Environment and Natural Resources Trust Fund

2022 Request for Proposal

General Information

Proposal ID: 2022-052

Proposal Title: Produce carbon nanotube and hydrogen from waste plastics

Project Manager Information

Name: Roger Ruan

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

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Project Basic Information

Project Summary: Develop a catalytic chemical vapor deposition (cCVD) technology to produce high quality carbon nanotubes (CNTs) and hydrogen from non-condensable pyrolytic gas recovered from waste plastic pyrolysis.

Funds Requested: $200,000

Proposed Project Completion: June 30 2025

LCCMR Funding Category: Small Projects (H)

Secondary 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.

Over 3 million tons of municipal solid waste generated in Minnesota are disposed every year, and plastics contribute around 20%. Currently, the most common solution to recycle the plastic waste is thermomechanical processing that is constrained by many challenges. The recycled plastics after melting and remolding have poorer properties than those of the virgin plastics, limiting the recycled plastics to lower quality products. This downcycling process makes the waste plastic recovery financially unattractive in the industry. Pyrolysis technology can convert waste plastics to value-added transportation fuels or chemicals, addressing the challenges of waste plastic management and increasing global energy demand simultaneously. It has been regarded as the most promising technology for waste plastic upcycling. However, the 35-45% non-condensable gas produced from plastic pyrolysis is generally burned for heat or electricity, causing serious greenhouse gas emission. Therefore, a clean and promising approach to recover the non-condensable gas for valuable products is highly sought after from both climate change and economic standpoints.

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.

In previous testing, we have seen highly encouraging results using certain catalysts in conjunction with the catalytic microwave assisted pyrolysis (CMAP) technology to produce naphtha as feedstock for new plastic manufacturing, with ~40 wt.% non-condensable gas (mainly composed of hydrogen, C1-C4 hydrocarbon) being left to be treated. Here, the proposed high temperature catalytic vapor deposition technology is designed to convert non-condensable gas to high quality CNTs and hydrogen, with the hope of improving the economic potential of plastic-to-fuels/chemicals technology and minimizing greenhouse gas emission in mind. In a nutshell, the proposed technology uses the novel porous metal oxides as coating material to catalytically decarburize the non-condensable gases for high quality CNTs and hydrogen production.

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 outcomes will include designing promising catalysts and optimizing the process for higher quality CNTs, the development of a structured catalytic reactor for CNTs growth, and cost-effective CNTs separation and purification. These outcomes will move our plastic-to-naphtha, CNTs, and hydrogen technology closer to commercial implementation, which will help will provide a sustainable way to utilize waste plastics, improve financial outlook of the plastic waste recycling industry, reduce fossil energy demand and CO2 emission, and thus reduce environmental impacts of plastic waste recycling industry.

Activities and Milestones

Activity 1: To develop promising catalysts and optimize the CVD process

Activity Budget: $75,000

Activity Description:

Our approach for waste plastic recycling is to convert waste plastics to naphtha for new plastic manufacturing and non-condensable gas by pyrolysis-catalysis. In this activity, the non-condensable pyrolysis gases containing abundant carbon sources (CH4 and C1-C4 hydrocarbons) will be introduced into a high temperature chemical vapor deposition process for CNTs production. After element carbon is consumed, the residual gas would be mainly composed of hydrogen. A wide variety of existing metal oxides, such as Ni, Co, Fe, Cu, will be tested for producing high performance CNTs and hydrogen. To improve the CNTs yield and quality, the bi/multifunctional metal oxides will be designed. The focus will be on how to increase the surface area, tailor the pore structure, and improve the metal dispersion of metal oxides by different techniques, such as sol-gel, impregnation, atomic vapor deposition, and hard template methods. The improvement of the cCVD process will be realized through processing parameter optimization such as gas composition, temperature, and residence time.

