M.L. 2019 ENRTF Project Abstract
For the Period Ending June 30, 2023

PROJECT TITLE: Sustainable Solar Energy from Agricultural Plant Byproducts
PROJECT MANAGER: Ted Pappenfus
AFFILIATION: Morris Campus (Regents of the University of Minnesota)
MAILING ADDRESS: 600 E 4th Street
CITY/STATE/ZIP: Morris, MN 56267
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FUNDING SOURCE: Environment and Natural Resources Trust Fund
LEGAL CITATION: M.L. 2019, First Special Session, Chp. 4, Art. 2, Sec. 2, Subd. 07c as extended by M.L. 2022, Chp. 94, Sec. 2, Subd. 19 (c.1) [to June 30, 2023]

APPROPRIATION AMOUNT: $185,000
AMOUNT SPENT: $184,388
AMOUNT REMAINING: $612

Sound bite of Project Outcomes and Results
New materials were developed from agricultural byproducts for use in the fabrication of printed organic solar cells that will lead to a more sustainable, low-cost, renewable energy source in Minnesota.

Overall Project Outcome and Results

The overall objective of this project was to develop materials for alternative energy technologies for Minnesota residents. This objective was achieved by producing sustainable materials from agricultural byproducts that can be used in organic photovoltaics (OPVs). OPVs (i.e., organic solar cells) are a promising renewable energy technology driven by their capability to be printed across large areas using roll-to-roll processing techniques– thus, creating the vision of covering every roof and other suitable building surface with organic photovoltaics at extremely low cost. Although scientists across the planet have developed many petroleum-based materials for OPVs, it is imperative that we find sustainable routes to make these materials. In this project, furfural – an organic compound produced from a variety of agricultural byproducts – was used as an important component of the solar material.

Undergraduate students in Minnesota utilized furfural for making polymers that link many small molecules in long chains to make plastics. These newly developed plastics show properties similar to petroleum based plastics used in conventional OPVs. These plastics can then be used for the fabrication of printed organic photovoltaics that will lead to a more sustainable, low-cost, renewable energy source in Minnesota.

Over fifteen undergraduate students contributed to the project across two institutions. Numerous high school students also benefited from the project through hands-on activities. Project results were disseminated widely through scientific publications and conference presentations. Results of the project were used to submit a large five million dollar grant to the National Science Foundation for the creation of a global center for practical, economic, and sustainable OPV technologies that will be based in the Midwest.

Project Results Use and Dissemination
1. The following manuscript was published in the journal *Molecules* (with PI and co-PIs as coauthors):

   "Halogen-interactions in Halogenated Oxoindoles: Crystallographic and Computational Investigations of Intermolecular Interactions," *Molecules* **2021**, *26*, 5487.

2. Over fifteen presentations were made by undergraduate students at local, regional, and national venues.
3. Results of the project were communicated in the region – including invited presentations at local colleges/universities.
4. The overview of the project was featured on PBS.

Environment and Natural Resources Trust Fund (ENRTF)
M.L. 2019 ENRTF Work Plan Final Report

Today's Date: August 15, 2023

Final Report

Date of Work Plan Approval: June 5, 2019

Project Completion Date: June 30, 2023

PROJECT TITLE: Sustainable Solar Energy from Agricultural Plant Byproducts

Project Manager: Ted Pappenfus

Organization: Morris Campus (Regents of the University of Minnesota)

College/Department/Division: Division of Science and Mathematics

Mailing Address: 600 E 4th Street

City/State/Zip Code: Morris, MN 56267

Telephone Number: 320-589-6340

Email Address: pappe001@morris.umn.edu

Web Address: http://cda.morris.umn.edu/~pappe001/

Location: Statewide

Total Project Budget: $185,000

Amount Spent: $184,388

Balance: $612

Legal Citation: M.L. 2019, First Special Session, Chp. 4, Art. 2, Sec. 2, Subd. 07c as extended by M.L. 2022, Chp. 94, Sec. 2, Subd. 19 (c.1) [to June 30, 2023]

Appropriation Language: $185,000 the first year is from the trust fund to the Board of Regents of the University of Minnesota, Morris, to use regional plant-based agricultural by-products to fabricate solar cells for creating renewable and affordable energy.

M.L. 2022 - Sec. 2. ENVIRONMENT AND NATURAL RESOURCES TRUST FUND; EXTENSIONS. [to June 30, 2023]

I. PROJECT STATEMENT:

Envision every house in Minnesota capable of producing renewable energy using plastics made from agricultural byproducts such as corncobs. The objective of this project is to take this idea from the benchtop to the rooftop by producing sustainable chemicals from agricultural biomass that can be used in organic photovoltaics (OPVs). OPVs (i.e., organic solar cells) are a promising renewable energy technology driven by their capability to be printed across large areas using roll-to-roll processing techniques–thus, creating the vision of covering every roof and other suitable building surface with organic photovoltaics at extremely low cost.

