NARA Goal Two

3RD Cumulative Report

April 2014 - March 2015

Value-Added Polymer and Carbon Products from Lignin

Create valuable co-products made from lignin, which is an
industrial byproduct of the woody biomass to biojet process.

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SUMMARY

Based on current estimates, for every bone-dry ton of forest residue converted to isobutanol, 1450 dry pounds of co-product residuals are produced (Tom Spinks presentation at the Idaho Small Log Conference 2013). Approximately 37% of the co-product residual is lignin (550 dry pounds) with the remainder being cooking acids, non-reacted cellulose (polysaccharides), non-fermented monomeric sugars, extractives, bark, yeast bodies, and wood ash. The most common strategy for dealing with these residual solids is to recover their fuel value to assist in heating and providing electrical power for facilities. While this strategy remains as a potentially valid one, NARA researchers are developing new products such as (1) activated carbon products, (2) cement additives, (3) thermosetting resins, and (4) thermoplastic polymers from the residual solids to provide a higher value than current use for energy. Creating high-value products from the residual solids produced in the pretreatment and hydrolysis production stages is essential to establish a value-chain for improved bio-refinery profitability. In addition, NARA is exploring methods to modify the lignin-rich material to produce platform molecules used to make an even broader array of valued products.

Freeze dried lignin residues from Douglas-fir after various mechanical and chemical pretreatments. NARA image

RESIDUAL SOLIDS AS MATERIAL FOR ACTIVATED CARBON AND SUPERCAPACITORS

In the previous NARA Year-3 reporting period, activated carbon (AC) materials were made from fermentation residual solids (FRS) derived from the mild bisulfite and wet oxidation pretreatment procedures and initially characterized for structure and their ability to absorb vapor phase mercury from coal power plant flue gas. In this reporting period, the activated carbon products were modified, by increasing the activation time, and again tested for vapor mercury absorption. The tests showed that the increase in activation time improved vapor mercury saturation, however, equilibrium capacity for both AC products was less that offered by commercially available AC products.

Experimental results suggest that the improved capacity of the commercial product is due to a greater proportion of large mesopores and macropores; consequently, further experimentation is underway to establish an AC production process that extends the pore size of the FRS AC. In addition, the lignin-rich residuals derived from modified pretreatment protocols like milled wood (MW; Task E-8) will be evaluated and could potential produce AC with superior absorption capacity (Task C-CP-2).

LIGNIN USE AS THERMOPLASTIC MATERIAL

In the previous NARA Year-3 reporting period, methylated ball-milled softwood lignin (MBML), was used to develop protocols that could be applied to lignosulfonates generated from Douglas-fir residues after sulfite-based pretreatment and enzymatic hydrolysis. Polymeric material exhibiting ~50% tensile strength and elongations at break around 8% were generated from the MBML material.

During this reporting period, improved protocols were applied to methylated lignosulfonate (MLS) from

Douglas-fir residues, and polymeric materials were produced for the first time that are comparable in strength to those formed from methylated softwood ball-milled lignin. The plastics formed from MLS verses MBML are different, however, at a molecular level. Research is in progress to estimate and reduce the cost of producing plastic material from MLS feedstock (Task C-CP-1).

PARTIALLY DEPOLYMERIZED LIGNIN AS A BUILDING BLOCK FOR CHEMICAL SYNTHESIS

The goal of producing partially depolymerized lignin (PDL) is to create building blocks used to engineer high value polymers. In the previous NARA Year-3 reporting period, the mild hydrogenolysis and BCD depolymerization protocols were applied to the lignin derived from forest residuals pretreated by the mild bisulfite (MBS) and wet oxidation (WOX) process. For this reporting period, partial hydrogenolysis protocols using MBS lignin were further developed, and a PDL-based epoxy was produced with yields of 86.6% at 70 °C and 100% at 117 °C. The molecular structure for the PDL-epoxy was evaluated.

The PDL-epoxy was cured and compared with a similarly cured commercially available epoxy. The PDL-epoxy exhibited a lower curing temperature and a higher activation energy compared to the commercial epoxy. The comparison results indicate that the PDL-epoxy possessed a similar thermal stability to the commercial epoxy. Additional curing agents are being investigated for use with the PDL-epoxy.

Additional depolymerization protocols to generate organosolv (OL) and oleated organosolv lignins were developed by mechanochemical reaction ball milling with the intent to produce PDL-lignin under milder conditions compared to the mild hydrogenolysis and BCD depolymerization protocols. The molecular structures for the resulting modified lignins were determined. The OLs were blended with polylactic acid (PLA) and exhibited good processability (Task C-CP-3).

SIGNIFICANT OUTPUTS REPORTED THIS PERIOD FOR THE CO-PRODUCT DEVELOPMENT TEAMS

- An international patent application titled “Compositions Including Lignin” was filed March 13, 2015 (Task C-CP-1).
- For the first time, lignosulfonate-based plastics have been successfully produced from sulfite-based pretreated Douglas-fir residuals (Task C-CP-1).
- A partially depolymerized lignin-epoxy was produced that, when cured, shares similar properties to commercially available epoxies (Task C-CP-3).
- A peer-reviewed manuscript (Ma et al) was published titled “Catalytic Oxidation of Biorefinery Lignin to Value-added Chemicals to Support Sustainable Biofuel Production” doi: 10.1002/cssc.201402503 (Task CP-2).
- A peer-reviewed manuscript (Alvarez-Vasco et al) was published titled “Dilute acid pretreatment of Douglas fir forest residues: pretreatment yield, hemicellulose degradation, and enzymatic hydrolysability” doi: 10.1007/s12155-014-9496-7 (Task CP-2).

SIGNIFICANT OUTCOMES

- None reported

TRAINING

Name	Affiliation	Role	Contribution
Yi-ru Chen	Univ of Minnesota	Graduate Student	Lignin-based plastic formulations
Yun-Yan Wang	Univ of Minnesota	Graduate Student	NARA ligninsulfonate-based plastics formulations
Junna Xin	WSU, CMEC	Post-doc	Lignin depolymerization and epoxy asphalt
Xiaojie Guo	WSU, CMEC	PhD Student	Lignin modifications and blends
Mei Li	WSU, CMEC	Visiting PhD Student	Lignin modification and epoxies
Alvarez Vasco, C	WSU, BSEL	PhD Student	
Cassandra Sanders	WSU, BSEL	NARA SURE Undergraduate	
Ruoshui Ma	WSU, BSEL	PhD Student	

RESOURCE LEVERAGING

Resource Type	Resource Citation	Amount	Relationship or Importance to NARA
Scholarship			Funding for C. Alvarez Vasco
NARA SURE		$5,000	Cassandra Sanders

CONVERSION

CO-PRODUCTS TEAM

TASK C-CP-1: FORMULATIONS FOR CO-PRODUCT LIGNIN-BASED PLASTICS

Key Personnel	Affiliation
Simo Sarkanen	University of Minnesota

Task Description

As a result of the work carried out during Years 1–3, promising formulations have been developed for converting softwood lignins into plastics with the highest attainable lignin contents. These unprecedented achievements have paved the way for converting NARA ligninsulfonates into useful polymeric materials. A positive outcome will enable productive communication with Borregaard to explore translation from laboratory practice to industrial applications. The emphases given to the various components of the tasks listed below will depend upon the outcomes from the inter-related studies that are carried out.

Context:
For the first time in 40 years, simple native softwood lignin derivatives (namely, methylated ball-milled lignins) have been converted into plastics without the need for additional blend components. The new biodegradable polymeric materials possess mechanical properties that are better than those of polystyrene. This represents the most important development in the history of lignin-based plastics.

