PROCEEDINGS
Kraft Lignin Innovation Forum
October 11 & 12, 2017
Verso Quinnesec Mill
Iron Mountain, Michigan

Hosted by:
Michigan Forest Biomaterials Institute
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The shared speaker PowerPoint presentations can be found at:

mifbi.org/events/past-events/2017-kraft-lignin-forum

Agenda

Kraft Lignin Innovation Forum

October 11th & 12th, 2017
Iron Mountain, Michigan
W6791 US Highway 2
Verso, Quinnesec Mill, Conference Room

In the near future, Lignin separation and valorization is expected to be standard technology at all kraft pulp mills. However, each mill has different feedstock and processing that creates different lignin, therefore, development of technology platforms will be unique for each mill. Cost competitive business models need to be developed with potential customers and with those across the whole value chain. Whether a byproduct of papermaking or residual from biorefineries, the Michigan bio-circular economy is in need of creating value from lignin.

This forum intends to bring researchers and companies from across Michigan (and beyond) to learn firsthand the availability and opportunities surrounding residual black liquor from Michigan's largest pulp producer. This meeting will be kept small (~15 attendees) to encourage discussion that explores and business possibilities and key research needs.

This meeting will kick off the creation of an informed network of businesses, researchers and government, focused on pulp mill byproducts that cuts across sectors of the economy. MIFBI will serve to guide the network toward opportunities in the Michigan bioeconomy.

Special Invited Guest - Kirsten Maki, P. Eng. *Bio-economy Technology Centre, FPInnovations, Thunder Bay, ON*
Kirsten Maki has a degree in Chemical Engineering from Lakehead University. She worked as a process engineer and shift supervisor at the Resolute mill in Thunder Bay, Ontario before joining FPInnovations in 2009. Her work at FPInnovations' Bio-economy Technology Centre (BETC) in Thunder Bay has focused on scaling up the extraction of coproducts from wood pulping including lignin, methanol and sugars. The kraft lignin extraction process piloted at the BETC has been commercially deployed as the LignoForce process.

Agenda Overview (The agenda was arranged to accommodate flight schedule from Detroit to Iron Mtn.)

Wednesday, October 11th

11:30 – 12:30pm	Lunch and Introductions (Mark Rudnicki, MIFBI & Steve Brooks, Verso)
12:30 – 1:30pm	Presentations by Verso Corporation & group discussion
1:30 – 2:30pm	Short presentations by industry attendees & group discussion

Julie Manley, Guiding Green – Rethinking the value chain for a circular economy
Donna LaCourt, MDARD - Overview of MI Forest Product sector
Warren Suchovsky, Michigan Asso. Timberman – Perspective from the forest
Alper Kiziltas, Ford Motor Company – Sustainable Materials for Automotive Applications
Brad McPhee, Creative Composites – A market for lignin carbon fiber
Shakti Mukerjee, Resinate Materials Group – Sustainable Lignin Polyester Polyols

2:30 – 3:00pm	Break
3:00 – 4:30pm	Tour of Verso Quinnesec Mill
5:00 - 6:30pm	Private Cocktail Reception at Historic Chippewa Club (106 Carpenter Ave, Iron Mountain, MI)

Thursday, October 12th

8:30 – 9:30am	Special Invited Guest – Kirsten Maki, P.E., FPInnovations 'Lignin Application Development, and scaling up the LignoForce process'
9:30 - 10:30am	Short presentations by University faculty - interests and expertise

David Shonnard, Chemical Engineering, MTU - Guiding Sustainable Development in the Forest Bioeconomy: Environmental Life Cycle Assessment
Eric Hegg, Biochemistry and Molecular Biology, MSU - Strategies for Developing Clean Lignin Streams and Subsequent Depolymerization
Rebecca Ong, Chemical Engineering, MTU – Utilizing Lignin's Inherent Properties for the Production of Value-Added Products

10:30 -11:00am	Break
11:00 - 11:30am	(Cont.) Short presentations of University faculty interests and expertise

Mojgan Nejad, Forestry, MSU – Developing Lignin-based Resins for Adhesive, Coating and Foam Applications
Mike Mullins, Chemical Engineering, MTU – The production of renewable fuels from lignin- a perspective from Sweden
Xinfeng Xie, Forest Resources & Environmental Science, MTU – High glass transition lignin for carbon fiber production

Wen Zhou, Chemical Engineering, MTU – Process modeling and Life-cycle assessment of biomass conversion

11:30 – 12:30pm	Working lunch and continued discussion
12:30 – 2:00pm	Outlining steps of how to move forward
2:00pm	Wrap up of meeting

Summary

The forum on lignin brought together experts from academia, industry, and government to share knowledge and identify technical and economic opportunities and challenges for the pulp and paper industry with regard to the utilization of the lignin byproduct from the Kraft process. The forum concluded with several action items that participants could work on together to accelerate the advancing forest bioeconomy in Michigan.