At the heart of every OPV is an organic (i.e., carbon-based) material that absorbs sunlight and transfers its energy within the device to produce useful electrical current. Although scientists across the planet have made many of these light-harvesting materials with good solar cell efficiencies, the vast majority of these organic materials are petroleum based. As we have a finite supply of petroleum on the planet, it is imperative that we find sustainable routes to make materials. One attractive chemical for the production of organic photovoltaic materials is furfural – an organic compound produced from a variety of agricultural byproducts, including corncobs and corn stover. As part of a collaboration between the Morris and Twin Cities campuses of the University of Minnesota, we have found that furfural functions well as a petroleum substitute in small molecules. This project will utilize this technology for making polymers that link many small molecules in long chains to make plastics. These plastics can then be used for the fabrication of printed organic photovoltaics that will lead to a more sustainable, low-cost, renewable energy source in Minnesota.

II. OVERALL PROJECT STATUS UPDATES:

First Update March 1, 2020

Significant progress has been made on both project activities since its inception in July 2019. Numerous students have worked on the project and collaborative activities between the University of Minnesota Morris and Saint Catherine University have been both positive and productive. Most noteworthy project results are as follows: (a) several analytical methods have been tested for the analysis of bio-based furfural; and (b) synthetic routes to more promising bio-based monomers for solar cell polymers have been identified and supported with encouraging preliminary results.

Second Update September 1, 2020

Progress has been made on both project activities since the last report, despite challenges due to COVID-19. Numerous students have worked on the project and collaborative activities between the University of Minnesota Morris and Saint Catherine University continue to be positive and productive. Most noteworthy project results are as follows: (a) several methods have been tested for the analysis of bio-based molecules; (b) routes to more promising bio-based chemicals for solar cells have been identified; and (c) green chemistry has been used to improve earlier synthetic methods with encouraging preliminary results.

Third Update March 1, 2021

Progress has been made on both project activities since the last report, despite challenges due to COVID-19. Numerous students have worked on the project and collaborative activities between the University of Minnesota Morris and Saint Catherine University continue to be positive and productive. Most noteworthy project results are as follows: (a) several methods have been tested for the synthesis and analysis of bio-based molecules; (b) routes to more promising bio-based chemicals for solar cells have been identified; and (c) green chemistry and computational chemistry has been used to improve earlier synthetic methods with encouraging preliminary results.

Fourth Update September 1, 2021

Progress has been made on both project activities since the last report, despite challenges due to COVID-19. Numerous students have worked on the project and collaborative activities between the University of Minnesota Morris and Saint Catherine University continue to be positive and productive. Most noteworthy project results are as follows: (a) several methods have been tested for the synthesis and analysis of bio-based molecules in collaboration with staff from Kimball High School; (b) routes to more promising bio-based chemicals for solar cells have been identified; (c) numerous polymerization attempts on bio-based chemicals have been performed and show promising results; (d) green chemistry has been used to improve paths towards more sustainable synthetic methods; and (e) structural and computational methods have been used extensively to better understand materials in the current investigation.

Fifth Update March 1, 2022

Progress has been made on both project activities since the last report, despite challenges due to COVID-19. Project results combining aspects of experiment and theory have been published in the journal *Molecules*. Project partners have started experiments together in Europe on furfural-based polymers and model compounds. Current experiments at UMM are focusing on optimizing syntheses of organic materials. A requested COVID extension will allow for the completion of project activities in Australia.

Update as of June 30, 2022:

Project extended to June 30, 2023 by LCCMR 6/30/22 as a result of M.L. 2022, Chp.94, Sec. 2, Subd. 19, legislative extension criteria being met.

Sixth Update as of September 1, 2022:

Progress has been made on both project activities since the last report. Project partners continued experiments together in Europe on furfural-based polymers and model compounds. Results of those experiments led to the preparation of new furfural-based model compounds in the laboratory at UMM. Current experiments at UMM are focusing on optimizing syntheses of organic materials. Excellent progress has been made on preparing polymer starting materials using mechanochemical methods which has resulted in numerous presentations in public venues.

Seventh Update as of March 1, 2023:

Significant progress has been made on project activities since the last report. Project partners continued experiments together in Europe on furfural-based molecules. Preliminary experiments in the lab in Spain have shown such molecules are exhibiting unprecedented behavior which has direct implications for solar energy development. Results of those experiments led to the preparation of a new petroleum-based model compound in the laboratory at UMM which will be used to facilitate publication of the results. Current experiments at UMM are focusing on finalizing syntheses of materials for the project and experiments in Australia continue to focus on device optimization. Three presentations were given since the last update related to project activities at local or regional venues.

