Final Abstract

Final Report Approved on November 27, 2024

M.L. 2020 Project Abstract

For the Period Ending June 30, 2024

Project Title: Eco-Friendly Plastics From Cloquet Pulp-Mill Lignin

Project Manager: William Tai Yin Tze

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Funding Source:

Fiscal Year:

Legal Citation: M.L. 2021, First Special Session, Chp. 6, Art. 5, Sec. 2, Subd. 07b

Appropriation Amount: $193,000

Amount Spent: $192,282

Amount Remaining: $718

Sound bite of Project Outcomes and Results

Plastic pollution has a dire impact on Minnesota's water, land and many natural resources. This project contributes to better environmental stewardship by converting surplus lignin from Sappi mill in Cloquet to eco-friendly plastics. Several promising plastics formulations were developed. They can potentially replace non-biodegradable plastics such as polystyrene.

Overall Project Outcome and Results

Plastics are ubiquitous in everyday life. Yet plastic pollution poses both a serious threat to the environment and a hazard to human health. This project sought to develop eco-friendly plastics as alternatives to petrochemical-derived plastics many of which resist biodegradation and persist in the environment for centuries.

Lignin makes up 25% of the trunks and limbs of northern Minnesota aspen. During kraft pulping to produce cellulosic fibers for making paper, the lignin is dissolved in the spent pulping chemicals (black liquor). Currently these kraft lignins have little value because they are used as recovery-boiler fuels in pulp mills.

The aspen kraft lignin from Cloquet Sappi Mills black liquor was isolated and purified. The kraft lignin was then solution-cast into plastic test pieces. At 5–15% levels, commercially available blend components were investigated for their effects on the strength of these new lignin plastics.

We demonstrated that, without fractionation or modification, these aspen kraft lignin could be transformed into plastics. Indeed, we successfully devised several plastics formulations containing 85% aspen kraft lignin. These eco-friendly plastics possess tensile strengths (37 MPa) surpassing those of common plastics such as polyethylene (30 MPa) and approaching those of polystyrene (42 MPa).

By converting these aspen kraft lignin from the Cloquet Sappi mill into eco-friendly plastics would create additional revenues for pulp mills. Furthermore, it also addresses plastic pollution as potential alternatives to recalcitrant petroleum-based plastics. Moreover, our studies showed that the molecular size distributions and thermal behavior of these aspen kraft lignin starting materials were very comparable to those reported in the literatures. Thus the plastic formulations developed in this LCCMR-supported project would apply to aspen kraft lignins derived somewhere else.

Project Results Use and Dissemination

Support from LCCMR in developing eco-friendly aspen kraft lignin plastics was highlighted in an oral presentation at the 2023 International Symposium on Wood, Fiber and Pulping Chemistry in Venice, Italy. The LCCMR logo was prominently displayed in the PowerPoint slides. A conference proceedings paper where LCCMR support was fully acknowledged has been attached. A manuscript describing the development of functional plastics based on aspen kraft lignins derived from Sappi Cloquet Mill is in preparation. Support from Minnesota Environment and Natural Resources Trust Fund will be also fully acknowledged in this manuscript.

Environment and Natural Resources Trust Fund

M.L. 2020 Approved Final Report

General Information

Date: December 11, 2024

ID Number: 2020-018

Staff Lead: Noah Fribley

Project Title: Eco-Friendly Plastics From Cloquet Pulp-Mill Lignin

Project Budget: $193,000

Project Manager Information

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Project Reporting

Final Report Approved: November 27, 2024

Reporting Status: Project Completed & Additional Update Approved

Date of Last Action: November 27, 2024

Project Completion: February 28, 2024

Legal Information

Legal Citation: M.L. 2021, First Special Session, Chp. 6, Art. 5, Sec. 2, Subd. 07b

Appropriation Language: $193,000 the second year is from the trust fund to the Board of Regents of the University of Minnesota to reduce environmental pollution from plastics by creating eco-friendly replacements using lignin from the pulp mill in Cloquet, Minnesota. This appropriation is subject to Minnesota Statutes, section 116P.10.

Appropriation End Date: June 30, 2024

Narrative

Project Summary: We will reduce environmental pollution from plastics by creating eco-friendly replacements using lignin from the pulp mill in Cloquet. The lignin plastics will be similar in strength to polystyrene.