Activity Milestones:

Description	Completion Date
Screening the existing catalysts	December 31 2022
New bi/multifunctional metal oxides will be prepared, characterized, and tested	October 31 2023
CVD process will be optimized	March 31 2024

Activity 2: To develop a microwave-assisted structured CVD reactor for CNTs growth

Activity Budget: $85,000

Activity Description:

Structured catalysts will be employed in order to alleviate limitations associated with conventional catalytic reactors such as the high pressure drop, inefficient mass and heat transfer, and weak mechanical strength. In this activity, we will use SiC foam structure as a catalyst bed on which selected catalysts are loaded, and raise and maintain catalysis reaction temperatures using microwaves. A microwave-assisted structured cCVD reactor for CNTs growth will also be developed and improved. Various techniques such as dip-coating and in-situ hydrothermal synthesis will be improved to optimize the loading of the newly developed catalyst materials onto the SiC foam structures. Fundamental operational parameters of the reactor including space velocity and residence time will be fine-tuned to achieve the best catalytic activity.

Activity Milestones:

Description	Completion Date
Microwave-assisted structured CVD reactor will be developed and improved	June 30 2024
Structured catalysts will be developed and tested	December 31 2024
Fundamental operational parameters will be fine-tuned	December 31 2024

Activity 3: CNTs separation and purification

Activity Budget: $40,000

Activity Description:

CNTs grown on the structured catalysts will be exfoliated by acid washing and then separated by centrifugation. The acid

type and concentration will be optimized. Based on the microwave-assisted cCVD process, heterogeneous samples containing CNTs as well as other carbonaceous contaminants will be produced. However, many valuable applications, such as transparent conductors, biosensors, and nano-electronics, require individualized CNTs with high purity. We attempt to purify CNTs via high temperature oxidation of amorphous carbons and the effects of oxygen concentration, temperature, and oxidation time will be investigated. Overall, a practical separation and purification protocol will be developed and improved.

Activity Milestones:

Description	Completion Date
The CNTs separation protocol will be developed and improved	March 31 2025
The CNTs purification protocol will be developed and improved	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?

The waste plastics-to-naphtha technology is very promising, and many major companies are extremely interested in it. We are closely collaborated with several of them and they have provided some financial and other support for our preliminary work. More new scientific knowledge on recovery of non-condensable pyrolytic gas for CNTs, and hydrogen production acquired through research will significantly improve the economic potential of this technology and reduce the greenhouse gas emission. More grants would be obtained from industry partners and private, state, and federal government to further develop and eventually commercialize the plastic-to-naphtha, CNTs, and hydrogen 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 - 9 month appointment - summer salary requested		PI			36.5%	0.12		$23,622
Professor/faculty - contract appointment		Co-PI			36.5%	0.24		$33,460
1 Graduate Research Assistant		Researcher			45%	2.25		$126,289
							Sub Total	**$183,371**
Contracts and Services								
University of Minnesota	Internal services or fees (uncommon)	Lab analytical and characterization services				0		$5,000
							Sub Total	**$5,000**
Equipment, Tools, and Supplies								
	Tools and Supplies	Purchase raw materials, catalysts, chemicals for analysis, external analytical service.	For setting up a catalytic reactors and conducting proposed experiments in labs					$10,243
							Sub Total	**$10,243**
Capital Expenditures								
							Sub Total	**-**
Acquisitions and Stewardship								

							Sub Total	**-**
Travel In Minnesota								
	Miles/ Meals/ Lodging	9 one-day 2-person trips, 100 miles each round trip ($0.56/mile), meals @$49/person	Visit to industry collaborator sites and conduct on-site tests					$1,386
							Sub Total	**$1,386**
Travel Outside Minnesota								
							Sub Total	**-**
Printing and Publication								
							Sub Total	**-**
Other Expenses								
							Sub Total	**-**
							Grand Total	**$200,000**

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				
			Non State Sub Total	**-**
			Funds Total	**-**

Attachments

Required Attachments

Optional Attachments

Support Letter or Other

Title	File
Institutional Approval to Submit	aa2ed89d-537.pdf
Visual graphic	b24e59ad-e09.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