Acknowledgements

We would like to thank Steve Brooks at the Verso Corporation for generously providing the meeting venue and catered lunches. We would also like to thank Julie Manley at Guiding Green for her help in organizing this event.

Resulting Actionable items

As a result of the afternoon discussions, there emerged four actionable items. All four were subsequently pursued and the results were shared at a follow up meeting for researchers (pg. 14).

1. *Isolate pure lignin from the black liquor and measure its physical, chemical and thermal properties.*

   Verso will send black liquor samples to MSU, who will isolate out the lignin using standard TAPPI procedure and conduct comprehensive analyses of the obtained lignin samples using analytical techniques, such as HPLC, GPC, DSC, TGA, FTIR and NMR. MTU can provide thermal analyses (TGA and DSC) of the samples isolated at MSU, if needed.

2. *Based on characterization results predict products or applications best suited for the pure hardwood lignin produced by the Quinnesec Mill. This is a unique feedstock that could provide competitive advantage over mixed or just softwood lignin.*

   Quinnesec mill uses only hardwood species (primarily maple). Due to the low reactivity of hardwood lignin toward formaldehyde, it might be used for other applications, such as polyurethane resin for foam, coating and adhesives or as filler in biocomposites. Results from chemical characterization will provide more information about the potential applications of the lignin. MSU and MTU should provide recommendations for potential applications of the lignin based on the shared analysis results.

3. *Perform a technical and economic feasibility analysis on the separation process.*

   Based on the recommended potential applications of Verso lignin, MTU can perform the technical and economic feasibility analysis for each application identified by Verso. The analyses will be incorporated into MTU students' curriculum activities (e.g. capstone projects or Enterprise) in the Department of Chemical Engineering. Donna LaCourt mentioned a potential funding source to support this activity, and she will follow up then it is announced later this year.

4. *Document the forum with a proceedings to be publicly shared.*

   To share perspectives and accomplishments MiFBI will assemble abstracts and presentations into a proceedings of the forum. The proceedings and presentations will be put on its website and available for public download.

Speakers

Special Guest Kirsten Maki

Associate Research Leader
FPInnovations

Title: LignoForce Kraft Lignin Extraction: Process Scale-Up, and Product Development

Co-authors: Michael Paleologou, Yaolin Zhang, Martin Feng, and Pedram Fatehi

Abstract: Biorefineries will play a key role in the future of the forest industry, and lignin is a product that will feature prominently in the mix. Lignin is a plant derived source of aromatic chemicals and has long been studied in various applications; its potential as a 'green' chemical feedstock is being realized, now that extraction technologies have been commercialized.
The first commercial LignoForce system for extracting lignin from the Kraft pulping process began operation in 2016. This presentation reviews the development of the process, from lab scale through to the commercial plant, including the critical role played by the pilot plant in Thunder Bay. The goal of the pilot plant was to produce lignin samples for research into value-added applications, to produce sufficient quantities for large scale trials, to fine-tune operating conditions. These goals were achieved, and the pilot plant experience helped shape many aspects of commercial plant design, including material and equipment selection. This project also highlighted the importance of partners in new technology development; FPInnovations partnered with an engineering firm in scaling from lab to pilot, and from pilot to commercial scale, and also with a member mills (one of which supported early stage development through hosting the pilot plant, and another which invested in building and operating the first commercial unit). In parallel with the process development, lignin applications were also being developed, as developing products and markets is essential for ultimate success. The approach taken by FPInnovations was to focus the majority of early product development efforts on a launch market for early offtake; adhesives in wood products was a natural fit. Additional applications are of course essential for building and expanding the market, and a few of these are noted as well. The collaboration of various parties at all stages of the project was key to success both on the process and product development fronts.