Describe the opportunity or problem your proposal seeks to address. Include any relevant background information.

Future production of liquid fuels, plastics and chemicals will inevitably shift gradually from oil to renewable plant materials. These raw materials encompass wood (including forest residuals) and crops (including agricultural residues). The structures of tree limbs and trunks, plant stalks and stems, are upheld by cellulose fibrils (like cotton fibers) and a variety of hemicelluloses. The cellulose and hemicelluloses are composed of sugars (like glucose and xylose) that can be converted into fuels, plastics and chemicals. However, production costs are too high for profitability. Fortunately, 12 - 35% of structural plant materials and wood consist of lignins that are quite different from cellulose and hemicelluloses. Traditionally, the value of lignin has been very low: it is used primarily as recovery-boiler fuel in pulp mills. We will remedy this waste by transforming industrial byproduct lignin from the Sappi mill in Cloquet (Minnesota) into eco-friendly plastics. The Cloquet pulp mill employs the kraft process to convert aspen wood chips into cellulosic pulp, with kraft lignin as byproduct. We will demonstrate how surplus aspen kraft lignin, created during increased pulp production, is transformed at 90% levels into valuable biodegradable plastics that are similar in strength to polystyrene.

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.

(1) We will create eco-friendly plastics from the lignin that makes up 25% of the trunks and limbs of northern Minnesota aspen. The lignin will be the byproduct generated in the Sappi mill, Cloquet (Minnesota), when aspen wood chips are pulped using the “kraft” process to form cellulosic fibers for making paper.
(2) These eco-friendly lignin plastics will contain higher-than-90% levels of aspen kraft lignin. They will be similar in strength to polystyrene, which resists biodegradation and persists in the environment for centuries. On the other hand, lignin plastics will undergo complete biodegradation through a process open to total control (by adding a little sugar).
(3) Lignin plastics will increase the profitability of kraft pulp mills. After cellulosic fibers are formed during kraft pulping, the byproduct lignin is easily isolated. Currently, the value of this kraft lignin is very low because it is burned as fuel.
(4) Aspen kraft lignin will be washed with water and air-dried. For comparison, the effect of simple methylation will be evaluated. Thus, before and after methylation, purified kraft lignin will be cast into plastic test pieces. At 10% levels, commercial blend components will be introduced to enhance the strengths of these new lignin plastics.

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 project outcome exemplifies how plant lignocellulose can be completely transformed into biodegradable cellulosic components and lignin plastics. The result will be a model for the use of plant lignocellulose as a renewable raw material with minimal waste. The cellulose and hemicelluloses can be converted into fuels and platform chemicals, while the biodegradable lignin plastics will have production costs below half of the polystyrene selling price. These new lignin plastics can be used in computer consoles, automobile dashboards and a range of attractive consumer articles. The impending vista will promote unprecedented conservation and enhancement of Minnesota’s renewable natural resources.

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?

Region(s): Central, NE, NW,

When will the work impact occur?

In the Future

Activities and Milestones

Activity 1: Isolation, purification and characterization of aspen kraft lignin from Cloquet

Activity Budget: $95,000

Activity Description:
Aspen kraft lignin will be isolated by acidifying kraft black liquor from Cloquet. It will be thoroughly washed with water and air-dried. The purified aspen kraft lignin will be characterized in regard to its molecular weight distribution (by size-exclusion chromatography), glass-transition temperature by differential scanning calorimetry (Tg by DSC), structure (by nuclear magnetic resonance spectrometry (NMR)), and molecular organization (by X-ray powder diffraction).

Activity Milestones:

Description	Approximate Completion Date
Purified aspen kraft lignin for lignin plastics	February 28, 2023
Aspen kraft lignin molecular weight distributions and glass-transition temperatures	August 31, 2023
Aspen kraft lignin structure and molecular organization	November 30, 2023

Activity 2: Formulations for aspen kraft lignin plastics and their strengths

Activity Budget: $98,000

Activity Description:
Apen kraft lignin will be solution-cast into plastic test pieces on their own and with commercially available blend components at levels below 10%. Lignin-lignin blends will also be investigated. These plastics will be characterized with respect to tensile strength (Instron), glass-transition temperature by differential scanning calorimetry (Tg by DSC) and molecular organization (by X-ray powder diffraction).