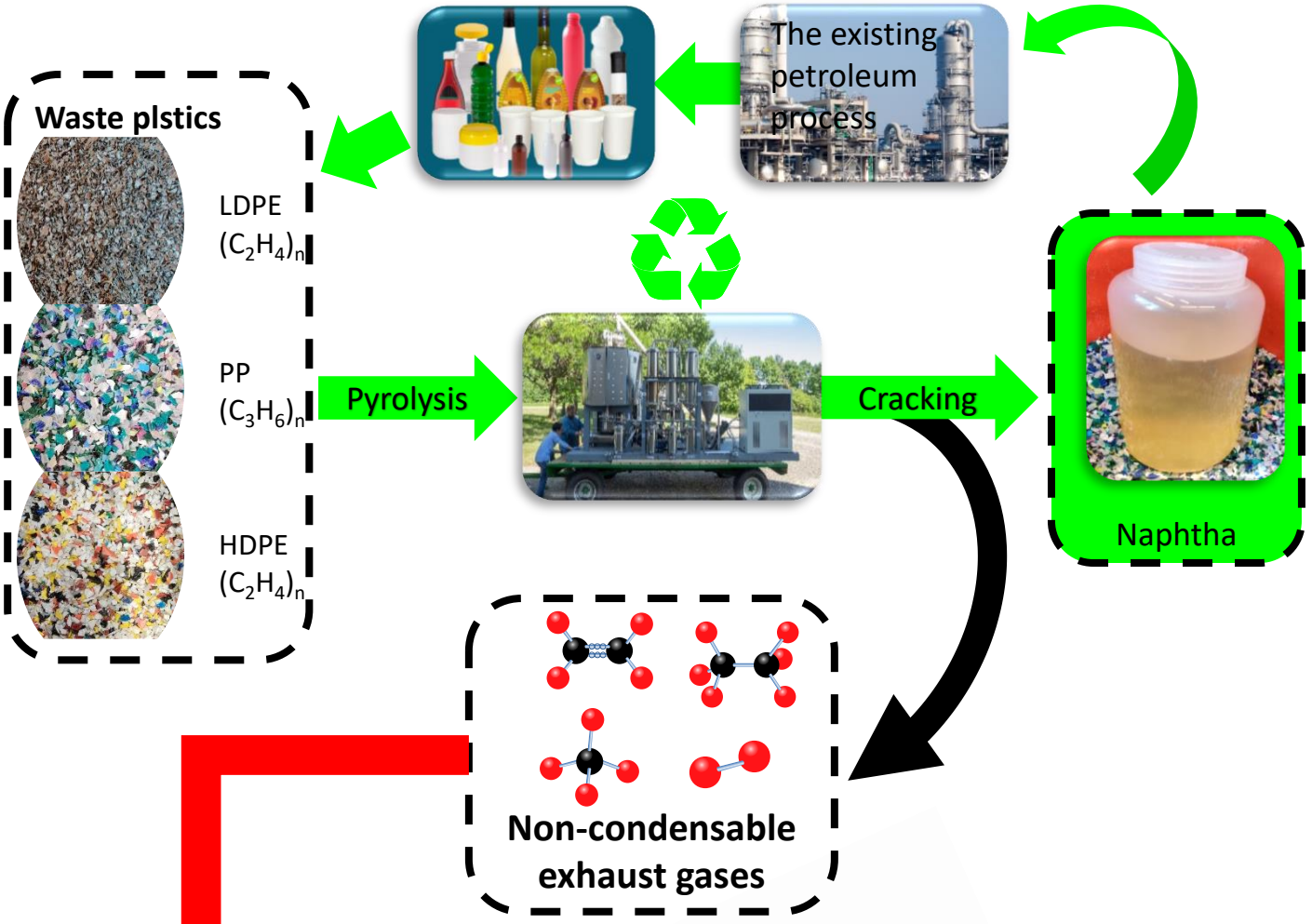
Does your project include original, hypothesis-driven research?

Yes

Does the organization have a fiscal agent for this project?

No

Converting non-condensable pyrolytic gas to carbon nanotubes and hydrogen



Chemical Vapor Deposition Process