Amendment Request May 30, 2023

We are requesting funds to be shifted from the equipment/tools/supplies budget line to personnel.

- Equipment/tools/supplies would be reduced by $2,219 to a revised budget of $18,213.
- Personnel would be increased from $101,675 to a revised budget of $103,894

These changes are being requested because fringe rates for salaries at the University of Minnesota increased from the originally proposed rate during the project.

Amendment APPROVED 6/28/2023

Final Report as of June 30, 2023 (to be submitted before August 15, 2023):

Overall Project Outcomes and Results

The overall objective of this project was to develop materials for alternative energy technologies for Minnesota residents. This objective was achieved by producing sustainable materials from agricultural byproducts that can be used in organic photovoltaics (OPVs). OPVs (i.e., organic solar cells) are a promising renewable energy technology driven by their capability to be printed across large areas using roll-to-roll processing techniques– thus, creating the vision of covering every roof and other suitable building surface with organic photovoltaics at extremely low cost.

Although scientists across the planet have developed many petroleum-based materials for OPVs, it is imperative that we find sustainable routes to make these materials. In this project, furfural – an organic compound produced from a variety of agricultural byproducts – was used as an important component of the solar material. Undergraduate students in Minnesota utilized furfural for making polymers that link many small molecules in long chains to make plastics. These newly developed plastics show properties similar to petroleum based plastics used in conventional OPVs. These plastics can then be used for the fabrication of printed organic photovoltaics that will lead to a more sustainable, low-cost, renewable energy source in Minnesota.

Over fifteen undergraduate students contributed to the project across two institutions. Numerous high school students also benefited from the project through hands-on activities. Project results were disseminated widely through scientific publications and conference presentations. Results of the project were used to submit a large five million dollar grant to the National Science Foundation for the creation of a global center for practical, economic, and sustainable OPV technologies that will be based in the Midwest.

III. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1 Title: Preparing and testing bio-based plastics for organic solar cells
Description: The objective of this activity is to develop furfural-based plastics that will function as light-absorbing materials in organic photovoltaics. The first step will be to prepare small molecules that contain furfural. These small molecules (or monomers) will then be polymerized to make the desired plastics. Fully petroleum-based plastics will also be prepared for control purposes. The physical properties of the plastics will be evaluated using a variety of analytical methods at the University of Minnesota, Morris and St. Catherine University. The performance of the plastics will be evaluated in small-scale devices (organic photovoltaics in collaboration with the University of Newcastle or organic transistors in collaboration with the University of Málaga) and the results of these initial devices will help guide second-generation furfural plastics. The synthesis of the best performing plastic(s) will then be explored at increased scale as candidates for large area organic photovoltaics. Results of the project will be readily available to LCCMR committee members and officials and will also be disseminated more broadly to the scientific community.

ACTIVITY 1 ENRTF BUDGET: $101,760

Outcome	Completion Date
1. Prepare initial sustainable molecules and polymers using mechanochemical and DArP methods; compare the materials to non-sustainable (petroleum-based) materials	*Dec. 31, 2019*
2. Fabricate and test initial devices using materials prepared in Outcome 1 (approximately two new polymers will be tested).	*May 31, 2020*
3. Prepare improved corn-based sustainable molecules and plastics and compare to non-sustainable (petroleum-based) materials	*Dec. 31, 2020*
4. Fabricate and test a second round of devices using improved materials prepared in Outcome 3 (approximately three additional new polymers will be tested).	*May 31, 2021*
5. Scale-up production of corn-based sustainable molecules and plastics and compare to non-sustainable (petroleum-based) materials	*June 30, 2022*

First Update March 1, 2020

Initial sustainable molecules and polymers have been prepared and compared to non-sustainable materials. A significant challenge resulted when the initially prepared molecules were found to exhibit the incorrect geometry needed for making suitable materials for solar cells. Collaborative activities between the University of Minnesota Morris and Saint Catherine University have shown that, with the assistance of molecular engineering efforts, molecules can be redesigned to exhibit the correct geometry for solar cell polymers. Although this was an unexpected barrier, it proved to be a great learning experience for students and investigators on the project. Project outcomes, however, are still on track as outlined.

Second Update September 1, 2020

Sustainable molecules redesigned as outlined in the previous progress report are very promising. Outcome two has not yet been completed due to two significant factors: (i) COVID-19 has limited in-person lab work on the project since March 2020; and (ii) one of our chemical suppliers provided us with an incorrect starting material that caused a significant delay in preparing our materials. Fortunately, we were able to identify two independent companies that have been able to supply us with the correct chemical. Experiments with these correct chemicals will take place immediately in fall 2020.