Activity Milestones:

Description	Approximate Completion Date
Solution-casting conditions optimized for aspen kraft lignin plastics	May 31, 2023
Formulations characterized for aspen kraft lignin-based plastics	December 31, 2023
Tensile strength of aspen kraft lignin-based plastics compares favorably with polyethylene	February 28, 2024

Project Partners and Collaborators

Name	Organization	Role	Receiving Funds
Tom Radovich	Sappi North America (in Cloquet)	Mr. Radovich will supply aspen black liquor from which aspen kraft lignin will be isolated. Aspen kraft lignin is the starting material for producing eco-friendly plastics.	No

Dissemination

Describe your plans for dissemination, presentation, documentation, or sharing of data, results, samples, physical collections, and other products and how they will follow ENRTF Acknowledgement Requirements and Guidelines.

The results will be disseminated through peer-reviewed journals such as Green Chemistry, ACS Sustainable Chemistry and Engineering, etc. Presentations at regional, national and international conferences also provide excellent opportunities to disseminate project results with respect to related scientific communities. Discussions with colleagues at other institutions can provide useful insights into future research directions.

The College of Food Agricultural and Natural Resource Sciences (CFANS) and the Department of Bioproducts and Biosystems Engineering (BBE) at the University of Minnesota have well established education and outreach programs which are in place and provide valuable opportunities to engage with members of the general public.

The ultimate target audience encompasses technical personnel in pulp mills and emerging biorefineries that seek to produce commodity organic chemicals (including liquid fuels) from lignocellulose in agricultural crop residues and forest residuals.

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.

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?

As our LCCMR project nears completion, funds will be sought for an injection-molding apparatus that can produce test pieces under conditions more closely allied to industrial practice. Adequate funding will be requested from DOE and/or USDA. Otherwise, when our work becomes sufficiently far advanced, companies and/or entrepreneurs will be approached for bringing lignin plastics to the market place. Articles can take many forms, ranging from automobile dashboards through stackable auditorium chairs to garden furniture, etc.

Budget Summary

Category / Name	Subcategory or Type	Description	Purpose	Gen. Ineligible	% Benefits	# FTE	Classified Staff?	$ Amount	$ Amount Spent	$ Amount Remaining
Personnel										
postdoctoral researcher		Development of functional lignin-based plastics from aspen kraft lignin. We found that it has been more time efficient and cost effective to analyze, by our own lab person, the instrumental data obtained from the shared equipment use facility. This is because our postdoctoral researcher is more familiar with the lignin plastic materials than those running the instruments in the use facility. Therefore, there has been an increased need for personnel from $187,800 to $189,728.			26.7%	2		$189,728	-	-
							Sub Total	**$189,728**	**$189,386**	**$342**
Contracts and Services										
Arrow Laboratory Specialists	Professional or Technical Service Contract	This budget was for the entity to provide repair of centrifuges, if necessary. But the equipment that has been critical for this project has been functioning well. Therefore, there is no need for the $200 in this category.		X		0		-	-	-
Characterization Facility and NMR Center at the University of Minnesota	Internal services or fees (uncommon)	Equipment/facility usage fees for characterizing kraft lignin plastics. We have significantly reduced numbers of samples needed for analysis at the characterization facilities. The expense associated with the equipment expert time is reduced since we interpret the data by ourselves. Thus, the $2,000 budget is reduced to $1,000.				0		$1,000	$634	$366
							Sub Total	**$1,000**	**$634**	**$366**

Equipment, Tools, and Supplies										
	Tools and Supplies	laboratory supplies: chemical reagents, nitrogen, solvents & laboratory consumables, etc.	We have been able to use the supplies and chemicals purchased earlier for this LCCMR project. In addition, we have developed a protocol to reduce the use of new blend components for our lignin plastics. Therefore, the required budget for supplies is reduced from $3,000 to $2,272.					$2,272	$2,262	$10
							Sub Total	**$2,272**	**$2,262**	**$10**
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										
							Sub Total	**-**	**-**	**-**

							Grand Total	**$193,000**	**$192,282**	**$718**

Classified Staff or Generally Ineligible Expenses

Category/Name	Subcategory or Type	Description	Justification Ineligible Expense or Classified Staff Request
Contracts and Services - Arrow Laboratory Specialists	Professional or Technical Service Contract	This budget was for the entity to provide repair of centrifuges, if necessary. But the equipment that has been critical for this project has been functioning well. Therefore, there is no need for the $200 in this category.	Arrow Laboratory Specialists, the provider, is the only local company capable of maintaining and repairing our centrifuges; they have been doing so for approximately 20 years.