Task 1.
(a) NARA ligninsulfonate derivatives will be created that alone, or in formulations with cheap commercially available blend components, can be transformed into polymeric materials with promising mechanical properties.
(b) Inchoate NARA ligninsulfonate-based plastics will be characterized using X-ray powder diffraction and atomic-force microscopy to establish trends that identify how new formulations may be efficiently optimized.
(c) The compatibility of ligninsulfonate-based plastics with flame-retardants will be determined.
(d) Conditions will be devised for converting ligninsulfonate-based plastics into foams with reasonable compressive strengths.
(e) The impact of molecular weight on the properties of ligninsulfonate-based plastics will be examined.

Task 2.
(a) The effects of incomplete derivatization on the properties of ligninsulfonate-based plastics will be explored.
(b) The effectiveness of additives that neutralize small quantities of acid liberated during casting of ligninsulfonate-based plastics will be investigated.
(c) Industrial conditions proposed by Borregaard to derivatize ligninsulfonates for incorporation into plastics formulations will be evaluated.
(d) Impact of polysaccharides (cellulose and hemicelluloses) on the mechanical properties of ligninsulfonate-based plastics will be determined.
(e) Efficacy of chemical foaming agents at different temperatures for producing ligninsulfonate-based plastic foams will be documented.
(f) In collaboration with Borregaard, production costs for the most promising ligninsulfonate-based plastics will be estimated.

Activities and Results

Methylated NARA ligninsulfonate-based polymeric materials have been reliably made. Technical proficiency in producing plastics from ligninsulfonates had necessitated extensive preliminary studies with ball-milled lignins. Hereby, the foundations created by the intrinsic lignin substructures can be differentiated from effects caused by the sulfonic acid groups.

Plastics composed exclusively of methylated ball-milled softwood lignins (MBMLs) can exhibit ~50 MPa tensile strengths with elongations-at-break around 8% (comparable to many commercial polymeric materials). Small quantities (5 – 10% w/w) of miscible low-Tg polymers or low-molecular-weight blend components can increase tensile strengths to 65 MPa or extend elongations-at-break to 15%. The constituent macromolecular species are associated complexes that are assembled from individual components as a result of strong noncovalent forces between lignin substructures. Interacting aromatic rings within the interiors are cofacially offset with respect to one another, while those in the peripheral domains of the complexes are often positioned in edge-on arrangements. X-ray powder diffraction reveals that continuity between complexes is established through their peripheral domains during casting of lignin-based plastics. Thus, a marked increase in the ratio of peripheral to interior aromatic rings in the complexes occurs as the MBML is cast to form a cohesive plastic (Figure C-CP-1.1).

In regard to the tensile behavior of the MBML-based polymeric materials, a roughly linear relationship between toughness and elongation-at-break holds (Figure C-CP-1.2) providing that the stress–strain curve does not embody undue plastic deformation.

The correlation between tensile strength and modulus is less exacting (Figure C-CP-1.3), but the relationship between toughness and tensile strength is very tenuous.

The first production trials for NARA ligninsulfonate-based plastics involved softwood ligninsulfonates (M_w and M_n estimated to be 23,000 and 12,900, respectively) derived from forest residues primarily composed of Douglas-fir (J.Y. Zhu et al., Bioresource Technology, 2015, 179, 390-397). After consecutive ultrafiltration through 200 kDa and 4 kDa nominal-molecular-weight-cutoff membranes, the phenolic hydroxyl groups of the retained ligninsulfonate were methylated with dimethyl sulfate in aqueous 50% dioxane at pH ~12. After acidification to pH 9, the dioxane was removed and the remaining aqueous solution was ultrafiltered with water through a 1 kDa membrane, whereupon the retentate was freeze-dried. The partially methylated ligninsulfonate was protonated using Amberlite IR120 in methanol before the sulfonic acid groups were methylated with diazomethane in chloroform.

Solution-casting of the methylated ligninsulfonate (MLS) in DMSO with small proportions of miscible blend components produces polymeric materials that are comparable in strength to those formed from methylated softwood ball-milled lignin. For example, MLS-based blends with 15% poly (trimethylene glutarate) exhibit the same tensile strengths and elongations-at-break as MBML-based blends with 30% poly(ethylene succinate). However, at a molecular level MLS-based plastics are fundamentally different from their MBML-based counterparts. X-ray powder diffraction studies demonstrate that the proportion of cofacially offset aromatic rings increases dramatically in materials composed entirely of MLS as they are cast (Figure C-CP-1.4). Such an effect is the reverse of what is observed when materials containing only MBML are cast (Figure C-CP-1.1). Estimates for the cost(s) of producing MLS-based materials are being evaluated at the time of writing.

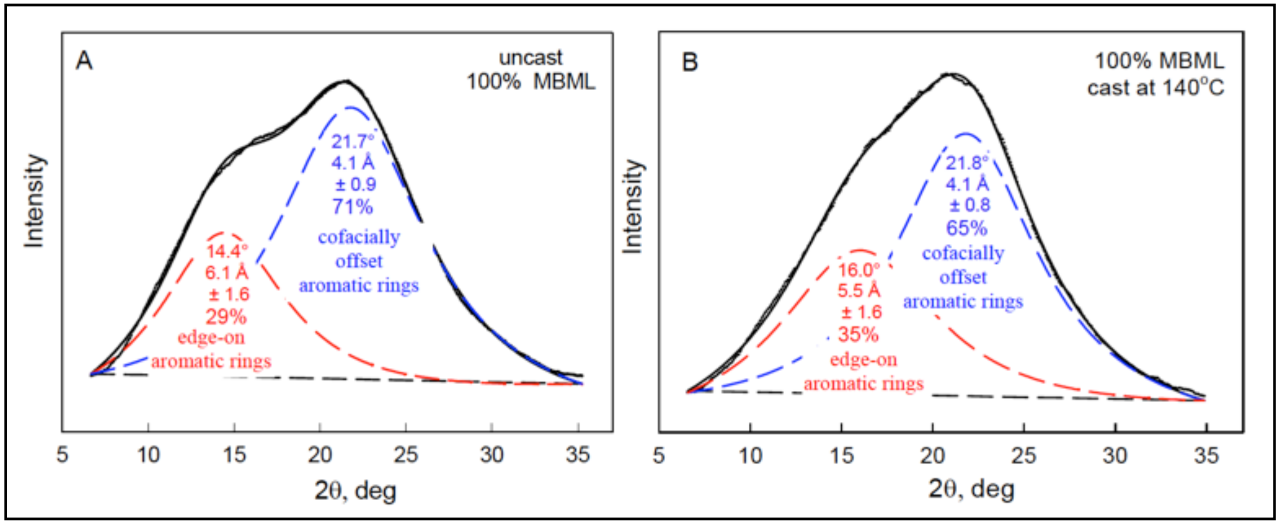


Figure C-CP-1.1. X-ray powder diffraction patterns of uncast and cast methylated ball-milled lignin-based materials can be described as sums of two Lorentzian functions $I(x) = I(0)/(1 + x2/hwhm2)$, $x = 2\theta - 2\theta k$, where $I(x)$ is the scattered intensity at x from the Bragg angle 2θk for the peak, 2θ is the scattering angle, and hwhm is the half-width at the half-maximum of the peak. During casting, the proportion of aromatic rings in edge-on arrangements with respect to one another increases so as to establish continuity between neighboring methylated lignin complexes.