Julie Manley

President
Guiding Green LLC

Title: Rethinking the value chain for a circular economy

Abstract: The linear supply chain paradigm of “take, make, waste” incurs cost and waste to all segments of the value chain from the initial extractor of the raw material to the product manufacturer to the consumer, and beyond. We have the opportunity to curve the value chain to enable a circular economy; rethinking technology, resources, customers, and markets to keep materials at their highest use value for as long as possible. Kraft lignin, a byproduct of pulp & paper mills, is commonly used for energy, but there is indication that Kraft lignin has higher value as a source for bio-based materials (adhesives, coatings, carbon fiber, flavors/fragrances, etc.). It has been reported that circular supply chains that increase the rate of recycling, reuse and remanufacturing could generate more than $1 trillion a year by 2025 (Towards the Circular Economy, Ellen MacArthur Foundation and McKinsey & Company, 2014). Yet, the price of oil, available technologies, and other factors can challenge the feasibility of a circular supply chain. Navigating and optimizing the interfaces requires innovative thinking, scientific advances, and collaboration. This presentation summarizes the development of Guiding Green’s experience in designing for sustainability, highlighting learnings from development and management of collaborations to help industry integrate green chemistry, the design of processes & products to use and generate less hazardous materials. Development and use of bio-based materials, such as Kraft lignin, is an integral component to green chemistry. Identifying and communicating industry needs allows academia, small business, other industrials sectors, and government to deliver solutions. The value chain in a circular economy is complex, arguably not even sufficiently understood, and requires active collaboration to develop opportunities and resources that create value for all components of the chain. Guiding Green has started working in this space to enable circular economy regionally. Understanding the availability and properties of Kraft lignin, as well as the performance specifications in various markets, can help develop an informed perspective on the value of Kraft lignin, and define the technology and information needs to transform it into valuable biomaterials.

References:

http://pubs.rsc.org/en/Content/ArticleLanding/2007/GC/b703488c#!divAbstract
http://pubs.rsc.org/en/content/articlelanding/2015/gc/c4gc02261k#!divAbstract
http://pubs.acs.org/doi/abs/10.1021/op100327d

Donna LaCourt

Economic/Community Development Specialist
Michigan Department of Agriculture and Rural Development

Title: Michigan's Forest Products Sector and Economic Development

Abstract: Michigan's Governor held Forest Product Summits in 2013 and 2015. The summits focused efforts to grow Michigan's forest product sector both in value and in jobs. Michigan's forest product sector as of 2016 was $20.3 billion in output with over 96,000 jobs. Adding more value to forest products in Michigan before exporting domestically or internationally and substituting Michigan products for exports are strategically key to support growth of the sector. Economic development efforts are being focused on understanding the forest product supply chain to address weaknesses, utilize strengths and fill gaps, along with pursuit of wood innovation opportunities. Supporting development of a robust, efficient, and innovative supply chain, along with coordination of economic development resources will inspire investment to pull growth opportunity rather than push.

Warren Suchovsky

Board Member
Michigan Association of Timbermen

Title: Perspective from the Forest

Abstract: From the perspective of a logger and forestland owner, historically our concerns were to control operational costs and ensure that there is an adequate supply of timber to harvest. Timber supply is no longer an issue. Our objective needs to shift from supply to increasing marketing opportunities. We need to increase our utilization of components of harvested trees as well as salvage from dead trees. We need to extract higher value products perhaps through chemistry. More opportunities in local communities for value added activities from products of the forest need to be created. We must be able to compete in the global market. We must better utilize the natural, human and financial resources of local communities. Certification of forest lands and industry is more than can we continue to grow trees. It is about sustaining the viability of local rural communities.

Alper Kiziltas

Ford Motor Company
Research Scientist

Title: Sustainable Materials for Automotive Applications

Slides available at mifbi.org

Brad McPhee

President
Creative Composites, Inc.

Title: Lignin-Based Carbon Fiber: A Case for Sustainable Advanced Technology Manufacturing in Michigan's Upper Peninsula

Slides available at: mifbi.org

Shakti Mukerjee

Resinate Materials Group

Title: Flame Retardant Characteristics of Recycled and Lignin-Based PET Polyols for Rigid Foam Applications

Co-Authors: Kevin A. Rogers, Joshua N. Cupp, Rick L. Tabor

Abstract: Halogenated flame retardant agents have protected the public from injury and death by
helping to prevent fires in buildings and dwellings for many decades. Today, new flame retardant options are being sought that are based on green chemistry and that contain no halogens for use in rigid foam applications. Resinate Materials Group, Inc. has developed green-content aromatic polyester polyols that provide improved flame retardant performance in polyisocyanurate (PIR) insulating foams. The green content of these new polyol products originate from biorenewable lignin and recycled polyethylene terephthalate. This paper details the performance of these emerging sustainable-content polyols in PIR foam applications.