Third Update March 1, 2021

Experiments with the new chemical from new suppliers occurred late 2020 and early 2021. Molecules redesigned as outlined in the previous progress reports continue to be very promising. The key bio-based polymer was prepared and duplicated and the control petroleum-based monomer has been prepared. Some aspects of Outcomes 2 and 3 have not been completed, however. Full completion of these outcomes has not occurred due to two significant factors: (i) COVID-19 has limited in-person lab work on the project since March 2020; and (ii) as mentioned in our previous reports, one of our chemical suppliers provided us with an incorrect starting material that caused a significant delay in preparing our materials (this issue has been fortunately resolved).

Fourth Update September 1, 2021

Since the last update, numerous additional experiments have been performed on preparing bio-based molecules and polymers for organic solar cells. A number of undergraduate students contributed to the project in this project period which expanded on our results from late 2020 and early 2021. Efficient and reproducible syntheses have been developed for the materials. Experimental results related to the structural characterization of the materials using X-ray diffraction have been outstanding and led to the submission of a manuscript based

on these investigations (vide infra). Outcomes related to device testing, however, have not been completed due to the COVID-19 lockdown in Australia which has limited the ability of our collaborators at the University of Newcastle to perform experiments. Specifically, Outcomes 2 and 4 have been delayed. A suite of polymers resulting from Outcomes 1 and 3 have been prepared and will be tested once staff personnel at the University of Newcastle are able to resume activities upon reduced COVID-19 restrictions. A new collaborator was engaged (at no cost to the grant) to better understand the starting materials for the polymers in this study. Dr. Demetrio da Silva Filho (professor of Physics at the University of Brasilia and head of the department of Materials Structure in the Institute of Physics; University of Brasilia, Brazil) and his graduate student Rodrigo Lemos Silva have supported the project with computational investigations to complement experimental measurements performed at SCU.

Fifth Update March 1, 2022

Experimental results related to the structural characterization of the materials using X-ray diffraction have been outstanding and led to the publication of a paper based on these investigations (vide infra). Additional polymers and model compounds were prepared by project manager Pappenfus and undergraduate students using the furfural building block. Project partner Daron Janzen traveled to Málaga, Spain in February 2022 to work with project partner Juan Casado. Much data has already been taken on these materials in Spain at the time of writing this report. Outcomes related to device testing, however, have not been completed due to the COVID-19 lockdown in Australia which has limited the ability of our collaborators at the University of Newcastle to perform experiments. Specifically, Outcomes 2 and 4 have been delayed. A suite of polymers resulting from Outcomes 1 and 3 have been prepared and will be tested once staff personnel at the University of Newcastle are able to resume activities upon reduced COVID-19 restrictions. Because of these pandemic-related delays, a COVID extension was requested.

Update as of June 30, 2022:

Project extended to June 30, 2023 by LCCMR 6/30/22 as a result of M.L. 2022, Chp.94, Sec. 2, Subd. 19, legislative extension criteria being met.

Sixth Update as of September 1, 2022:

Polymers and model compounds were prepared by project manager Pappenfus and undergraduate students were investigated by project partner Daron Janzen in Málaga, Spain. Work on these materials continued by project partners in Spain. These experiments resulted in the need for two additional compounds which were prepared by project manager Pappenfus. Pappenfus and Janzen will work on the purification and characterization of the new compounds over the next reporting period. Outcomes 2 and 4 related to device testing, however, have not been completed in Australia as one of the final polymers does not have sufficient solubility to prepare a device. Project manager Pappenfus will prepare a new polymer with the goal of enhanced solubility. Excellent progress has been made on preparing polymer starting materials using mechanochemical methods which has resulted in numerous presentations in public venues (vide infra).

Seventh Update as of March 1, 2023:

Project activities with collaborators in Málaga, Spain have been very successful. Furfural-based molecules outlined in the previous update have shown unprecedented behavior. Project manager Pappenfus prepared the analogous petroleum-based material to complement existing studies and samples have been sent to Spain for analysis. Collaborator Seth Rasmussen (North Dakota State University) and students went to Australia to facilitate experiments in Outcomes 2 and 4 and those activities remain in progress. Excellent progress has been made on preparing polymer starting materials using traditional and mechanochemical methods which has resulted in three presentations in public venues (vide infra).