Non ENRTF Funds

Category	Specific Source	Use	Status	$ Amount	$ Amount Spent	$ Amount Remaining
State						
			State Sub Total	-	-	-
Non-State						
			Non State Sub Total	-	-	-
			Funds Total	-	-	-

Attachments

Required Attachments

Visual Component

File: 15211286-bee.pdf

Alternate Text for Visual Component

Eco-friendly lignin plastics from Minnesota pulp mill will increase profitability of making paper by replacing polystyrene and other plastics from petrochemical sources....

Supplemental Attachments

Capital Project Questionnaire, Budget Supplements, Support Letter, Photos, Media, Other

Title	File
Background Check Certification Form	c7461ec9-48c.pdf
ISWFPC conference paper	570b79f0-70a.pdf
Visual 10072024	2fa54169-398.pdf

Difference between Proposal and Work Plan

Describe changes from Proposal to Work Plan Stage

No changes have been made to the workplan.

Additional Acknowledgements and Conditions:

The following are acknowledgements and conditions beyond those already included in the above workplan:

Do you understand and acknowledge the ENRTF repayment requirements if the use of capital equipment changes?

N/A

Do you understand that travel expenses are only approved if they follow the "Commissioner's Plan" promulgated by the Commissioner of Management of Budget or, for University of Minnesota projects, the University of Minnesota plan?

N/A

Does your project have potential for royalties, copyrights, patents, sale of products and assets, or revenue generation?

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?

Yes, Sponsored Projects Administration

Work Plan Amendments

Amendment ID	Request Type	Changes made on the following pages	Explanation & justification for Amendment Request (word limit 75)	Date Submitted	Approved	Date of LCCMR Action
1	Project Manager	Previous Manager: Simo Sarkanen (sarka001@umn.edu) New Manager: William Tai Yin Tze (wtze@umn.edu)	Dr. Sarkanen passed away in June of 2022	November 14, 2022	Yes	November 14, 2022
2	Amendment Request	• Budget • Project Collaborators - Project Manager Info • Narrative • Activities and Milestones • Budget - Personnel • Budget - Professional / Technical Contracts • Budget - Capital, Equipment, Tools, and Supplies	Budget change after re-evaluation of research approach (milestones adjustment) and future needs for funds (budget rearrangement). Overall scope remains unchanged. Specific justifications for the fund rearrangement of the respective budget categories are provided on the budget page.	February 1, 2023	Yes	February 7, 2023
3	Completion Date	Previous Completion Date: 07/31/2023 New Completion Date: 02/28/2024	Delayed project starting date, change of PI, and revising of work approach (without changing the project scope).	January 30, 2023	Yes	February 1, 2023
4	Project Manager	Previous Manager: William Tai Yin Tze (wtze@umn.edu) New Manager: William Tai Yin Tze (wtze@umn.edu)	Not able to submit requests/reports due to name matching issue	February 1, 2023	Yes	February 1, 2023
5	Amendment Request	• Budget • Project Collaborators - Project Manager Info • Budget - Personnel • Budget - Professional / Technical Contracts • Budget - Capital, Equipment, Tools, and Supplies • Attachments	Request for budget amendment after re-evaluation of research approach. The overall scope remains unchanged. Specific justifications for the fund reallocation of the respective budget categories are provided on the budget page.	April 12, 2024	Yes	August 23, 2024

Additional Status Update Reporting

Additional Status Update October 7, 2024

Date Submitted: October 7, 2024

Date Approved: October 30, 2024

Overall Update
Final status update was approved on Aug 23, 2024.

Activity 1
This activity was previously marked complete.
(This activity marked as complete as of this status update)

Activity 2
This activity was previously marked complete.
(This activity marked as complete as of this status update)

Dissemination
A conference proceedings paper where LCCMR support was fully acknowledged has been added to the attachment during submission of the final status update on Apr 12, 2024. A manuscript describing the development of functional plastics based on aspen kraft lignins derived from Sappi Cloquet Mill is in preparation. Support from Minnesota Environment and Natural Resources Trust Fund will be fully acknowledged in this manuscript.