David Shonnard

Professor, Chemical Engineering
Michigan Technological University

Title: Guiding Sustainable Development in the Forest Bioeconomy: Environmental Life Cycle Assessments

Abstract: This short presentation exhibits the capabilities of the Sustainable Futures Institute (SFI) at Michigan Tech in environmental life cycle assessment (LCA) that can be used to support the future development of a forest-based bioeconomy in Michigan. The SFI is a multidisciplinary research and teaching institute focused on sustainability, with participation by nearly 200 faculty, staff, and students at the university, and with partnerships involving institutions throughout the Pan American region. In cooperation with several emerging biofuel and bioenergy companies, LCAs have been conducted on emerging advanced biofuels from a wide range of biomass feedstocks and industrial residues. The main goal of the LCAs is to compare the carbon footprints of advanced biofuels with conventional and alternative petroleum fuels. The presentation concludes with a slide showing a novel two-stage micropyrolysis reactor for the chemical recycling of waste plastics. The new reactor is providing insights on the reaction mechanisms and kinetics of plastics pyrolysis for chemical recycling.

Eric Hegg

Professor, Protein Structure and Molecular Biophysics
Director of MSU Operations, Great Lakes Bioenergy Research Center
Michigan State University

Title: Strategies for Clean Lignin Streams and Subsequent Depolymerization

Co-authors: Aditya Bhalla[1,2], Namita Bansal[1,2], Grace E. Klinger[1,2,3], James E. Jackson[2,3], David Hodge[2,4,5,6], and Eric L. Hegg[1,2]

[1]Department of Biochemistry & Molecular Biology, Michigan State University
[2]DOE Great Lakes Bioenergy Research Center (GLBRC)
[3]Department of Chemistry, Michigan State University
[4]Department of Biosystems and Agricultural Engineering, Michigan State University
[5]Department of Chemical Engineering & Material Science, Michigan State University
[6]Department of Civil, Environmental and Natural Resources Engineering, Luleå University of Technology

Abstract: Our novel two-stage copper-catalyzed alkaline hydrogen peroxide (Cu-AHP) pretreatment process effectively delignifies hybrid poplar and results in glucose yields of up to 96% following enzymatic hydrolysis.[1-3] The solubilized lignin can be easily recovered, is only lightly colored, and has properties very similar to native lignin, making it particularly amenable to valorization. To improve the economic sustainability of the two-stage Cu-AHP process, we are developing strategies to utilized the lignin obtained from Cu-AHP pretreatment. In addition to its potential application in resins, coatings, and foams, lignin isolated from the Cu-AHP pretreatment process is also amenable to depolymerization because it retains its β-O-4 bonds and has not been modified extensively with additional crosslinks.

In collaboration with researchers at the University of Wisconsin, we are testing the efficacy of an oxidative depoymerization strategy.[4] In addition, we are also developing a biomimetic reductive depolymerization strategy. *Sphingobium* sp. strain SYK-6 employs a glutathione-dependent enzyme to reductively cleave β-O-4 bonds, a ubiquitous linkage in lignin. Utilizing small organic thiols to mimic the etherase chemistry, we have demonstrated 100% conversion and up to 95% yield of lignin model compounds. In addition, using this approach we have also observed considerable reduction in molecular weight of authentic poplar lignin. To our knowledge, this work exemplifies the first reductive biomimetic approach to lignin degradation by mimicking small molecule-mediated enzymatic ether cleavage.

1 *Biotechnol. Biofuels* 2013, *6*, e119
2 *Biotechnol. Bioeng.* 2013, *110*, 1078-1086
3 *Biotechnol. Biofuels* 2016, *9*, e34.
4 *Nature*, 2014, *515*, 249-252.

Rebecca Ong

Assistant Professor, Chemical Engineering
Michigan Technological University

Title: Using Lignin's Inherent Properties for the Production of Value-Added Products

Slides available at: mifbi.org

Mojgan Nejad

Assistant Professor, Green Bioproducts
Michigan State University

Title: Developing Lignin-based Resins for Adhesives, Coatings, and Foam Applications

Abstract: Lignin is a 3D-complex natural polymer made of phenylpropane units that has a great potential to replace petrochemicals in polymeric industries. Lignin contains both aliphatic and aromatic functional units, which makes it an excellent candidate to replace petroleum-based polyols in formulation of polyurethanes for foam, adhesive and coating applications. In addition, lignin is a natural polyphenolic compound, which can replace 100% of phenol in phenolic adhesive formulations that are used in the production of plywood and orientated strand board (OSB) in building constructions. Depending on the source (hardwood, softwood or annual crop) and isolation process (Kraft, organosolv, soda, sulfite and enzymatic hydrolysis), there are significant variations in structure and properties of the lignin. In order to use lignin in different products, first it needs to be completely characterized then determine its suitability for that specific application.