Final Report as of June 30, 2023 (to be submitted before August 15, 2023):

Final Report Summary:

Sustainable molecules and polymers have been prepared and compared to non-sustainable materials. A significant outcome of this activity is that the sustainable polymers show comparable properties to conventional, non-sustainable materials. In addition, collaborative activities between the University of Minnesota Morris and Saint Catherine University have shown that, with the assistance of molecular engineering efforts, molecules can be redesigned to exhibit the correct geometry for solar cell polymers. Although this was an unexpected barrier, it proved to be a great learning experience for students and investigators on the project. Two items that were not fully completed in this activity: full testing of all solar cell materials and scale-up of the most promising material. To address these two items, results of the project were used to submit a large five million dollar grant request to the National Science Foundation for the creation of a global center for practical, economic, and sustainable OPV technologies that will be based in the Midwest.

ACTIVITY 2 Title: Production and quantification of corn-based furfural as a sustainable chemical
Description: The objective of this activity is to find improved methods for the production and quantification of furfural from agricultural biomass (where quantification refers to determining how much furfural is produced in a given chemical reaction). The first step will be to find cheap and rapid methods to quantify furfural using 3D printed colorimeters. The quantitative work will take place as a collaborative effort between undergraduate and high school students and will serve as a great introduction to this overall project for the students. The second step will utilize advanced quantification methods for furfural using high performance liquid chromatography (HPLC) which will provide more detailed results in order to confirm the validity of the simple methods from 3D printed spectrometers. Once quantification methods have been established, furfural production will be developed on the benchtop scale using simple sugars as they are the basic components of biomass. The bulk of the work for Outcomes 2-4 will take place on the Morris and St. Catherine campuses.

ACTIVITY 2 ENRTF BUDGET: $83,240

Outcome	Completion Date
1. Develop simple quantification methods of furfural with visible spectroscopy using 3D printed colorimeters	*Aug. 31, 2020*
2. Use advanced quantification methods (HPLC and NMR) to test the validity of the simple quantification methods of furfural developed in Outcome 1	*Dec. 31, 2020*
3. Production of furfural from simple sugars using solid-acid catalysts	*May 31, 2021*
4. Optimize production of furfural from simple sugars using solid-acid catalysts	*June 30, 2022*

First Update March 1, 2020

Efforts to produce 3D printed colorimeters have been successful and preliminary quantification methods have been tested for the analysis of furfural. The advanced quantification method of HPLC has also been tested. An alternative method, nuclear magnetic resonance (NMR) spectroscopy, has also been tested which has shown very promising preliminary results. Given the success of the NMR methods, we have added efforts to produce furfural from simple sugars are well ahead of schedule as initial experiments for furfural production have already occurred. Lastly, one initially proposed project partner (Michael Maudal) has been removed from this project activity as he has relocated out of state to a different position. The remaining project partners remain intact, however.

Second Update September 1, 2020

This activity is on schedule and collaboration between UMM and Kimball High School (KHS) has been very successful – most notably the design, printing and testing of 3D printed devices for analysis is proceeding very well. Current efforts are focusing on advanced methods of preparation and analysis of bio-based molecules.

Third Update March 1, 2021

To date, this activity is on schedule and collaboration between UMM and Kimball High School (KHS) continues to be very successful. Last summer, a UMM student performed an updated literature search on effective routes toward bio-based chemicals using sugars. KHS also secured additional funding for their own 3D printer which will aid the project significantly. Current efforts are focusing on advanced methods of preparation and analysis of bio-based molecules.

Fourth Update September 1, 2021

To date, this activity is on schedule and collaboration between UMM and Kimball High School (KHS) continues to be very successful. This past summer, a UMM student performed numerous experiments on producing bio-based chemicals using sugars. Staff at KHS completed their studies on spectroscopic methods of preparation and analysis of bio-based molecules.

Fifth Update March 1, 2022

To date, this activity is on schedule and collaboration between UMM and Kimball High School (KHS) has been very successful. Outcomes 1-3 have been fulfilled and current efforts are focusing on optimizing production of organic molecules using solid-acid catalysts with and without mechanochemistry.

Update as of June 30, 2022:

Project extended to June 30, 2023 by LCCMR 6/30/22 as a result of M.L. 2022, Chp.94, Sec. 2, Subd. 19, legislative extension criteria being met.

Sixth Update as of September 1, 2022:

To date, this activity is mostly on schedule and collaboration between UMM and Kimball High School (KHS) has been very successful. Outcomes 1-3 have been fulfilled. Efforts focusing on optimizing production of organic molecules using solid-acid catalysts with and without mechanochemistry were put on hold to focus on Activity 1 experiments.

Seventh Update as of March 1, 2023:

Outcomes 1-3 have been fulfilled. Efforts focusing on optimizing production of organic molecules using solid-acid catalysts with and without mechanochemistry were put on hold to focus on Activity 1 experiments which have yielded more promising and unprecedented results.