Status Update Reporting

Final Status Update April 13, 2024

Date Submitted: April 12, 2024

Date Approved: August 23, 2024

Overall Update
Up to 35% of lignocellulosic biomass is lignin. The goal of this project was to provide a viable avenue for lignin valorization by creating eco-friendly plastics using hardwood aspen kraft lignin derived from Sappi mill in Cloquet (Minnesota). By converting the surplus kraft lignin (which is burned as fuel) to plastics would not only create additional revenues for pulp mills, but also mitigate the environmental impact of its disposal.

We have successfully devised several formulations for plastics with 85 wt% aspen kraft lignin (without fractionation nor modification). These eco-friendly plastics possess tensile strengths surpassing those of polyethylene (30 MPa) and approaching those of polystyrene (46 MPa).

The molecular weight and glass-transition temperature (Tg) of our aspen lignin are within the respective range of the reported values. NMR analysis suggested that its structural characteristics are similar to those reported in the literature. X-ray powder diffraction studies revealed that the molecular organization of aspen lignin (containing similar proportions of guaiacyl and syringyl units) is more complex than their softwood counterparts (composed mainly of guaiacyl residues). This may explain that it had been challenging to develop aspen kraft lignin plastics with tensile strength comparable to those composed of softwood kraft lignin.

Activity 1
We devised a protocol to fully remove sulfur particles formed from black-liquor polysulfide under acidic isolation conditions. This was critical in obtaining useful starting materials for aspen lignin plastics. The weight-average (Mw) and number-average (Mn) molecular weights of our acetylated aspen kraft lignin preparation were estimated to be 3100 and 1400, respectively, which were comparable with those reported in the literature. On the other hand, it had more uniform lignin chain lengths as reflected by its polydispersity (Mw/Mn) value of 2.2 as opposed to 3-4 in the literature.

The X-ray powder diffraction patterns of softwood lignin revealed the existence of two distinct domains. They are manifested by two overlapping Lorentzian peaks arising from cofacially offset and edge-on orientations of interacting aromatic rings respectively representing inner and peripheral regions of lignin associated complexes. However, the X-ray powder diffraction patterns of aspen kraft lignin and the resulting plastics cannot always be deconvoluted into two peaks alone. It appeared that their constituent aromatic rings have more complex interacting patterns. This could compromise the material continuity of associated complexes as aspen kraft lignin plastics are being formed. As a result, the materials are weaker compared to their softwood counterparts.
(This activity marked as complete as of this status update)

Activity 2
Among the solvents evaluated, dimethyl sulfoxide was most viable for solution casting aspen kraft lignin plastics; it yielded plastic specimens that could successfully be tested for tensile strengths. The casting conditions were also optimized where casting temperature was raised step-wise until it surpassed the Tg of aspen kraft lignin in such a way that the solvent was nearly completely removed.

Non-crystalline polymers like lignins possess Tg which affect many material properties. Not surprisingly, increasing a blend component from 5-15 wt% resulted in progressively lower Tg of the ensuing aspen kraft lignin plastics. This reflects an increased mobility of associated complexes within lignin plastics.

At 15 wt% level, a blend component improved the tensile strength of aspen plastics 3-fold reaching those of polyethylene (30 MPa). On the hand, a synergistic effect was observed where the presence of two different plasticizers engendered 85 wt% aspen kraft lignin plastics with 37 MPa in tensile strength with 6~8% in strain approaching those of polystyrene (46 MPa, 2% strain). Moreover, a plastic composed of equal weight-percent of aspen kraft lignin and Jack pine ball-milled (native) lignin possessed 50 MPa in tensile strength and 7% in strain surpassing polystyrene.
(This activity marked as complete as of this status update)

Dissemination
An oral presentation highlighting progress made in this LCCMR-funded project was given at the 2023 International Symposium on Wood, Fiber and Pulping Chemistry in July 2023. A manuscript describing the development of functional plastics based on aspen kraft lignins derived from Sappi Cloquet Mill is in preparation. Support from Minnesota Environment and Natural Resources Trust Fund will be fully acknowledged.

Status Update Reporting

Status Update October 1, 2023

Date Submitted: September 29, 2023

Date Approved: November 9, 2023

Overall Update

This project seeks to valorize aspen kraft lignin derived from the Sappi Mill in Cloquet, Minnesota by developing eco-friendly plastics with mechanical properties comparable with polyethylene.