Michael Mullins

Professor of Chemical Engineering
Michigan Technological University

Title: Renewable Fuels from Lignin- A Swedish Perspective

Abstract: While serving as the Distinguished Fulbright Chair in Alternative Energy at Chalmers University (Gothenburg, Sweden), Dr. Mullins explored processes to produce renewable transportation fuels fully compatible with existing engines and the fuel distribution infrastructure. The work was done in collaboration with Michigan Technological University, Chalmers University, Valmet, and the Swedish refiner Preem. Preem currently produces >250,000 m^3 of renewable fuels/year but needs additional feed materials to reach goal of >1M m^3/year. The team also examined the co-production of value-added chemicals (e.g. BTEX) as a possible credit toward the cost of production. Pyrolysis oil is a less than an ideal starting point for fuel production processes, due to small molecule size and oxygen content (>30wt%), therefore our work focused on the development and optimization of a pilot-scale hydrothermal process for lignin depolymerization to produce a suitable bio-oil. Hydrothermal liquefaction (HTL) in near-critical water is promising due to larger product molecules and low oxygen content (<13wt%). It produces a higher average molecular weight distribution than pyrolysis oil, making it more suitable for renewable gasoline, and chemical production. Experimental studies using catalytic hydro-deoxygenation (HDO) of the products produced a significant product range of C6 to C8 with minimal coking. These results have been incorporated into detailed process-level models to simulate the entire process and to conduct techno-economic analyses (TEA) and Life Cycle Assessments (LCA) for several lignin-to-fuels process scenarios.

Xinfeng Xie

Assistant Professor of Forest Biomaterials
Michigan Technological University

Title: High Glass Transition Lignin for Carbon Fiber Production

Abstract: Lignin is the second most abundant renewable biopolymer in nature. It has been considered as a renewable precursor for carbon fiber production because of its low prices (~$500 per ton), high carbon yield (>40%), and broad availability. Lignin recovered from Kraft black liquor has great potential to fill the low-cost raw material need and to improve profitability of the pulp and paper industry. In North America alone, the potentially available Kraft lignin was estimated at 1.5 million tons per year. However, the major technical barriers of heterogeneous structure and unique reactivity that are associated with the origin and isolation method of the lignin need to be overcome before utilization of lignin in developing lignin-based carbon fiber products. Lignin fractionation is the first step toward tailoring lignin to specific carbon fiber products. Our preliminary study on integrated liquefaction/fractionation of lignocellulosic biomass using subcritical methanol produced a high-purity lignin fraction with a glass transition temperature higher than 180C, showing a great potential for melt-spinning lignin for fiber production. This method will be tested with Kraft hardwood lignin in our future studies.

Wen Zhou

Assistant Professor, Chemical Engineering
Michigan Technological University

Title: Process Modeling and Life Cycle Assessment of Biomass Conversion

Abstract: In this presentation, Dr. Zhou talked about the computational capability in his lab for both biochemical conversion pathway and thermochemical conversion pathway for producing biofuels and value-added products from biomass. These detailed mechanistic modeling at process level and whole flowsheet simulation at plant level could be very useful for the scale-up procedure of the technology we are seeking for innovative utilization of lignin.

Follow-up Meeting

An online follow-up meeting was held on July 3, 2018. Researchers reviewed the progress that had been made on the actionable items that emerged from the forum. The meeting allowed faculty from the two institutions to come back together to discuss potentials for further collaboration and establishing federal funding- from NIFA and NSF. Currently, two collaborative grant proposals have been submitted, focusing on hardwood lignin valorization.

Attendees:

Mark Rudnicki, MiFBI mark@mifbi.org
Steven Brooks, Verso steve.brooks@versoco.com
Mojgan Nejad, MSU nejad@anr.msu.edu
Richard Kobe, MSU kobe@anr.msu.edu
David Shonnard, MTU drshonna@mtu.edu
Rebecca Ong, MTU rgong1@mtu.edu

Agenda for July 3rd, 2018 online meeting
9:00am - Start of meeting and welcome - Mark Rudnicki
Steven Brooks - opening remarks
Mojgan Nejad - 10-15min
Xinfeng Xie -10-15 min
David Shonnard - 10-15min

10:30am - General discussion about shared results
11:00am - Discussion about future joint opportunities