



Environment and Natural Resources Trust Fund

2021 Request for Proposal

General Information

Proposal ID: 2021-347

Proposal Title: Renewable and Green Polymers from Pennycress

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 novel technology to convert pennycress straw and oil into polyols for making renewable and green polymers such as biopolyurethane.

Funds Requested: \$559,000

Proposed Project Completion: 2024-06-30

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.

Polyurethane (PU) is the fifth largest plastic in the world, which is widely used in medical, aviation, spinning, chemicals, and automobiles on account of its outstanding properties of stability, chemical resistance, resilience and mechanical. The worldwide PU consumption was about 60.5 billion USD in 2017, and it is estimated to be over 79 billion USD by 2021. In general, PU is produced by using polyols and isocyanate via polymerization reaction. As one of the primary ingredients, polyols are originated from petrochemical origin. However, the petroleum-based PU is hardly biodegradable and has negative impact on the environment. More importantly, petroleum is a non-renewable resource, and thus the petroleum-based PU production is unsustainable in the long term. Therefore, it is urgent to select a renewable material to replace the petroleum polyols, and satisfy the demand for green polymers.

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.

Pennycress is an oil crop, which is rapidly being domesticated as a third crop to be grown between the corn harvest and the soybean establishment in the following year, and hence it has a great economic value, in addition to providing important ecosystem services, e.g., reducing soil erosion and unused nutrients contaminating water, etc. Overall, the harvested pennycress could be divided into two part: straw (PS) and oil (PO). PS is mainly comprised of cellulose, semi-cellulose, and lignin. PO is consisted of triacylglycerols (TAGs), especially the unsaturated fatty acid, which could be transformed into epoxidized PO through epoxidation reaction in the presence of peroxy acid. On this basis, epoxidized PO could be further converted into polyols via ring-opening reaction. Non-thermal plasma (NTP) is demonstrated to be efficient in oxidation, which is supposed to reduce the usage of peroxy acid materials.

The PS can be transformed into polyols via liquefaction using liquefacients like polyethylene glycol and glycerol at high temperature and concentrated sulfuric acid. However, the downstream purification would generate wastewater. Due to the strong polarity of hydroxy, liquefacients are naturally characterized with excellent microwave absorbing ability. Hence, microwave is expected to replace the traditional heating thereby reducing energy consumption.

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?

Our project is expected to enable the conversion of pennycress straw and oil to biopolymers and adding value to pennycress planting operation. This will on the one hand produce renewable and green materials alternative to fossil based products, and on the other hand make pennycress planting profitable, which can help promote this rapid cycling winter cover crop providing crucial environmental services including nutrient scavenging, weed suppression, soil erosion protection and runoff reduction.

Activities and Milestones

Activity 1: Pennycress straw liquefaction in the presence of microwave

Activity Budget: \$284,000

Activity Description:

The concentrated sulfuric acid is commonly used as catalyst in traditional liquefaction process. A concern is that not only the sulfuric acid cannot be reused, but also the products purification would generate wastewater. Hence, high efficient solid acids will be employed as catalyst in pennycress straw (PS) liquefaction. Furthermore, owing to the strong polarity of liquefacient, microwave could be utilized to enhance the PS liquefaction and reduce the energy consumption. Therefore, the effects of catalyst type, solid-to-liquid ratio, liquefacient amount, reaction temperature, microwave power, microwave time on the polyols yield and quality will be studied. Furthermore, dielectric properties of dielectric constant (ϵ), loss factor ($\tan\delta$), and penetration depth (D_p) will be evaluated to reveal the microwave absorbing characteristic of the mixed reactants. Based on that, the relationship between microwave absorbing property of reactants and polyols yields will be revealed. These designed experiment are expected to offer us the basic information and data to build up a continuous PS liquefaction equipment.

Activity Milestones:

Description	Completion Date
Screen solid acid catalyst	2023-03-31
Optimize of pennycress straw liquefaction	2023-06-30
Evaluate dielectric property and reveal microwave absorbing characteristic	2023-12-31
Set up the continuous PS liquefaction equipment	2024-06-30

Activity 2: Epoxidization of pennycress oil with the aid of plasma and conversion to polyols

Activity Budget: \$275,000

Activity Description:

According to the reported data, pennycress oil (PO) is rich in unsaturated fatty acid, in which the C=C could be epoxidized (POE) in the presence of peroxy acid. To obtain the peroxy acid, hydrogen peroxide and formic acid are required to be added into the reaction system. In order to obtain the optimized conditions, the effect of temperature, residue time, ratio of catalyst, H₂O₂ amount, formic acid amount on the epoxidation conversion will be studied. With that, plasma is used to reduce the usage of peroxy acid materials and the catalytic activity of plasma will be further elucidated. The obtained POE will be converted into polyols via the ring-opening reaction, in which the epoxy -O- in POE is protonized with acid catalyst. Moreover, effects of molar ratio of POE to sorbitol, catalyst dosage, reaction temperature, and time on polyols yield are evaluated, especially the relationship between catalyst structure and polyols yield will be illuminated. Above all, the optimized parameters would be used to construct the large scale trial system for evaluation of commercial potential.