It is generally assumed that lignin fractionation and/or modification, both of which are costly on a large scale, is a prerequisite for industrial viability. Our group has demonstrated neither step is required for lignin-based plastics. This is the approach we are taking by developing functional plastics based on unfractionated underivatized aspen kraft lignin preparation.

The molecular weight of our purified aspen kraft lignin is within the range of the reported values in the literature. However, it has a narrower molecular weight distribution. The glass transition temperature, on the other hand, is much higher than other hardwood kraft lignin preparations reported. This may explain the challenges we have encountered in developing functional plastics composed of 95 wt% aspen kraft lignin. Nevertheless, we have identified an eco-friendly polymer that, at a 15 wt% level, improved the tensile strength of aspen kraft lignin plastics by 3-fold bringing us closer to that of polystyrene. The effects of the blend component on the molecular organization of resulting plastics are being evaluated.

Activity 1

Previous work has demonstrated that mechanical properties of lignin plastics strongly depend on the molecular weight distributions of lignin preparations. Thus our purified aspen kraft lignin was acetylated to make it dissolve in tetrahydrofuran so that it could be analyzed through gel permeation chromatography.

The weight-average (Mw) and number-average (Mn) molecular weights of our acetylated aspen kraft lignin preparation were estimated to be 3100 and 1400, respectively, which were comparable with those reported in the literature. Yet it had a slightly narrower molecular weight distribution as reflected by its lower polydispersity (Mw/Mn) value compared to the published values of about 3-4.

Another characteristic of non-crystalline polymers such as lignin is the presence of a glass transition temperature (Tg) which affects the mechanical properties and service temperature range of a polymer. Our lignin exhibits a Tg of 175°C, as determined by differential scanning calorimetry (DSC), which is much higher than those reported in the literature. This could reflect the heterogeneous chemical structure and composition of the lignin preparation. Casting aspen kraft lignin into cohesive plastics increased the Tg by over 30°C.DSC studies so far indicate that the Tg increase was not attributed to blend compositions.

Activity 2

As mentioned in the previous report, dimethyl sulfoxide was the most viable solvent examined for solution-casting aspen kraft lignin-based plastics for mechanical testing. The solution-casting conditions have been optimized in such a way that the solvent is nearly completely (97-100%) removed before the lignin plastics can be tested for mechanical properties. A promising blend component has been identified which, when introduced at 5 to 15 wt% levels, improved the tensile strengths of the resulting aspen plastics up to 3-fold. It is plausible that this polymer blend component provides favorable material continuity in these 85-95 wt% aspen kraft lignin plastics. Our goal of producing 90 wt% aspen kraft lignin plastics possessing >30 MPa in tensile strength is within reach. This is the focus of current work.

Dissemination

An oral presentation highlighting progress made in this LCCMR-funded project was given at the 2023 International Symposium on Wood, Fiber and Pulping Chemistry in July 2023. A corresponding Conference Proceedings paper was also published. Support from Minnesota Environment and Natural Resources Trust Fund was fully acknowledged on both instances. A manuscript describing the development of functional plastics based on aspen kraft lignins will be submitted for publication toward the end of this project.

Status Update Reporting

Status Update April 1, 2023

Date Submitted: March 30, 2023

Date Approved: April 6, 2023

Overall Update

The annual global production of lignin in the pulp and papermaking industry is estimated to be about 80 million tons. Indeed, kraft lignins have been touted as "raw material for the future", but currently they are almost exclusively used as fuel in the pulp mill recovery boiler. This project seeks to improve profitability in traditional pulp mills by developing plastics formulations based on aspen kraft lignin derived from the Sappi mill in Cloquet, Minnesota. These new plastics can eventually be eco-friendly alternatives to polymeric materials produced from petrochemical sources. Several miscible plasticizers investigated so far can slightly improve the tensile strengths of aspen kraft lignin-based plastics. We have also identified plastic blends containing Jack pine ball-mill and aspen kraft lignin preparations that surpass polystyrene (46 MPa, 2% strain) in tensile strength.

