Environment and Natural Resources Trust Fund

2024 Request for Proposal

General Information

Proposal ID: 2024-080

Proposal Title: Capturing and Converting Carbon Dioxide from Flue Gas

Project Manager Information

Name: Hua Zhao

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

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Project Basic Information

Project Summary: This project aims to develop a green and effective route for carbon dioxide capture and conversion, especially from flue gases generated by various industries in Minnesota.

Funds Requested: $505,000

Proposed Project Completion: June 30, 2027

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?

Region(s): Metro

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.

In 2020, >137 million tons of CO_2-equivalent greenhouse gases (GHG) were produced in Minnesota including 26.3% from transportation, 20.9% from crops and animal agriculture and oil, 19.1% from electricity generation, 14.8% from industries, and 10.7% from commercial sources (GHG emissions data, Tableau Public). Flue gases from power plants and industrial operations account for 33.9% of all GHG released to the atmosphere in Minnesota. In 2022, all power plants in Minnesota emitted over 22.8 million tons of carbon dioxide (CO_2), 82% of which was generated by four coal power plants (EPA data). State regulators have approved the Minnesota Power plan to retire coal by 2035, and add renewables over next 15 years. As a major GHG, increasing CO_2 release to air is a major contributor to the climate change in Minnesota and around the globe.

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.

Flue gas contains ~12-14 vol% CO_2 from coal-fired power plants and around 3-4 vol% from a natural gas turbine. CO_2 has a poor solubility in water (2.9 g/L at 25 °C). Conventional chemical absorption of CO_2 using amine solutions (e.g., monoethanolamine) are effective but have several drawbacks including equipment corrosion, amine volatility, high construction cost, amine degradation, and high energy for absorbent regeneration.

Our goal is to develop a green and effective route for CO_2 capture and conversion. We plan to capture CO_2 and particulate matter (PM) by environmentally benign solvent systems under ambient conditions, followed by a conversion to a baking-soda-salt known as bicarbonate using an enzyme called carbonic anhydrase (see Visual Component). This enzyme is found in human lung and all living creatures for catalyzing very fast, reversible hydration of CO_2 during breathing. Bicarbonate becomes a solid carrier for CO_2 storage and is a valuable chemical for many applications. In addition, CO_2 could be released from bicarbonate by carbonic anhydrase when needed to produce valuable commodities such as methanol.

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 successful completion of this project will enable a green and robust method for capturing CO_2 and particulate matter from flue gas generated by various manufacturing and production industries in Minnesota. Furthermore, captured CO_2 will be converted to bicarbonate via an enzyme. The implementation of this project will greatly reduce the GHG and particulate matter releases to the environment, improve the air quality, produce a valuable chemical, and minimize the carbon footprint of these industries in Minnesota.

Activities and Milestones

Activity 1: Design environmentally benign solvent systems to capture a high concentration of CO_2 and remove particulate matter (PM)

Activity Budget: $165,814

Activity Description:
We will investigate aqueous solutions of inexpensive poly(ethylene glycol)s (PEGs), PEG amines and choline chloride-based salts and deep eutectic mixtures to dissolve a high concentration of CO_2 (> 10 wt%) under ambient conditions. Past studies used high pressure (>10 bar) to dissolve CO_2, but we will target atmospheric pressure to reduce the equipment and energy costs. We hypothesize that functional groups in solvents allow strong CO_2-solvent interactions to promote CO_2 solubilization. PEGs have low cost, negligible vapor pressure, high chemical/thermal stability, low toxicity, and high CO_2 affinity. PEG amines have amine groups that bind with CO_2. Choline chloride (i.e., vitamin B4) is used as an additive in chicken feed, and as an essential micronutrient for humans. Choline chloride mixtures with glycerol or glycols could form 'deep eutectic solvents' that are capable of dissolving CO_2. An amino acid salt of choline chloride, choline prolinate, is a green salt that can solubilize CO_2 in aqueous solutions.

In addition to examining various aqueous mixtures at different concentrations for CO_2 solubility at ambient conditions, we will also study how effectively these solutions can entrap particulate matter from flue gas and how particulate matter can be filtered off the solutions.

Activity Milestones:

Description	Approximate Completion Date
Prepare environmentally benign solvent systems	December 31, 2024
Determine CO_2 solubility	June 30, 2025
Measure the amount of particulate matter in solvent systems	June 30, 2025

Activity 2: Develop enzyme mutants of carbonic anhydrase that are more efficient for CO_2 conversion and more tolerant to solvent systems

Activity Budget: $168,258

Activity Description:
Processes that convert CO_2 into the ions bicarbonate (HCO_3^-) and carbonate through the action of the enzyme carbonic anhydrase are well established in the literature, and biological enzymes that perform this reaction are among the most efficient enzymes known. In some cases, these processes lead to the formation of insoluble carbonates, such as calcium carbonate ($CaCO_3$), which is more commonly known as limestone. Other ions can also be used to precipitate the carbonate. We plan to produce carbonic anhydrase mutants by modifying surface residues so the enzyme is more tolerant to ions and organic solutes.