Activity Milestones:

Description	Completion Date
Investigation of pennycress oil epoxidization process	2021-12-31
Plasma device construction and catalytic mechanism elucidation	2022-03-31
Optimization of POE ring-opening process	2022-06-30
Set up pilot reaction system combining epoxidation and ring-opening reaction	2022-12-31

Project Partners and Collaborators

Name	Organization	Role	Receiving Funds
Yanling Cheng	University of Minnesota	co-PI	No
Paul Chen	University of Minnesota	co-PI	Yes

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 and experience on polyols production from pennycress assisted by microwave and non-thermal plasma will be obtained through this project. The processes of liquefaction and epoxy-open

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, Center for Biorefining and Department of Bioproducts and Biosystems Engineering, University of Minnesota, Fellow of ASABE and Fellow of IFT, is the project manager of the proposed project. Dr. Ruan's research focuses on renewable energy technologies, solid and liquid waste treatment and utilization, and environmental engineering. 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) gasification and pyrolysis, airborne pathogen disinfection, catalysis, non-thermal plasma, ammonia synthesis, etc. He is a top-cited author in the area of agricultural and biological sciences with an h-index of 63, i10-index of 255, and over 15,400 citations, and has received over 180 projects totaling over \$45 million in various funding for research, including major funding from USDA, DOE, DOT, DOD, LCCMR, and industries. He was the project manager of several earlier LCCMR funded projects which resulted in the issuance of a US patent and licensing of a technology. Therefore he has the technical expertise and project management experience to ensure the execution of proposed projects.

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

Organization Description:

The Center for Biorefining is a University of Minnesota research center and help coordinate the University efforts and resources to conduct exploratory fundamental and applied research; provide education on bioenergy, biochemicals and biomaterials; 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 funded 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								
Paul Chen		Co-Principal Investigator			36.5%	0.48		\$64,621
Roger Ruan		Principal Investigator			36.5%	0.12		\$24,328
Post Doc		Researcher			25.4%	3		\$193,799
Graduate Research Assistant		Research Assistant			45%	1.5		\$150,933
							Sub Total	\$433,681
Contracts and Services								
							Sub Total	-
Equipment, Tools, and Supplies								
	Tools and Supplies	Materials and lab supplies including chemicals for analysis, liquefaction agents, catalysts, consumable supplies for analytical instruments, thermocouples, glassware, etc.	For running experiments and operating the systems					\$19,319
	Equipment	Components for fabrication of experimental apparatus, including NTP reactors, power supply, microwave magnetrons, microwave guide, mixer, tanks, pumps, control, etc.	To fabricate experimental apparatus and small system for running experiments, conducting performance analysis, and demonstration					\$100,000
							Sub Total	\$119,319
Capital Expenditures								
							Sub Total	-
Acquisitions and Stewardship								
							Sub Total	-

Travel In Minnesota								
							Sub Total	-
Travel Outside Minnesota								
							Sub Total	-
Printing and Publication								
							Sub Total	-
Other Expenses								
		Repairs and Maintenance	Repairs and Maintenance of analytical instruments					\$6,000
							Sub Total	\$6,000
							Grand Total	\$559,000

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: [4a5fe19c-b09.pdf](#)

Alternate Text for Visual Component

- 1) Issues with current production and use of polyurethane
- 2) Pennycress as an oil crop
- 3) Our approach to utilization of Pennycress oil and biomass
- 4) Expected outcomes of the project

Optional Attachments

Support Letter or Other

Title	File
UMN authorization letter	87510dbb-096.pdf
UMN financial audit report	581e4deb-171.pdf

Administrative Use

Does your project include restoration or acquisition of land rights?

No

Does your project have patent, royalties, or revenue potential?

Yes,

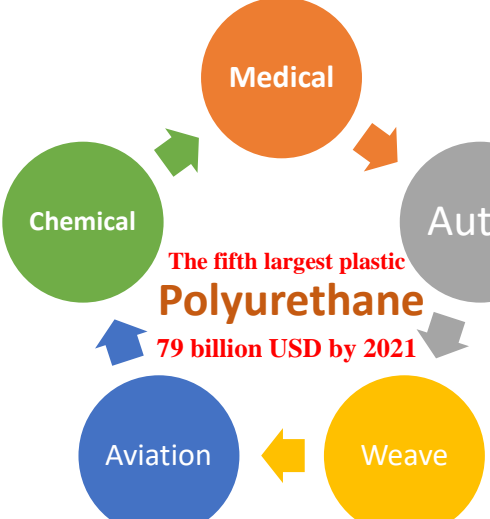
- Patent, Copyright, or Royalty Potential

Does your project include research?