Final Report as of June 30, 2023 (to be submitted before August 15, 2023):

This activity between the University of Minnesota Morris (UMM) and Kimball High School (KHS) has been very successful – most notably the design, printing and testing of 3D printed devices for analysis proceeded very well. The advanced quantification method of HPLC was also tested by UMM undergraduate students. An alternative method, nuclear magnetic resonance (NMR) spectroscopy, was also tested by undergraduate students which displayed very promising results. Given the success of the NMR methods, we added efforts to produce furfural from simple sugars as model studies for producing bio-based molecules from agricultural byproducts. Although we did not publish any results from this activity in a scientific journal, our results from spring 2023 are worthy of publication and will be reported in the next year.

IV. DISSEMINATION:

Description: Results of the project will be readily available to LCCMR committee members and officials and will also be disseminated more broadly to the scientific community. Results of the project will be presented locally at the various respective institutions. Data, results, and samples will also be shared across institutions. Undergraduate students will present results at national meetings and completed project activities will be submitted for publication in peer-reviewed scientific journals when appropriate.

The Minnesota Environment and Natural Resources Trust Fund (ENRTF) will be acknowledged through use of the trust fund logo or attribution language on project print and electronic media, publications, signage, and other communications per the ENRTF Acknowledgement Guidelines.

First Update March 1, 2020

The following presentations were made by undergraduate students working on the project at the fall 2019 University of Minnesota Morris Summer Research Program: (a) Synthesizing Furfural from Xylose and Quantitative Analysis via HPLC and NMR (students Isaac Sanchez and Mitch Scanlan); and (b) Polymerization of (Furanylmethylene)oxindole and (Thienylmethylene)oxindole Derivatives and their Physical and Electronic Properties (students Hanna Kennedy, Luke Lippert, Jacqueline Schneider, and Ike Hills).

The following presentations were made by undergraduate students working on the project during 2019-20 at St. Catherine University in the Chemistry Seminar Course CHEM 4850: (a) Green and Sustainable Solar Energy Materials (Megan Moberg); and (b) Synthesis of Green and Sustainable Materials for Photovoltaic Cells (Rachel Morgan). The undergraduate student Megan Moberg also has been accepted to present her research in oral format at the National Conference on Undergraduate Research to be held in March 2020 at the University of Montana.

Second Update September 1, 2020

The following posters were communicated by UMM undergraduate students working on the project at the spring 2020 national meeting of the American Chemical Society (meeting posters were communicated fully online): (a) Synthesizing Furfural from Xylose and Quantitative Analysis via HPLC and NMR (students Isaac Sanchez and Mitch Scanlan); and (b) Polymerization of (Furanylmethylene)oxindole and (Thienylmethylene)oxindole Derivatives and their Physical and Electronic Properties (students Hanna Kennedy, Luke Lippert, Jacqueline Schneider, and Ike Hills).

SCU students Hope Holte, Badraa Al-Jasi, and Hil Ngouajio worked on this project and presented an oral presentation of their work as part of the St. Catherine University Summer Scholars Research Program showcase (online oral/poster session). The presentation was entitled "Green Synthesis of Solar Cell Materials".

Third Update March 1, 2021

SCU students Hil Ngoujio and Badraa Al-Jasim have submitted an abstract (with PI and co-PIs as coauthors) to present work of this project to the 2021 Spring National Meeting of the American Chemical Society (April 2021) and await acceptance status. Also, SCU students Hil Ngoujio and Badraa Al-Jasim submitted an abstract (accepted) for an oral presentation of their work on this project to the 2021 National Conference on Undergraduate Research where they will present in April 2021.

Fourth Update September 1, 2021

The following manuscript was submitted to the journal *Molecules* (with PI and co-PIs as coauthors):

"Halogen-interactions in Halogenated Oxoindoles: Crystallographic and Computational Investigations of Intermolecular Interactions."

Two papers were presented at the 2021 Spring National Meeting of the American Chemical Society: (a) SCU students Hil Ngoujio and Badraa Al-Jasim presented a paper titled, "Green methods for the synthesis of solar cell materials" and (b) SCU student Megan Moberg presented a paper titled, "Semi-sustainable monomers for organic photovoltaic donor polymers." These papers were also presented at the National Conference of Undergraduate Research (NCUR).

Fifth Update March 1, 2022

The following manuscript was published in the journal *Molecules* (with PI and co-PIs as coauthors):

"Halogen-interactions in Halogenated Oxoindoles: Crystallographic and Computational Investigations of Intermolecular Interactions," *Molecules* **2021**, *26*, 5487.