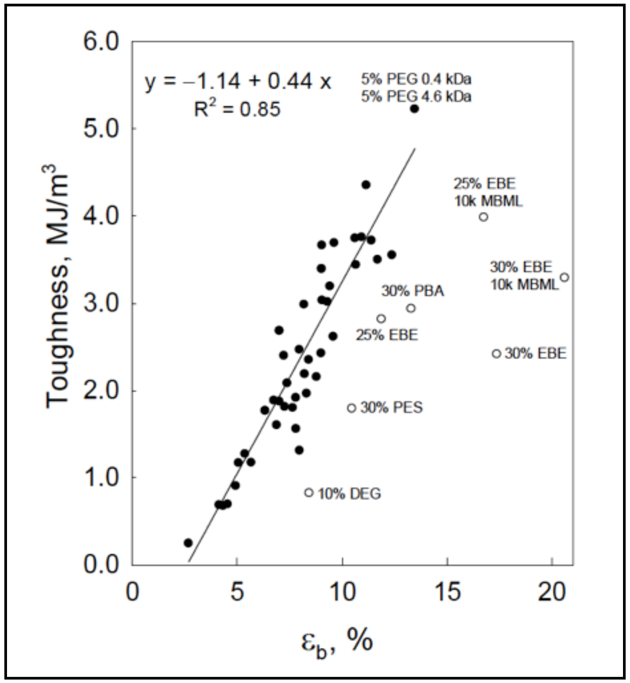


Figure C-CP-1.2. Correlation between toughness and elongation-at-break (εb) for polymeric materials with the highest attainable MBML contents. (Open circles denote data points that are not included in the linear regression analysis: they represent tensile behavior that embodies substantial plastic deformation.) Abbreviations: DEG, diethyl glutarate; EBE, poly(ethylene oxide-b-1,2-butadiene-b-ethylene oxide); PBA, poly(butylene adipate); PEG, poly(ethylene glycol); PES, poly(ethylene succinate).

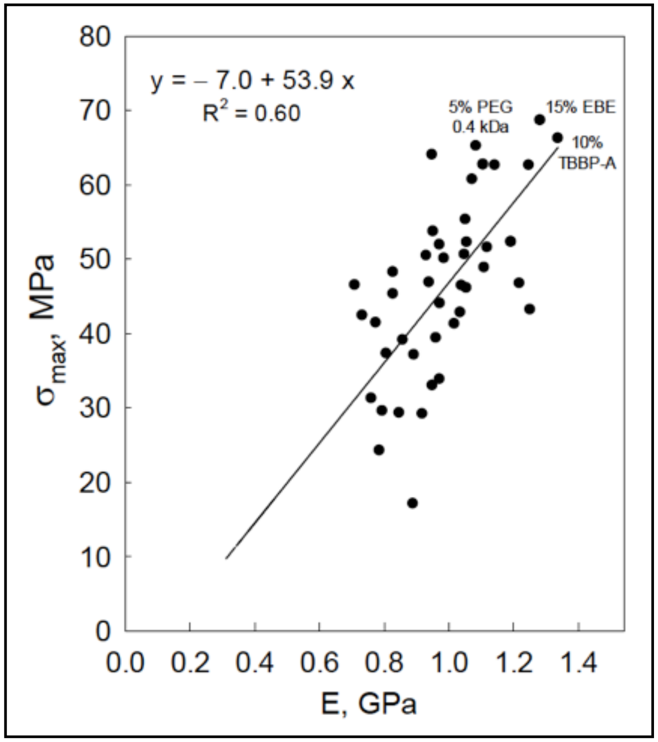


Figure C-CP-1.3. Correlation between tensile strength (σ_{max}) and modulus (E) for polymeric materials with the highest attainable MBML contents. Abbreviations: EBE, poly(ethylene oxide-b-1,2-butadiene-b-ethylene oxide); PEG, poly(ethylene glycol); TBBP-A, 3,3′,5,5′-tetrabromobisphenol A.

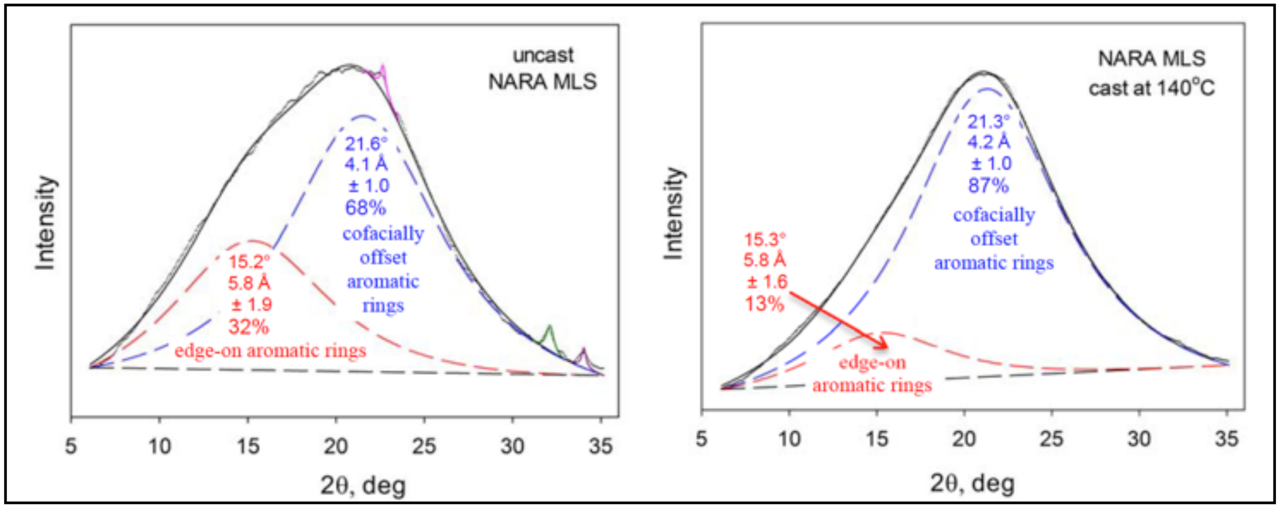


Figure C-CP-1.4. X-ray powder diffraction patterns of uncast and cast methylated ligninsulfonate-based materials can be described as sums of two Lorentzian functions I(x) = I(0)/(1 + x2/hwhm2), x = 2θ – 2θk, where I(x) is the scattered intensity at x from the Bragg angle 2θk for the peak, 2θ is the scattering angle, and hwhm is the half-width at the half-maximum of the peak. During casting, the proportion of aromatic rings in cofacially offset arrangements with respect to one another increases dramatically, as opposed to what is observed with 100% MBML-based materials.

Recommendations | Conclusions

For the first time, NARA ligninsulfonate-based plastics have been successfully produced as a result of methylating the phenolic hydroxyl groups and sulfonic acid residues in the starting material (supplied by Dr. J.Y. Zhu at the Forest Products Laboratory). Formulations with small proportions of miscible blend components have resulted in plastics that possess quite similar tensile properties to analogous blends based on methylated ball-milled softwood lignins.

Production costs are, of course, augmented by two consecutive methylation steps requiring different reagents. Therefore, at the time of writing, conditions are being developed through which derivatization is limited to a single methylation step that can be readily adapted to industrial practice. Preliminary results have confirmed that such a goal is well within reach. Accordingly, in future work, simple methylation conditions will be developed for producing methylated ligninsulfonate-based blend formulations that compare favorably in their mechanical properties with a range of commercial polymeric materials (Table C-CP-1.1). Accompanying techno-economic analyses will be used for guidance in recommending alternatives for this important segment of the overall NARA process.

Table C-CP-1.1. Tensile properties of selected engineering

Thermoplastic	Tensile strength (MPa)	Elongation at break (%)
Polystyrene	46	2.2
Styrene-acrylonitrile	72	3
Acrylonitrile-butadiene-styrene (ABS)	48	8
Flame-retardant ABS	40	5.1
Polypropylene	32	15
Polyethylene	30	9

*Davis, J.R., Tensile Testing 2nd ed., ASM International, Materials Park, OH, 2004

Physical and Intellectual Outputs

RESEARCH PRESENTATIONS

Oral Presentation entitled "Formulations for Coproduct Lignin-based Plastics" by Simo Sarkanen, Yun-Yan Wang and Yi-ru Chen at NARA Coproducts Team Meeting, Spokane, WA, July 10, 2014.

Oral Presentation entitled "Prospects for Lignin-based Plastics from Biorefineries" by Simo Sarkanen, Yun-Yan Wang and Yi-ru Chen at Lignin 2014 Conference, Umeå, Sweden, August 24–28, 2014.

Oral Presentation entitled "Lignin-based Plastics from Biorefineries" by Simo Sarkanen, Yun-Yan Wang and Yi-ru Chen at VTT Technical Research Centre of Finland, September 3, 2014.