We will further use spectroscopic tools including infrared, fluorescence emission spectra, and far-UV circular dichroism (CD) spectroscopy to probe enzyme structural changes. Dr. Gary Baker at University of Missouri will assist with the interpretation of these spectra (no cost to this project). Dr. Katie Mitchell-Koch at Wichita State University will assist us with molecular dynamics (MD) simulations of CO_2-solvent system interactions, and enzyme interactions with solvent systems and CO_2 (no cost to this project). This will enable a molecular-level understanding of how carbonic anhydrase interacts with the substrate (CO_2) and solvent molecules.

Activity Milestones:

Description	Approximate Completion Date
Develop systems to produce high yields of active extracellular alkaline carbonic anhydrase	December 31, 2024
Identify ideal water/solvent systems to enhance the precipitation of carbonates and bicarbonates	December 31, 2025
Engineer enzyme mutants by modifying enzyme's surface residues	June 30, 2027
Spectroscopic and MD simulations studies of enzyme structures under different solvent systems	June 30, 2027

Activity 3: Construct a continuous process for CO2 capture and conversion

Activity Budget: $170,928

Activity Description:
To improve the enzyme stability and recyclability, we will immobilize the enzyme (carbonic anhydrase) on solid carriers such as silica sol-gel matrices, chitosan, and polystyrene beads, and compare the residual enzyme activity and stability after the immobilization.

We will design a laboratory-scale and later pilot-scale stirred tank reactor for CO2 capture, followed by a continuous flow reactor packed with an immobilized enzyme to capture and convert CO2 on a continuous basis. This will allow future process being scaled-up for industrial applications.

We will demonstrate the capture of flue gases from a power plant and a brewery respectively, and run pilot tests using our capture-conversion reaction system. These pilot testing will provide valuable data for future large-scale CO2 capture and conversion.

Activity Milestones:

Description	Approximate Completion Date
Design a stirred tank reaction for CO2 capture	December 31, 2026
Investigate different methods for enzyme immobilization	February 28, 2027
Design a continuous packed-bed reactor for CO2 conversion	June 30, 2027

Project Partners and Collaborators

Name	Organization	Role	Receiving Funds
Gary Baker	University of Missouri	Assisting with enzyme spectroscopic data analysis	No
Katie Mitchell-Koch	Wichita State University	Molecular dynamics simulations of enzyme interactions with CO2 and solvent molecules	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?

Zhao, Barney and their graduate students will lead research design and experiments to implement proposed activities. Their collaborators on this project will be funded by different sources for their efforts. Results generated in this project will enable a fundamental understanding of interactions between CO2, solvents and enzymes. These preliminary data will allow us to acquire a larger Department of Energy (DOE) grant that involve multiple institutions to tackle a much bigger scale of the carbon capture, sequestration, and utilization (CCSU). Our goal is in line with the DOE's Carbon Negative Shot objective by providing CO2 capture, storage, and conversion systems.

Project Manager and Organization Qualifications

Project Manager Name: Hua Zhao

Job Title: Professor and Head

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

PI Dr. Hua Zhao is a professor and department head in the Department of Bioproducts and Biosystems Engineering at University of Minnesota. He has been working on biocatalysis and renewable fuels (such as cellulosic ethanol and biodiesel) for the past 20 years since he was a chemical engineering Ph.D. student at New Jersey Institute of Technology and a postdoctoral researcher at Rutgers University. He received a combined training and preparations in chemical engineering, chemistry and food science. He has led multiple research and student research training projects funded by National Science Foundation (NSF), National Institutes of Health (NIH), and American Chemical Society – Petroleum Research Fund (ACS-PRF). His current and past projects include enzymatic catalysis for the synthesis of biosurfactants, new asymmetric medicinal molecules, and biopolymers, as well as enzymatic coal treatment, desulfurization of liquid fuels, and DNA-base hybrid catalysis.

Co-PI Dr. Brett Barney is a professor in the Department of Bioproducts and Biosystems Engineering and a member of the Biotechnology Institute at the University of Minnesota. Dr. Barney's laboratory is focused on minimizing the environmental impacts associated with biofuels and agriculture, and finding innovative methods to capture and sequester CO2. Dr. Barney has 30 years of experience in both basic and applied research in both academia and industry, including experience managing projects and laboratories in a range of settings. Previous research funding has come from the National Science Foundation (NSF), the United States Department of Agriculture (USDA), the United States Department of Energy (DOE), the Defense Advanced Research Projects Agency (DARPA), the Legislative-Citizen Commission on Minnesota Resources (LCCMR), Minnesota's Discover, Research and InnoVation Economy (MnDRIVE) and the Initiative for Renewable Energy and the Environment (IREE).