Update as of June 30, 2022:

Project extended to June 30, 2023 by LCCMR 6/30/22 as a result of M.L. 2022, Chp.94, Sec. 2, Subd. 19, legislative extension criteria being met.

Sixth Update as of September 1, 2022:
Numerous presentations were made at local and national venues related to project outcomes and are outlined below:

Access to Unique Products From a Mechanochemical Synthesis. Bendel, K.*; Pappenfus, T.M.; Janzen, D.E. Associated Colleges of the Twin Cities Summer Seminar in Chemistry, St. Catherine University, 2022.

Green Synthesis of Conducting Polymers for Organic Photovoltaic Applications. Biermeier, H.*; Pappenfus, T.M.; Janzen, D.E. Minnesota Academy of Science, Winchell Undergraduate Symposium, Hamline University, St. Paul, MN., oral presentation, 2022.

Green Synthesis of Conducting Polymers for Organic Photovoltaic Applications. Biermeier, H.*; Pappenfus, T.M.; Janzen, D.E. National Conference of Undergraduate Research, virtual conference oral presentation, 2022.

Green Synthesis of Conducting Polymers for Organic Photovoltaic Applications. Biermeier, H.*; Pappenfus, T.M.; Janzen, D.E. Sr. Seraphim Gibbons Undergraduate Research Symposium, St. Catherine University, poster presentation, 2022.

Seventh Update as of March 1, 2023:

Three presentations were made at local and regional venues related to project outcomes and are outlined below:

Access to Unique Products from a Mechanochemical Synthesis. Bendel, K.*; Pappenfus, T.M.; Janzen, D.E. Summer Scholars Research Symposium, St. Catherine University, 2022.

Access to Unique Products From a Mechanochemical Synthesis. Abstract accepted for oral presentation, National Conference on Undergraduate Research, University of Wisconsin Eau Claire, 2023.

Green and Sustainable Methods for Solar Energy Materials. Pappenfus, T. M. South Dakota State University Chemistry Seminar, 2022

Final Report as of June 30, 2023 (to be submitted before August 15, 2023):

Final Report Summary:

1. The following manuscript was published in the journal *Molecules* (with PI and co-PIs as coauthors):

   "Halogen-interactions in Halogenated Oxoindoles: Crystallographic and Computational Investigations of Intermolecular Interactions," *Molecules* **2021**, *26*, 5487.

2. Over fifteen presentations were made by undergraduate students at local, regional and national venues.

3. Results of the project were communicated in the region – including invited presentations at local colleges/universities.

4. The overview of the project was featured on PBS.

V. ADDITIONAL BUDGET INFORMATION:

A. Personnel and Capital Expenditures

Explanation of Capital Expenditures Greater Than $5,000: Two Benchtop Ball Mills for Solid State Reactions ($10,590 ea.); One for use on the Morris Campus; One for use at St. Catherine University. This equipment will be used during its useful life for the research described in this proposal and for similar environmental research after this specific project has ended.

Explanation of Use of Classified Staff: N/A

Total Number of Full-time Equivalents (FTE) Directly Funded with this ENRTF Appropriation:

Enter Total Estimated Personnel Hours for entire duration of project: 2226	Divide total personnel hours by 2,080 hours in 1 yr = TOTAL FTE: 1.1

Total Number of Full-time Equivalents (FTE) Estimated to Be Funded through Contracts with this ENRTF Appropriation:

Enter Total Estimated Contract Personnel Hours for entire duration of project: 400	Divide total contract hours by 2,080 hours in 1 yr = TOTAL FTE: 0.2

VI. PROJECT PARTNERS:

A. Partners outside of project manager's organization receiving ENRTF funding

Name	Title	Affiliation	Role
Dr. Daron Janzen	**Associate Professor of Chemistry**	**St. Catherine University, St. Paul, MN**	**Analysis of materials; solid-state syntheses**
Mr. Zachary Boser	**Science Instructor**	**Kimball High School, Kimball, MN**	**Furfural Detection; Mentor for Students**

B. Partners outside of project manager's organization NOT receiving ENRTF funding

Name	Title	Affiliation	Role
Professor Paul Dastoor	**Professor of Physics**	**University of Newcastle, New S. Wales, Australia**	**Organic Solar Cell Device Fabrication and Testing**
Professor Juan Casado	**Professor of Chemistry**	**University of Málaga, Málaga, Spain**	**Organic Transistor Device Fabrication and Testing**

VII. LONG-TERM- IMPLEMENTATION AND FUNDING:

At the conclusion of the project, both Activities 1 and 2 will continue. Funds will be sought from the Minnesota Corn Growers Association to scale up furfural production methods developed as part of this project. Additional funding will be sought (from the Department of Energy and/or Xcel Energy's Renewable Development Fund) for a large area photovoltaic test site on the UMM campus using these corn-based plastics. Prof. Dastoor has two organic photovoltaic test sites currently operating in Australia; an additional site in a climate such as MN would provide valuable data. Long term, we will seek funding from the Gates Foundation to construct a printing center in MN to deliver corn-based organic photovoltaics to low income Minnesota families.

