
Visual graphic	43321dad-796.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

Catalytic non-thermal plasma nitrogen fixation system

Nitrate concentration system

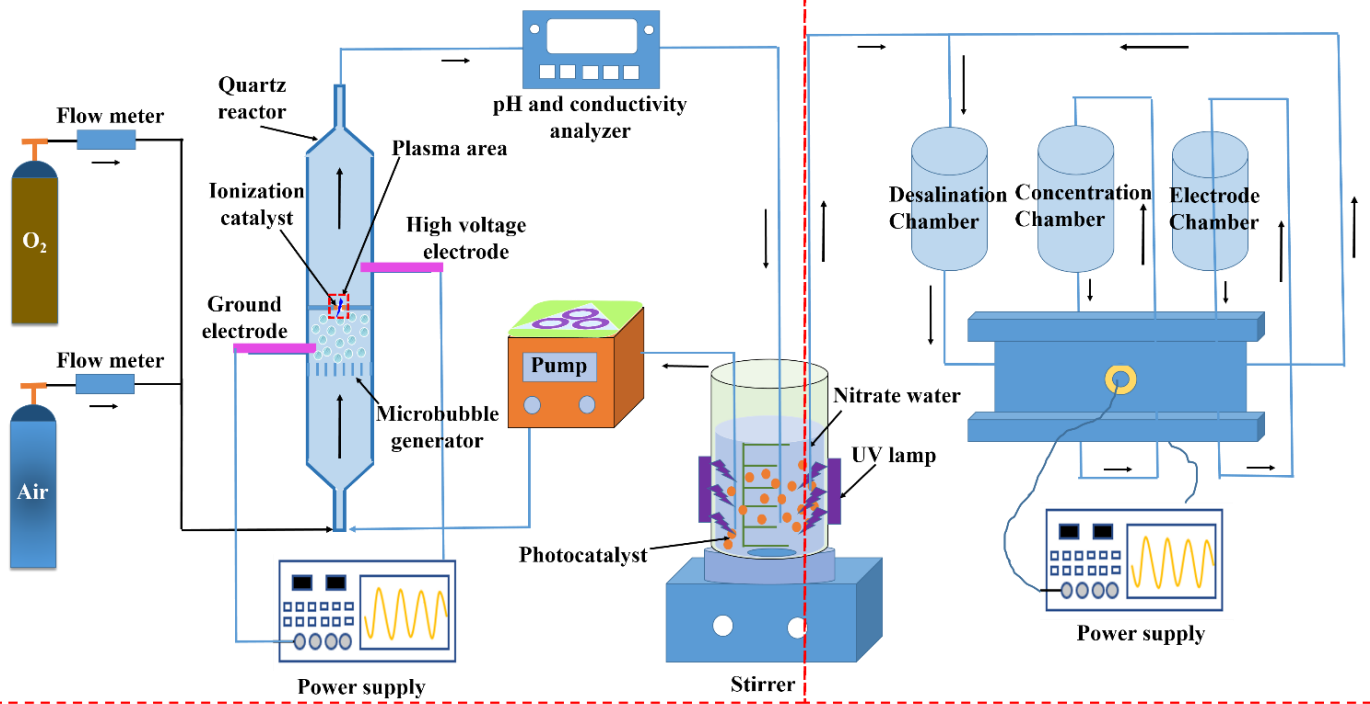


Figure 1 Schematic diagram of the integrated catalytic high-concentration nitrate production system

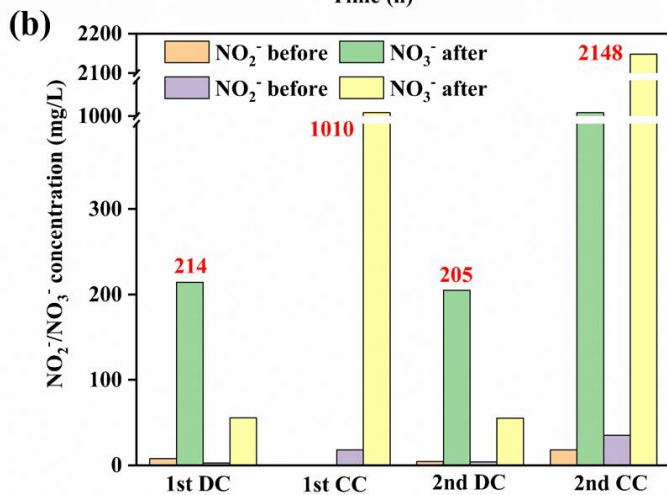
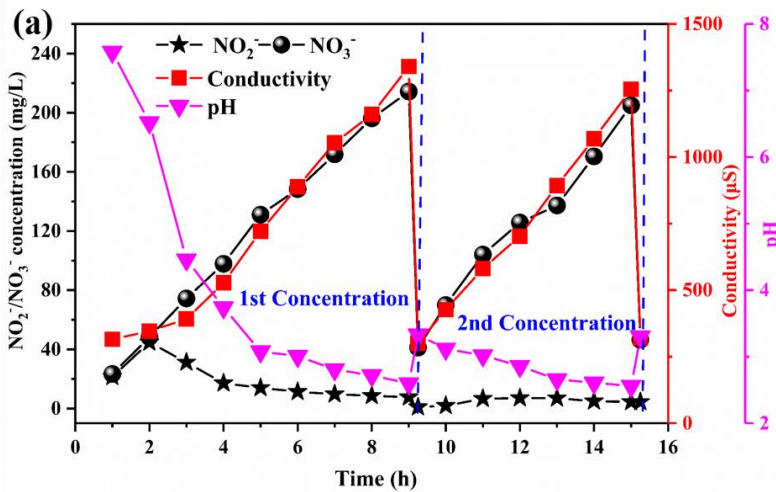


Figure 2 shows the preliminary results of integrated catalytic high-concentration nitrate production system. The catalytic non-thermal plasma system can effectively produce nitrate water, with over 200 mg/L in 6 h. And then the concentration system can rapidly enrich the nitrate concentration (from 205 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.