Poster presentation entitled "Plastics Containing 85-100% Levels of Simple Lignin Derivatives" by Yun Yan Wang, Yi-ru Chen and Simo Sarkanen at 2014 NARA Annual Meeting, Seattle, WA, September 15–17, 2014.

Oral Presentation entitled "Highest Attainable Lignin Contents in Polymer Materials from Biorefineries" by Simo Sarkanen, Yun-Yan Wang and Yi-ru Chen at Lignobiotech III Symposium, Concepción, Chile, October 26–29, 2014.

Oral Presentation entitled "Formulations for Coproduct Lignin-based Plastics" by Simo Sarkanen, Yun-Yan Wang and Yi-ru Chen at NARA Coproducts Team Meeting, Pullman, WA, November 19, 2014.

Oral Presentation entitled "Formulations for Coproduct Lignin-based Plastics" by Simo Sarkanen, Yun-Yan Wang and Yi-ru Chen at NARA Coproducts Team Meeting, Pullman, WA, March 19, 2015.

Oral Presentation entitled "Macromolecular Characterization of Plastics with 85-100% Levels of Methylated Native Softwood Lignin" by Yun-Yan Wang, Yi-ru Chen, and Simo Sarkanen at the 249th American Chemical Society National Meeting, Denver, Colorado, March 22–26, 2015.

INTELLECTUAL PROPERTY

Compositions Including Lignin: Chen, Y.-r.; Sarkanen, S.; Wang, Y.-Y. 2015, International Patent Application No. PCT/US2015/020599, filed March 13.

TASK C-CP-2: CONVERSION OF LIGNIN TO HIGH VALUE, LARGE MARKET PRODUCTS

Key Personnel	Affiliation
Manuel Garcia-Perez	Washington State University

Task Description

In this project, the sources of lignin will be from one or more processes identified in the NARA project and from one or more steps in the process. This process is being used to supply the carbohydrates for the fermentation to isobutanol for fuel production. A key component of the proposal is to create high value products from the residual lignin. The lignin produced from the various pretreatment processes is significantly different from traditional Kraft lignins. The first part of the work was to characterize the lignin with respect to molecular weight, G/S ratio, hydroxyl content, thermal properties, and other properties thought important by the Co-Products Team. This information is essential to developing suitable end-uses for the various lignins.

We have focused our efforts on two target products to be produced from the lignin: moderate value activated carbon (AC) and high value AC for us in energy storage devices. It was found that with the new EPA requirements that coal-burning facilities must reduce their mercury emissions, the market for AC designed to clean up flue gas emission has grown rapidly. Our primary goal has become to develop an AC that will be effective in mercury capture from coal combustion flue gases. The market size for this application is so large that it should consume a significant amount of the lignin produced. Furthermore the value generated should be significant. The second is a new and emerging market, where there is a need for a sustainable, low-cost alternative to current materials. There are also numerous other known applications for AC materials. The key to designing AC materials for specific applications is to develop methodologies to prepare materials with precisely engineered pore structures and surface chemistry. We anticipate that thorough characterization of the properties of the AC materials prepared for the applications mentioned above will provide insight into other potential applications, such as the adsorption of metals, organic compounds, phosphates, and other environmental contaminants released into air and water. The research conducted on AC materials will therefore provide a platform for the development of a family of carbon products from lignin-rich biorefinery residues.

Another more traditional area that we are pursuing is the use of the lignin sulfonate produced by the mild bisulfite process as a viscosity modifier for wet cement.

Activities and Results

In previous work, two series of activated carbon (AC) materials were prepared from Ca^{2+} fermentation residual solids (FRS) derived from mild bisulfite (MBS) pretreated residuals (referred to herein as MBS FRS), and also from FRS from the wet oxidation (WOX) process. The AC materials were prepared at 700oC using physical activation with CO_2. The pore structures of these AC materials have been characterized in detail with gas physisorption and samples have been tested for elemental mercury (Hg0) capture from flue gas at the laboratory scale. The results of the last two rounds of testing conducted in April 2014 (Round 1) and November 2014 (Round 2) for Hg adsorption capacity are shown in Figures C-CP-2.1, C-CP-2.2 and C-CP-.3. The equilibrium vapor phase Hg0 adsorption capacities (herein referred to as the Hg0 adsorption capacity) are plotted vs. the activation time (which was previously shown to be correlated with the porous structure of the AC materials).

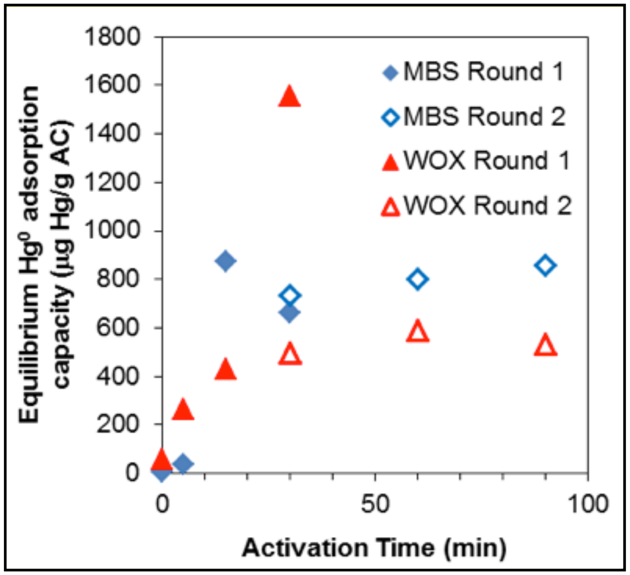


Figure C-CP-2.1. Equiibrium Hg^0 adsorption capacities measured in bench scale fixed bed test. Experiments were conducted at 300°F (149oC). Simulated coal flue gas composition was 1500 ppm SO_2, 400 ppm NO_x, 50 ppm HCl, 7% H2O, 12% CO_2, 6% O_2, and either 24 or 56 µg Hg^0/Nm^3 in Round 1 and 2, respectively. Gas flow rate was 1 L/min measured at 70°F.

The first round of testing showed that chars and AC with low degree of activation were ineffective for Hg0 capture under these flue gas conditions. The working hypothesis during preparation for Round 2 was that longer activation times would lead to better performance in Hg0 capture. The main results from analysis of the equilibrium capacity data from Round 2 were:

1) The MBS based AC had higher adsorption capacities compared to the WOX AC.
2) The rather high adsorption capacity of the WOX material activated for 30 minutes measured in Round 1 was not reproduced in Round 2.
3) Increasing activation time from 30 to 90 minutes only slightly increased the Hg0 capacity of the MBS AC.

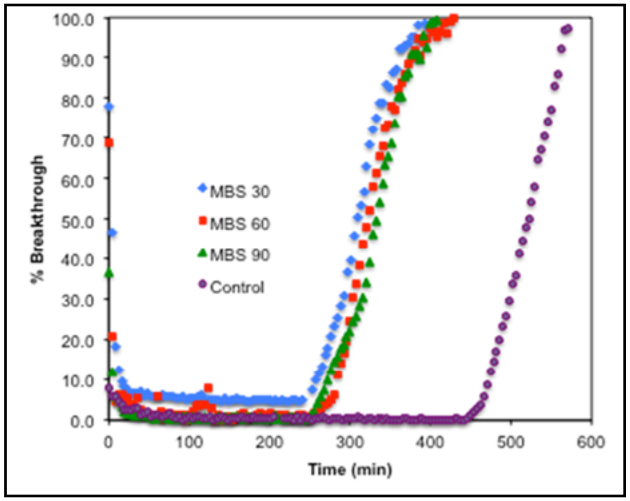


Figure C-CP-2.2. Breakthrough curves for MBS FRS AC prepared with activation times of 30, 60, and 90 minutes (denoted MBS 30, MBS 60, and MBS 90), respectively) showing the percentage of the inlet Hg concentration measured at the outlet.