VIII. REPORTING REQUIREMENTS:

- Project status update reports will be submitted March 1 and September 1 each year of the project
- A final report and associated products will be submitted between June 30 and August 15, 2023

IX. SEE ADDITIONAL WORK PLAN COMPONENTS:

A. Budget Spreadsheet
B. Visual Component or Map
C. Parcel List Spreadsheet (N/A)
D. Acquisition, Easements, and Restoration Requirements (N/A)
E. Research Addendum

Attachment A:
Environment and Natural Resources Trust Fund
M.L. 2019 Budget Final Spreadsheet
Legal Citation: M.L. 2019, First Special Session, Chp. 4, Art. 2, Sec. 2, Subd. 07c
Project Manager: Ted Pappenfus
Project Title: Sustainable Solar Energy from Agricultural Plant Byproducts
Organization: Morris Campus (Regents of the University of Minnesota)
Project Budget: $185,000
Project Length and Completion Date: 4 Years, June 30, 2023
Today's Date: August 15, 2023

ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Revised Budget (06/28/2023)	Amount Spent	Balance
BUDGET ITEM			
Personnel (Wages and Benefits): University of MN, Morris	$ 103,894	$ 103,894	$ -
Professor Ted Pappenfus, Project Manager: 18 % FTE YR 1-3 (66% salary; 34% fringe) (1.5 mo. summer salary in YR 1-3; 2 credit fall semester release to work with undergraduates in YR 1-3)			
Undergraduate Research Assistant: 21% FTE YR 1-3 (100% salary) (8 weeks; 32 hrs/wk @$12/hr)			
Summer Contracts for High School Instructors ($3,000/summer in YR 1 and 2 for each of two instructors) (5 weeks @20 hrs/wk)			
Professional/Technical/Service Contracts: St Catherine University			
Associate Professor Daron Janzen, Co-PI (St. Catherine Univ.): 11% FTE YR 1-3 (83% salary; 17% fringe) (1.0 mo. summer salary in YR 1-3)	$ 26,353	$ 26,353	$ -
Undergraduate Research Assistant (St. Catherine Univ.): 21% FTE YR 1-3 (100% salary) (8 weeks; 20 hrs/wk; @$12.25/hr(2019) $13.25/hr(2020), $14.25/hr(2021))	$ 6,360	$ 6,360	$ -
Lab materials, chemicals and lab supplies for project activities: $2,000/yr for 3 yrs for St. Catherine U	$ 6,000	$ 6,000	$ -
Equipment/Tools/Supplies: University of MN, Morris	$ 18,213	$ 17,625	$ 588
Lab materials, chemicals and lab supplies and analytical services for sample analysis for project activities: (a) $6,144/yr for 3yrs for UMM; (b) $1,000 for each high school in YR 1			
Capital Expenditures Over $5,000	$ 21,180	$ 21,156	$ 24
Two Benchtop Ball Mills for Solid State Reactions ($10,590 ea.); One for use on the Morris Campus; One for use at St. Catherine Univ.			
Travel expenses in Minnesota: University of MN, Morris	$ 3,000	$ 3,000	$ -
Domestic, in-state travel for Project Manager Pappenfus to travel to Project Partners ($1,000/yr) (Travel will be reimbursed per University of MN travel policies)			
COLUMN TOTAL	$ 185,000	$ 184,388	$ 612

OTHER FUNDS CONTRIBUTED TO THE PROJECT	Status (secured or pending)	Revised Budget (05/30/2023)	Spent	Balance
Non-State: UMM Chemistry Undergraduate Research Fund: Funds will be available to cover a second undergraduate student in YR 1-3 at UMM ($3,072/yr) plus housing for both students in each summer ($500/summer for each student)	Secured	$ 12,216	$ 12,216	$ -
State: N/A	N/A		$ -	$ -
In kind: The 54% in foregone federally negotiated ICR funding constitutes a portion of the University of Minnesota, Morris's cost share to the project.	Secured	$ 88,463	$ 88,145	$ 318

PAST AND CURRENT ENRTF APPROPRIATIONS	Amount legally obligated but not yet spent		Spent	Balance
Current appropriation: N/A	N/A		$ -	$ -
Past appropriations: N/A	N/A		$ -	$ -