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

Organization Description:

In the College of Food, Agricultural and Natural Resources Sciences (CFANS) at the University of Minnesota, we look at the bigger picture. When we envision a better tomorrow, it includes disease-resistant crops, products that protect our health, lakes free from invasive species, and so much more. We use science to find answers to Minnesota and the world's grand challenges and solve tomorrow's problems. Almost 93 percent of students who earn CFANS undergraduate degrees find jobs in their career field or enter graduate school within six months of graduation.

The Department of Bioproducts and Biosystems Engineering, in CFANS, discovers and teaches solutions for the sustainable use of renewable resources and the enhancement of the environment. We discover innovative solutions to address challenges in the sustainable production and consumption of food, feed, fiber, materials, and chemicals by integrating engineering, science, technology, and management into all degree programs.

We have a public impact through community engagement and extension efforts. We develop and deliver high quality, regionally and nationally-recognized research-based programs to meet current and emerging needs of industry and communities. We also have a long-standing tradition of close partnerships with alumni, industry professionals, organizations, government agencies, donors, and community members.

Budget Summary

Category / Name	Subcategory or Type	Description	Purpose	Gen. Ineli gible	% Bene fits	# FTE	Class ified Staff?	$ Amount
Personnel								
Two graduate students		Research design and conduct experiments as proposed			46.2%	6		$323,728
Two undergraduate students		Receive research training and collect experimental data			0%	1.14		$45,000
Dr. Brett Barney, co-PI		Mentor students to develop enzyme carbonic anhydrase and its mutants			36.8%	0.75		$33,827
							Sub Total	**$402,555**
Contracts and Services								
							Sub Total	-
Equipment, Tools, and Supplies								
	Tools and Supplies	Funds ($20,000 in Year 1, $20,000 in Year 2, and $20,175 in Year 3) are requested to purchase laboratory chemicals (PEGs, PEG amines, and choline chloride-based salts), reagents (acetone, methanol, and HPLC-grade water), enzymes (carbonic anhydrase, formate dehydrogenase, formaldehyde dehydrogenase, alcohol dehydrogenase, glucose dehydrogenase), media, and reagents ($400 per month), and kits for performing routine molecular biology ($400 per kit), analytical reagents, DNA synthesis of primers ($100 per month), liquid nitrogen for strain storage ($400 per year).	These chemicals and enzymes are needed to carry out the proposed experimental work.					$60,175
							Sub Total	**$60,175**
Capital Expenditures								
							Sub Total	-

Acquisitions and Stewardship								
							Sub Total	**-**
Travel In Minnesota								
	Conference Registration Miles/ Meals/ Lodging	One conference trip per year for PI and two students per year, $150 registration per person ($450 total per year), 200 miles per year ($120), lodging for 3 persons and 2 nights ($900), and meals ($620 for 3 persons, two days per year)	PI and two students each year will present and share research results in in-state conferences, and network with peers.					$6,270
							Sub Total	**$6,270**
Travel Outside Minnesota								
							Sub Total	**-**
Printing and Publication								
	Publication	Open-access journal publication cost	Publish research results in open-access journal, about $2,000 per year for one paper					$6,000
							Sub Total	**$6,000**
Other Expenses								
		Protein sample analysis by infrared, fluorescence emission spectra, and far-UV circular dichroism (CD) spectroscopy	The spectroscopic data will enable us to know the enzyme-solvent molecules interactions at microscopic level. These measurements require specific instruments.					$30,000
							Sub Total	**$30,000**
							Grand Total	**$505,000**

Classified Staff or Generally Ineligible Expenses

Category/Name	Subcategory or Type	Description	Justification Ineligible Expense or Classified Staff Request

Non ENRTF Funds

Category	Specific Source	Use	Status	Amount
State				
			State Sub Total	**-**
Non-State				
In-Kind	Both state allocation from legislature and non-state tuition, fees, etc.	Facilities and Administration (hr, finance, purchasing) involved in proposal execution at 2023 55% Federally Negotiated Rate	Secured	$218,494
			Non State Sub Total	**$218,494**
			Funds Total	**$218,494**

Attachments

Required Attachments

Visual Component

File: 1cfd5528-188.docx

Alternate Text for Visual Component

The top graph (part a) shows carbon dioxide from flue gas is converted to bicarbonate (baking soda salt) in a solvent system via an enzyme called carbonic anhydrase. The bottom graph (part b) shows a stirred tank reactor for CO2 capture and a packed-bed reactor for CO2 conversion....

Optional Attachments

Support Letter, Photos, Media, Other

Title	File
Authorization from UM sponsored projects office	9f26d9b4-ff9.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

Does your project include the design, construction, or renovation of a building, trail, campground, or other capital asset costing $10,000 or more?

No

Do you propose using an appropriation from the Environment and Natural Resources Trust Fund to conduct a project that provides children's services, as defined in Minnesota Statutes section 299C.61 Subd.7?

No