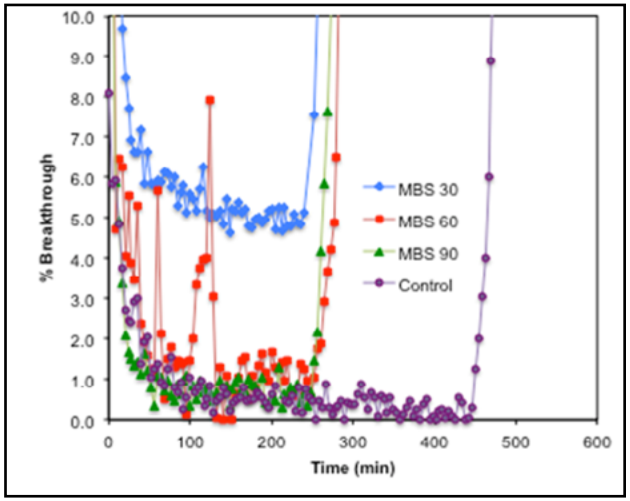


Figure C-CP-2.3. Zoomed in view of breakthrough curves in Fig. 1 for MBS FRS AC prepared with activation times of 30, 60, and 90 minutes showing the percentage of the inlet Hg concentration measured at the outlet.

The results also showed that all of the FRS-based AC had lower Hg0 capacities compared to the control materials, which had an average capacity of 1319 µg Hg/g AC (number of controls tested, n = 2).

Closer inspection of the raw adsorption data offered some additional information regarding the effectiveness of the AC materials in Hg0 capture. Breakthrough curves for the MBS AC materials prepared in Round 2, which show the concentration of Hg in the vapor phase at the outlet of the fixed bed as a percentage of the inlet Hg concentration, are shown in Figures C-CP-2.2 and C-CP-2.3, for MBS AC activated for 30, 60, and 90 minutes.

Recommendations | Conclusions

The transition of the AC work from Weyerhaeuser to Washington State University was a significant disruption to the progress of the AC project. The AC work has regained momentum, albeit with fewer personnel. The above results taken together with previous results suggest that it is possible to produce effective Hg0 adsorbents from FRS, but more work needs to be done to improve the performance in Hg0 capture. The data in Figure C-CP-2.1 shows that the equilibrium Hg0 adsorption capacities are consistently lower than the control material (an unidentified, commercially available, untreated powdered AC used for Hg capture). Figure C-CP-2.1 also suggests that increased activation time had relatively little effect on the equilibrium capacities. However, the breakthrough curves shown in Figure C-CP-2.2 and C-CP-2.3 show that the efficiency of Hg removal from the simulated flue gas was increased from around 95% to greater than 98% (here efficiency is defined as 1 - % breakthrough) when the activation time was increased from 30 to 90 minutes. The MBS 90 sample actually performed quite similarly to the control prior to saturation, but became saturated at an earlier time compared to the control, leading to its lower measured equilibrium capacity. These results suggest that the activation did create an appropriate pore size distribution (PSD) for efficient Hg removal from the simulated flue gas.

Comparing the results from MBS and WOX (data for WOX not shown), the mesopore volume and mesopore size appear to be critical for achieving high efficiency removal of Hg from the simulated coal combustion flue gas.

Comparison of the adsorption isotherms and corresponding PSD for a commercially available untreated AC used for mercury capture provides some additional insight to guide future work. N2 adsorption isotherms and corresponding PSDs for MBS FRS AC, wood powder AC, and Norit Darco Hg are shown in Figures C-CP-2.4 and C-CP-2.5.

Figures C-CP-2.4 and C-CP-2.5 show that MBS FRS AC is comparable to the commercial sorbent in terms of micropore volume and total nanopore volume, but the commercial AC used for Hg capture has a greater proportion of large mesopores and macropores, whereas the maximum pore size in the MBS FRS AC is around ~11-12 nm. The data gathered to date suggest that strictly microporous carbons, such as FRS carbons with low activation, chars, and the wood powder AC included in Figure C-CP-2.4 and C-CP-2.5 are not suitable for Hg capture from coal combustion flue gas. Assuming that the AC used in the bench scale Hg0 adsorption capacity test was similar to Darco-Hg, it appears that it would be beneficial to modify the AC production process to produce a greater amount of larger mesopores and possibly macroporosity. Based on the results shown, modifications to the AC production process will be investigated to increase the amount of larger pores for Hg capture. Furthermore, the relocation of the AC work started at Weyerhaeuser to WSU in September 2014 presents some opportunities to explore synergies between some ongoing research in the Biosystems Engineering (BSE) department, CMEC, and the ongoing AC research described above. A reproducible and simple physical activation method has been shown to generate interesting mesoporous carbon materials from FRS. Now that the porosity of the physically activated materials is well-characterized, there are opportunities to build on this technology platform and study the adsorption of other environmental pollutants such as heavy metals and organic compounds from the aqueous phase. Studies on adsorption of some known environmental pollutants will allow comparison with other types of materials and will provide insight on the range of potential adsorption applications of the materials that have been made from the FRS.

Research aimed at understanding the effects of processing variables and different activation conditions on porous structure is also being extended to the application of AC in electrochemical capacitors. The goal of this research is to modify the processing steps to obtain AC with abundant narrow microporosity and some degree of mesoporosity, high electrical conductivity, and high purity. Washing of precursors and carbons is being investigated both to understand the effect of inorganic species on porosity development and to reduce the ash content to meet the higher purity specifications of electrode carbons. Exposing the carbons to different acids or bases during washing has the potential to also influence the surface chemistry of AC, and so the effect of washing on surface chemistry also needs to be investigated. This research is intertwined with the study of combining chemical activation with physical activation to generate a higher microporosity for electrosorption of ions coupled with sufficient meso- and macroporosity to facilitate rapid diffusion of ions at high charge/discharge rates. Chemical activation involves impregnation of the solid AC precursor material with acids, bases, or other salts prior to carbonization and requires a washing step to remove and potentially recover the activation agent after thermal treatment. In order to produce a material with lower cost, it is desirable to minimize the complexity of the activation and purification processes and energy consumption during thermal treatment.

Lastly, the applicability of the AC production process developed for the MBS FRS is being evaluated on newer batches of lignin recently delivered to WSU. The goal of this work is mainly to determine whether slight modifications to the pretreatment, hydrolysis, and fermentation processes affect the characteristics of the AC materials produced. More specifically, it has not yet been determined whether the choice of cation (Ca2+ vs. Mg2+) or the use of FRS vs. SRS (fermented vs. saccharified but not fermented solids) have significant effects on the yield, char reactivity, or porosity of the AC materials. These issues are the subject of current ongoing research.

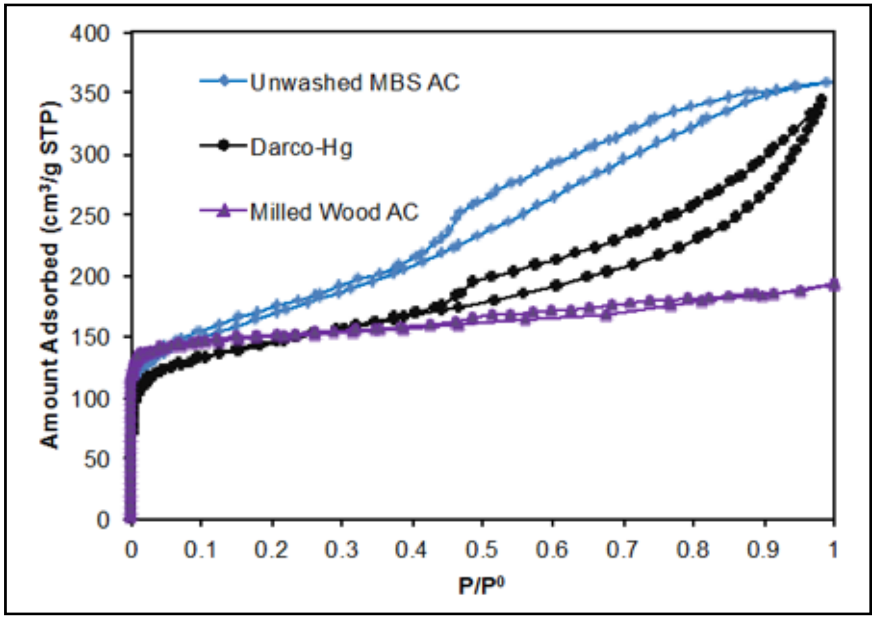


Figure C-CP-2.4. Nitrogen adsorption-desorption isotherms of AC materials measured at 77K.