Activity 1

As detailed in our January 2023 report, we had solved a significant issue with aspen kraft lignin isolation. By introducing an additional centrifugation step at pH 11 in the isolation process, colloidal sulfur can be completely removed. This has enabled us to routinely obtain aspen kraft lignin with high purity from Sappi Cloquet Mill black liquor. The focus of attention for Activity 1 is now the characterization of aspen kraft lignin preparations in terms of their molecular weight distributions and molecular organization. The first step in size-exclusion chromatographic studies of molecular weight distributions is acetylation of aspen kraft lignin preparation which is currently underway.

Activity 2

Aspen kraft lignin can readily be dissolved in solvents such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF), or γ-valerolactone (GVL). However, only solution-casting in DMSO so far yields aspen kraft lignin-based plastics that can be filed to test specimens with measurable tensile strengths. Several plasticizers (ranging from monomers to polymers) form homogeneous blends with aspen kraft lignin preparations. None investigated so far significantly improves the tensile behaviors of the resulting plastics. On the other hand, when incorporated with 40 wt% Jack pine ball-milled lignin (BML), the tensile strength of the resulting 60 wt% aspen kraft lignin-based plastics increases to 25 MPa. Blending BML and aspen kraft lignin in equal proportion engenders plastics surpassing polystyrene (46 MPa, 2% strain) in tensile strength. Other promising plasticizer candidates are being evaluated.

Dissemination

We are committed to disseminate our results to the general public and scientific community at the earliest opportunities. An oral presentation at the forthcoming 2023 International Symposium on Wood, Fiber and Pulping Chemistry will highlight the progress made in this LCCMR-funded project. A manuscript describing the development of functional plastics based on aspen kraft lignins will be submitted for publication toward the end of this project.

Status Update Reporting

Status Update October 1, 2022

Date Submitted: February 1, 2023

Date Approved: February 7, 2023

Overall Update

Wood and plant materials are mainly composed of polysaccharides (cellulose and hemicelluloses) and an aromatic polymer (lignin). Lignins account for up to 35% of renewable lignocellulose. Profitability for converting lignocellulosic polysaccharides to biofuels or organic chemicals depends on valorization of coproduct lignins. Kraft lignin, the most abundant industrial co-product lignin, is almost exclusively used as a (low-value) fuel in the pulp mill recovery boiler, which houses the rate-limiting step of the operation. This project seeks to convert aspen kraft lignin derived from the Sappi mill in Cloquet (Minnesota) to higher-value commodity thermoplastics. Utilization of the surplus kraft lignin in making plastics would not only eliminate the adverse environmental consequences of its disposal, but also create eco-friendly substitutes for polymeric materials from petrochemical sources. We have documented several homogeneous aspen kraft lignin plastic blends with measurable strengths. Further studies are underway to identifying other blend components that can result in biodegradable aspen kraft lignin plastics with tensile properties surpassing those of polyethylene.

Activity 1

The most important progress during this reporting period is improvement in the isolation protocol for aspen kraft lignin from Sappi Cloquet Mill. The significance is two-fold. First, a 10% increase in the aspen kraft lignin yield was obtained. Second, the resulting lignin preparation could be successfully made into plastics for mechanical testing. Previously during solution-casting, the majority of aspen kraft lignin plastics became deformed around 150°C regardless of formulations and/or casting conditions. The final casting temperatures, however, need to exceed 150°C to attain the rubbery state of lignin preparations. This is a critical parameter for plastics formulations. To overcome such a serious deformation problem, several remedies were explored. Ultimately, an extra centrifugation step at pH 11 added to the previous protocol (April 2022 report) to remove colloidal sulfur during the initial acidification (to pH 3.0) was the most significant. The ensuing aspen kraft lignin sample was a far better starting material. Deformation is now a rare occurrence; it is mostly observed in the presence of certain blend components being investigated. It is conjectured that more lower-molecular weight aspen kraft lignin components are retained during the new isolation procedure. Molecular weight distribution studies will provide some insight.