Yes

Does the organization have a fiscal agent for this project?

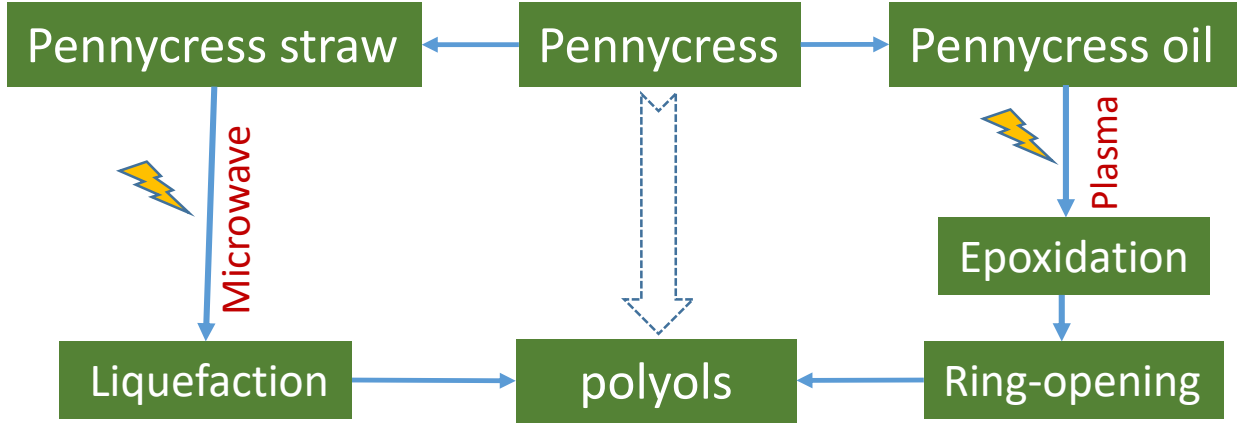
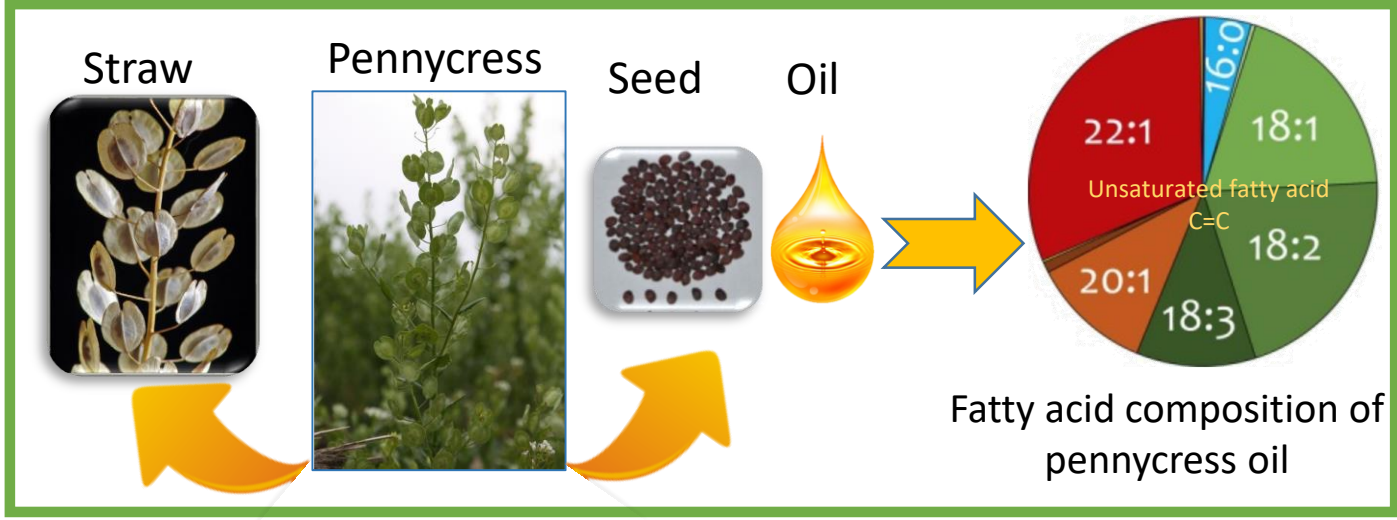
No



Disadvantages

Gradients are non-renewable

Deposition is non-biodegradable



Outcome of the Project

- Pennycress oil epoxidized with the aid of plasma and conversion to polyols
- Pennycress straw liquefaction in the presence of microwave for polyols production
- Stakeholders will be presented with the research findings and recommendations for further actions
- The research findings will be used for seeking industrial partnerships and external funds for further R & D efforts