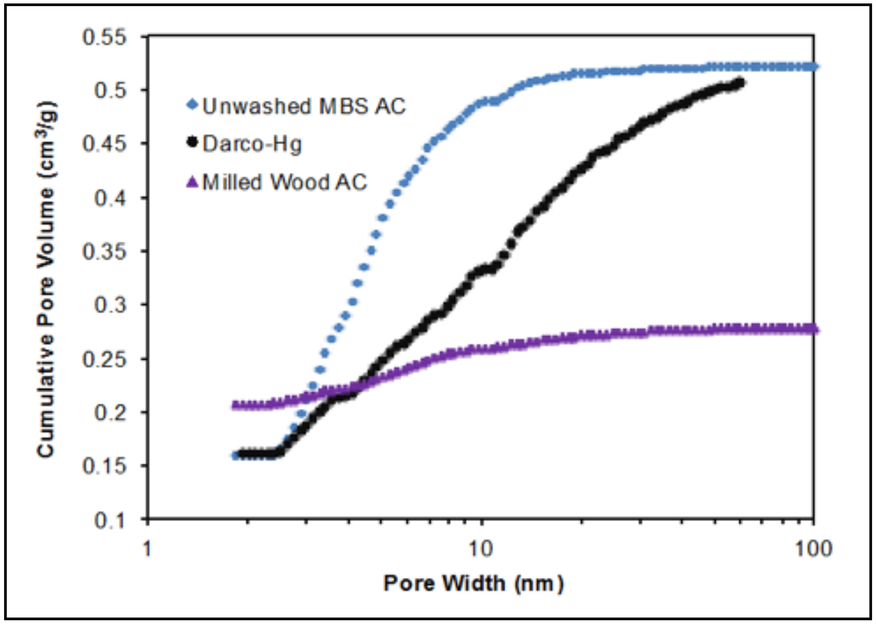


Figure C-CP-2.5. Cumulative pore size distributions of AC materials calculated from N2 adsorption isotherms by nonlocal density functional theory (NLDFT).

TASK C-CP-3: NOVEL ENGINEERING POLYMERS FROM LIGNIN-DERIVED BUILDING BLOCKS

Key Personnel	Affiliation
Jinwen Zhang	Washington State University
Michael Wolcott	Washington State University

Task Description

Using lignin for polymer materials has received extensive investigations from academia and industry. However, neither the direct use of lignin as polymeric component nor the use of depolymerized lignin as a monomeric feedstock for polymer materials have achieved significant progress to date. Currently, commercially available lignin is mainly limited to the Kraft lignin (KL) and sulfonated lignin (lignosulfonate). KL and lignosulfonate are recovered from the spent pulping liquids of their respective pulping processes and are available in various product forms. While lignosulfonates are mainly used as industrial dispersants, KL has far fewer practical applications. Nonetheless, in recent years KL has received tremendous interest in polymer applications. As our nation strives to advance the technology of lignocellulosic biorefinery, a huge amount of hydrolysis lignin is expected to be available.

Lignin-to-chemical conversion is a highly desirable approach in lignin utilization and could potentially produce many important aromatic chemicals including intermediate monomeric feedstock. Scientists are striving to explore various technologies to selectively cleave lignin for desirable chemicals. Meanwhile, plant scientists and biochemists also seek means to interrupt the normal biosynthesis of lignin and harvest the precursor chemicals directly. While these efforts may eventually result in significant progress and advance the related sciences, they are not likely to achieve breakthrough technologies any time soon.

As seen in the growing number of scientific publications, the presence of both phenolic and alcohol hydroxyls makes lignin an attractive substance to directly incorporate into existing thermosetting resins as a reactive ingredient or extender. However, compatibility remains the major issue in these applications. Similar compatibility issues are also present when lignin is used as volume filler for thermoplastic polymers. The poor compatibility between lignin and other systems is rooted in its highly branched molecular structure, which makes it neither miscible with nor accessible to others for good interactions. In addition, lignin as a base material for thermoplastics is another important application but still faces many processing problems.

Complete lignin depolymerization is an energy-negative process aimed at deconstructing what nature has constructed. Instead, increasing the use of and adding value to the lignin polymer that nature has already provided is more attractive for the chemical industry. *In this project, we propose to develop new technologies for the preparation of engineering polymers from hydrolysis lignin and to explore the applications.* The characteristic structure of lignin makes lignin insoluble in most organic solvents and hinders the access of hydroxyls for modification reactions. As indicated above, to completely disintegrate the lignin structure and use the resulting monomeric chemicals for construction of new polymers is far not practical and may not be economically advantageous. In this project, our hypothesis is that partially depolymerized lignin (PDL) with enhanced solubility will provide accessible hydroxyls to enhance modification, thereby converting the lignin into effective building blocks for engineering polymers. Epoxy resin is the target polymer in this current effort but it will not be the only application interest long-term. Attention will be given to other engineering polymers when an appropriate application is identified. Furthermore, PDL is expected to possess an improved performance when directly incorporated as an active ingredient to thermosets because the reduced molecular weight and increased accessibility and content of hydroxyls promote compatibility and/or even the miscibility. The implementation of this project consists of three major tasks.

Task C-CP-3.1. Preparation of epoxies using lignomers

Although utilization of lignin-derived monomers is not a favorable route in producing lignin-based polymers, the approach serves as a useful step in route to utilizing lignin. We selected eugenol as the model compound for synthesis of epoxies. Eugenol can be obtained from a number of plant extractives and is also claimed by some researchers to be present in materials produced from a lignin cracking process. We have demonstrated in an earlier task that eugenol can be converted to epoxies with excellent physical and mechanical properties. However, because the current lignin depolymerization technology is not able to economically and efficiently produce eugenol or related chemicals that could be used as feedstock for engineering polymers, this task is not our major focus and is currently complete. Detailed results and data on this part of project can be found in our 4th quarterly report. A manuscript has also submitted recently for publication.

Task C-CP-3.2. Development of lignin-based epoxies using partially depolymerized lignin (PDL)

First, a though review of lignin depolymerization was conducted. Based on the survey, two methods were selected to show potential: (1) base catalyzed depolymerization in supercritical solvent (BCD) and (2) hydrogenolysis under catalysis of Raney nickel. To achieve oligomeric compounds rather than the more commonly targeted monomeric compounds, we focused on cracking methods that could be deployed with milder conditions. The reaction conditions are regulated to selectively cleave ether bonds of lignin to improve the PDL solubility, dispersabiltiy, and functionality. PDL can be functionalized much more effectively than the native lignin. Furthermore, preparation, processing and performance of the lignin-derived epoxies will be thoroughly studied.

Task C-CP-3.3. Application development for PDL-based epoxy asphalt

Our central hypothesis is that the PDL-based epoxy resins will demonstrate higher performance than those based on unmodified lignin but incorporating lignin tends to always increase stiffness and brittleness of the resulting polymer. In this project, we plan to explore the application of PDL-based epoxies in an underexplored but increasingly important product, i.e., epoxy asphalt. To this application, the designs of PDL-based epoxies and curing agents will be customized to meet the specific requirements for asphalt application, and formulation and preparation of the epoxy asphalt will be studied. Finally, the performance of the PDL-based epoxy asphalt will be evaluated.