Activity 2

We continued our intensive efforts in creating plastics formulations containing high levels of aspen kraft lignin preparation. As mentioned in the Activity 1 of the current report, the focus of effort was on solving the problem with plastic deformation which occurred around 150 °C during casting. Three different solvents (dimethyl sulfoxide, dimethylformamide and γ-valerolactone) were investigated as a possible remedy. Once the purification protocol was improved (see Activity 1 report), dimethyl sulfoxide was the solvent of choice as it yielded plastic specimens that could be tested for mechanical properties. Candidate plasticizers were blended at 5% level with aspen kraft lignin. Several blend components resulted in successful mechanical testing. The tensile strengths of these aspen kraft lignin plastics had not yet met our goal (32–46 MPa), but we anticipate significant improvements are forthcoming as other candidate blend components are being explored. Another approach to creating eco-friendly aspen kraft lignin-based plastics is to blend with other lignin preparation (ball-milled Jack pine lignin, for example). The results obtained so far are very promising.

Dissemination

We are committed to disseminate our results to the general public and scientific community at the earliest opportunities. An oral presentation at an international meeting in 2023 has been planned. It is anticipated that a manuscript describing up to date progress on aspen kraft lignin plastics will be submitted for publication toward the end of this project.

Status Update Reporting

Status Update April 1, 2022

Date Submitted: April 29, 2022

Date Approved: May 6, 2022

Overall Update

After a delayed start, we have successfully negotiated the first two steps toward creating plastics from Sappi pulp-mill aspen kraft lignin in Cloquet. Profitable alternative production of fuels, biodegradable plastics and chemicals from renewable wood and plant materials is being vigorously pursued in response to global warming. Raw materials include wood in forest residuals, agricultural residues and specialty crops. Integrity in tree limbs and trunks, plant stalks and stems, is maintained by cellulose fibers (comparable to cotton) and hemicelluloses; all are composed of linked sugar units. These sugars can be converted into fuels (cellulosic ethanol and "biojet") and organic chemicals. Despite multibillion-dollar investments by DOE, however, costs remain too high. A compelling way of solving the problem involves gaining significant additional value from the lignins that make up 12–35% of all wood and plant materials. The best option for illustrating success lies with the industrial kraft process whereby lignin in wood chips is removed to form pulp for making paper. We are converting kraft lignin produced from aspen wood chips pulped in Cloquet into eco-friendly plastics that surpass non-biodegradable polystyrene in behavior. Positive outcomes will improve profitability in traditional pulp mills and future biorefineries alike.

Activity 1

Aspen kraft lignin was isolated as a precipitate that separated during acidification of alkaline "black liquor" formed by kraft pulping of aspen wood chips in the Cloquet Sappi pulp mill. Aspen kraft lignin purity was compromised by the persistent appearance of fine sulfur particles formed from black-liquor polysulfide under acidic conditions. Sulfur removal was necessary to avoid adverse effects upon the strengths of the aspen kraft lignin-based plastics to be created. "Black liquor" was acidified to pH 3.0, whereupon the precipitated kraft lignin was isolated by centrifugation. After dissolution of the precipitate at pH 11.0, the fine sulfur particles that separated from solution on standing were removed by centrifugation. The aspen kraft lignin was isolated by re-acidifying the solution with hydrochloric acid to pH 3.0, then washing the resulting precipitate three times with aqueous hydrochloric acid at the same pH (which remained clear and colorless). Upon re-dissolution, the kraft-lignin solution was allowed to stand at pH 8.8 until the fine sulfur particles had completely separated from solution for removal by J2-21 centrifugation. After final acidification of the solution to pH 3.0, the precipitated aspen kraft lignin was washed with water and air-dried.

Activity 2

We have solution-cast purified 100% aspen kraft lignin-based plastics into the shape of tensile test pieces. Casting conditions have been carefully adjusted in incremental steps to facilitate complete loss of solvent without the appearance of voids within the plastics being formed. Each distinct material being studied as a possible candidate for creating eco-friendly plastics requires an individually tuned protocol. The first sign of a promising outcome is the development of material continuity and measurable strengths in the formulations being investigated. We are privileged to report that this has been achieved for the first time with 100% aspen kraft lignin-based plastics. Improvements in their mechanical properties are the subject of intensive investigations. While the glass transition temperature of purified uncast aspen kraft lignin can be readily determined, the same parameter for the corresponding plastic is difficult to discern. Possible reasons for the difference are being carefully evaluated.

Dissemination

At this first reporting stage of the project, it is premature to communicate our results to the general public or the private sector. However, we gave a presentation entitled "Biodegradable plastics with 95–98 wt% underivatized unfractionated industrial kraft lignin can well exceed polystyrene in mechanical behavior" at the American Chemical Society National Meeting in San Diego in March 2022.