The specific objectives of this project are: (1) to investigate the synthesis of important engineering polymers (e.g., epoxies) using lignin as feedstock; (2) to study the structure-property relationship of the resulting engineering polymers and; (3) explore the application development using the lignin-derived polymers.

Activities and Results

Task C-CP-3.1, preparation of epoxies using lignomers, has been successfully accomplished as summarized in our last cumulative report. To date, approximately 80% of task 2 development of lignin-based epoxies using partially depolymerized lignin (PDL) has been completed in 4th year. At the same time we also explored depolymerization and modification of lignin in solid-state reaction for the past year. Task C-CP-3.3 was preliminarily investigated.

Task 2.1. Development of partially depolymerized lignin (PDL) epoxies

Partial hydrogenolysis of NARA lignin was studied under the catalysis of Raney Ni. Most of the experiments were conducted in a 100 mL pressure reactor. The NARA lignin samples were obtained from different pretreatment methods in different batches. In the 4th year, we focused on the CLE 62 (A) lignin and performed the partial hydrogenolysis in a 2 L pressure reactor. We investigated the hydrogenolysis of NARA lignin at two different reaction temperatures, 180 °C and 200 °C, respectively. As shown in Table C-CP-3.1, the catalyst Raney Ni could be reused for the second run and the yields of PDL obtained from the second runs only decreased a little. Compared to the yields obtained from the small pressure reactor (100 mL), the yield in the large rector at 180 °C or 200 °C decreased by ~9%, which is considered to be acceptable from the viewpoint of commercialization. On the other hand, the hydroxyl values of PDLs collected from the large reactor (2 L) at 180 °C or 200 °C were moderately higher than that of PDL collected from the 100 mL reactor. These results may suggest the process of partial hydrolysis of NARA lignin is scalable.

Use of PDL for preparation of PDL-epoxy resins was fully exploited. Because of its higher hydroxyl value, the PDL from hydrogenlolysis at 200 °C in the 2 L reactor was used for all the following reactions. The PDL-epoxy was prepared by traditional glycidylization by reacting PDL directly with epichlorohydrin (ECD) (Scheme C-CP-3.1). Initially, ECD was used as both reactant and solvent for the first step of reaction and the reaction temperature was conducted at 70 or 117 °C. However, PDL exhibited a poor solubility in ECD, and the resulting PDL-epoxies were hardly soluble in any solvents, not even in the mixture solvent (CDCl3/pyridine) for 31P NMR analysis. It was also difficult to determine its epoxy value by a titration procedure which involves hydrolysis with HCl in actone followed back titration using NaOH aqueous solution. The result may suggest the low reaction efficiency of glycidylation of PDL without a suitable solvent or partial self-polymerization of the lignin derivative. In order to improve the reaction efficiency of glycidylation, DMSO was used as the reaction solvent as shown in Scheme 1. As reported in the previous report, DMSO is a good solvent for PDL and its use may avoid the partial self-polymerization and improve the reaction efficiency. The yields of PDL-epoxy were 86.6% at 70 °C and 100% at 117 °C, suggesting high temperature is helpful for completing glycidylation reaction. The solubility of PDL-epoxies in organic solvents increased with the reaction temperature increasing from 70 to 117 °C. For the rest experiments, the PDL epoxy samples used are all prepared by this method with DMSO as a co-solvent.

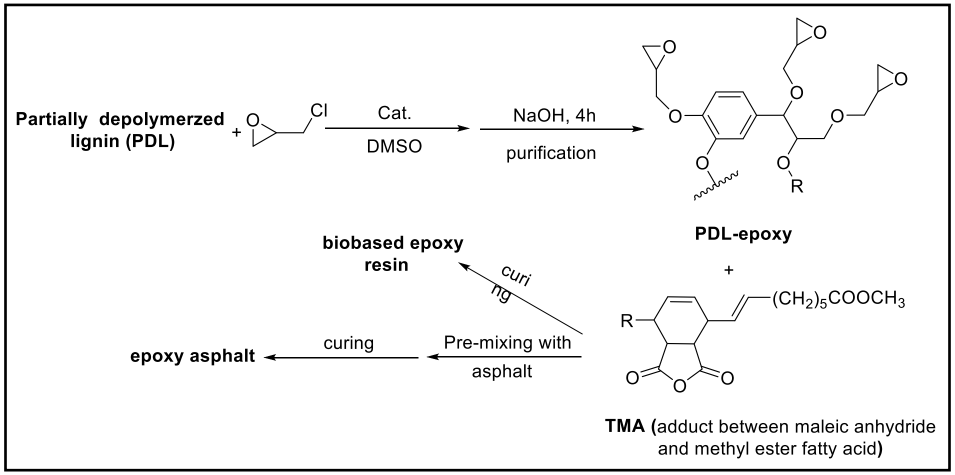
We also determined the hydroxyl value of PDL epoxies and PDL by 31P NMR as shown in Figure C-CP-3.1. The hydroxyl groups can be categorized in three groups, aliphatic, aromatic and carboxylic. The calculated hydroxyl values for three depolymerized lignin samples are summarized in Table C-CP-3.2. Compared to the original PDL (Figure C-CP-3.1), the signals for the aromatic hydroxyls of PDL-epoxies in the region of 136.6-144.7 ppm became very weak in PDL-epoxy-70 °C and almost disappeared in the spectrum of PDL-epoxy-117 °C. Further, the signal of the carboxylic acid hydroxyl in the range of 133.6-136.6 ppm completely disappeared in the spectra of both PDL-epoxy-70 °C and PDL-epoxy-117 °C. On the contrary, the intensity of aliphatic hydroxyl with chemical shift 145.5-150.0 ppm apparently became strong in the epoxy products. In Table C-CP-3.2, the hydroxyl value of aromatic OH decreased from 3.7 mmol/g in PDL to 1.7 mmol/g in PDL-epoxy-70 °C and to 0 mmol/g in PDL-epoxy-117 °C. That means the phenolic hydroxyl groups was fully reacted with reaction temperature increased from 70 to 117 °C. And the disappearance of carboxylic acid hydroxyls in both PDL-epoxies indicate that carboxylic acid OH was highly reactive even at the lower temperature of 70 °C. However, the aliphatic OH value increased greatly from 0.7 mmol/g of the original PDL to 2.4 mmol/g for the PDL-epoxy-70 °C and 2.7 mmol/g for PDL-117 °C. There were possible two reasons: one was when PDL reacted with ECH to produce PDL epoxy, some unreacted OH groups may react with the forming the epoxy ring grafted on PDL and the epoxy rings would be reopened to produce more aliphatic OH group. Another one was some of epoxy rings weren't formed in second closing step during preparation PDL-epoxy. Whatever, 31P NMR results proved that epoxy based on PDL was successfully synthesized by the conventional method using ECH.

Figure C-CP-3.2 shows the infrared spectra of the PDL and PDL-epoxies prepared at 70 and 117 °C, respectively. Figure C-CP-3.2 shows the FTIR of PDL and PDL-derived epoxies. All samples exhibited a broad band around 3460-3480 cm-1, which was attributed to the stretching of the phenolic and aliphatic hydroxyl groups. The bands around 2933 and 2832 cm-1, arising from the CH stretching in the aromatic methoxyl groups and the methyl and methylene groups of the side chains. The absorptions at 1700 cm–1, 1597 cm–1 and 1506 cm–1 were attributed to the carbonyl group and the aromatic skeletal vibration, respectively. The C-H deformations band of asymmetric methyl and methylene appeared at 1460~1470 cm–1. By comparing the spectra of PDL and PDL-epoxies, the apparent differences were seen at ~1700 cm–1 and the fingerprint region at ~908 cm–1. The absorption intensity of the carbonyl group at ~1700 cm–1 in the PDL-epoxies spectra shifted to a slightly higher wavenumber, which was due to the C=O groups in the newly formed glycidyl ester epoxy groups. Also, a new peak at 908 cm -1 in the spectra of PDL-epoxies appeared, which was attributed to the oxirane ring as noted. The FTIR results suggest that PDL was successfully converted to PDL-epoxies through direct glycidylation with ECH using DMSO as a co-solvent at 70 and 117 °C.

The resulting PDL-epoxies were cured by a tung oil fatty acid-derived anhydride, the adduct of methyl eleostearate and maleic anhydride (TMA) as shown in Scheme 1 C-CP-3.1. The curing procedure was as follows: epoxy and TMA were mixed in a weight ratio of 1:0.88. 2-ethyl-1-4-methylimidazole was used as the catalyst and added at 1.0 wt% on the basis of the total weight of curing agent and epoxy. The ingredients were mixed at 70 °C (preheated in an oven) and grounded to a homogeneous mixture. The mixture was transferred into an aluminum mold with dimensions of 30 mm×18 mm × 5 mm. The curing was performed at 150 °C for 2 h then at 200 °C for 1 h. The cured samples were carefully removed from the mold and used for the thermal analysis.
A commercial bisphenol A type epoxy DER332 was also selected to cure with TMA. The curing behavior and thermal properties of DER332/TMA and PDL-epoxy/TMA were compared. Figure C-CP-3.3 shows the DSC thermograms of the curing of the two epoxies at different heating rates and the plots of 1/(Tp) versus ln(ϕ). The DSC results are summarized in Table C-CP-3.2. The curing of each epoxy exhibited only one exothermic peak during the non-isothermal

Table C-CP-3.1. Results of hydrogenolysis of NARA lignin in a 2 L pressure reactor

Entry	Yield / %		Hydroxyl value / mmol/g		Note
1	66.7	75.3a	4.01	3.83a	180 oC
2	57.1	-	4.31	-	180 oC, Cat. reused
3	57.3	66.0a	5.07	4.38a	200 oC
4	53.3	-	5.52	-	200 oC, Cat. reused



Scheme C-CP-3.1. The synthesis route of PDL-epoxy

Table C-CP-3.2. Hydroxyl values of PDL and PDL-epoxies determined by 31P NMR

	Hydroxyl value mmol/g			Total / mmol/g
	Aliphatic	Aromatic	Carboxylic	
PDL-epoxy-117 °C	2.7	0	0	2.7
PDL-epoxy-70 °C	2.4	1.7	0	4.1
PDL	0.7	3.7	0.3	4.7

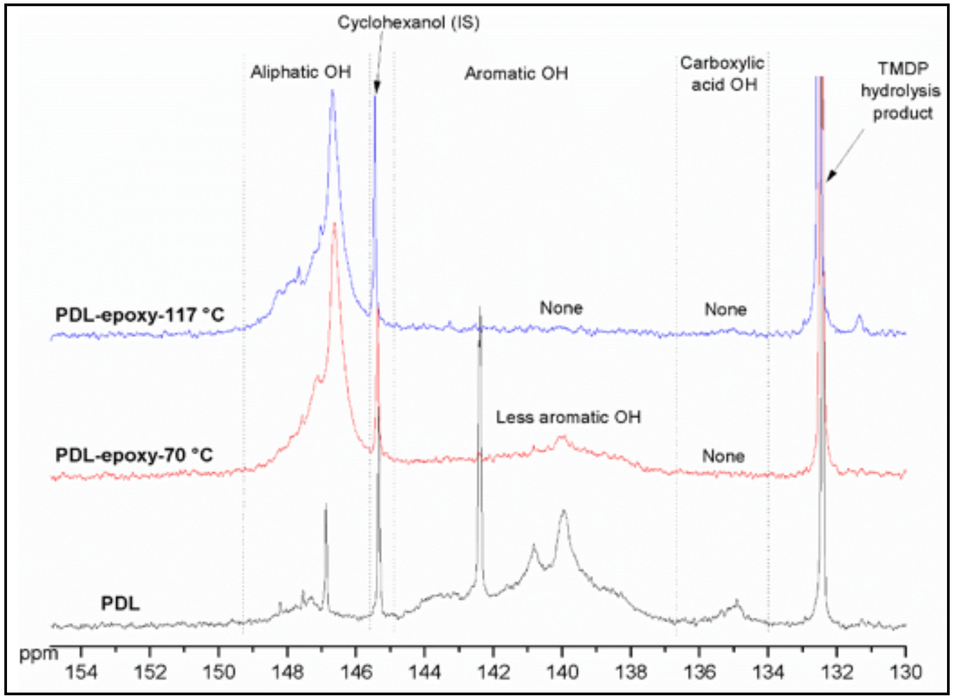


Figure C-CP-3.1. ^{31}P NMR spectra of before and after epoxidation of PDL-epoxy at different temperatures.

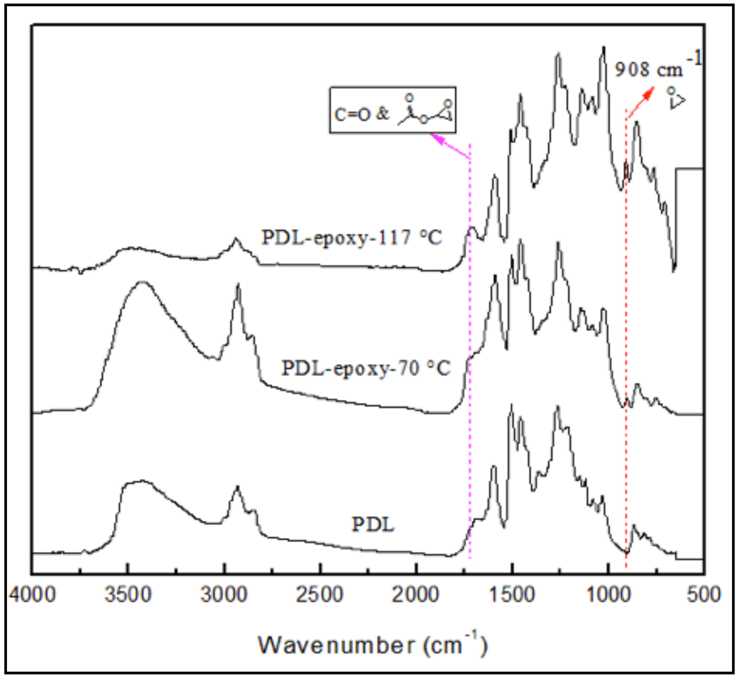


Figure C-CP-3.2. The FTIR spectra of PDL PDL-epoxy-70 °C and PDL-epoxy-117 °C.

test. As the heating rate (ϕ) increased, the peak exothermic temperature (Tp) shifted to higher temperature, which was a typical methodological phenomenon for non-isothermal curing. By extrapolating the results to the point of a infinitely slow heating rate, the calculated curing temperature at zero heating rate was obtained and could be used as a reference in the selection of isothermal curing temperatures. Table C-CP-3.2 shows that the calculated Tp at the zero heating rate is 129.9 °C for PDL-epoxy-117°C/TMA and 134.4 °C for DER332/TMA. These results indicate that the curing temperatures of PDL-epoxy-117°C was lower than the conventional epoxy curing temperatures. On the other hand, the activation energy of curing (Ea) of PDL-epoxy-117°C/TMA was 87.7 KJ/mol which was notably higher than that of curing of DER332/TMA (68.3 KJ/mol). The higher Ea of the PDL-epoxy-117°C/TungMA was likely due to the solid form of PDL-epoxy-117°C which would result in low compatability to diffuse with TMA in the stage of curing.

Figure C-CP-3.4 shows the curves of storage modulus (E′) and damping (tan δ) as functions of temperature for PDL-epoxy and DER332 epoxy resins cured with TMA. The glass transition temperatures (Tgs) of the cured samples were determined from the peak temperatures of the tan δ. The Ve of the cured epoxy resin can be estimated using the following equation based the theory of rubber elasticity:

$$v_e = \frac{E}{3RT} \qquad (1)$$

where E is the elastic modulus of the thermoset in the rubbery state, R is the gas constant and T is the absolute temperature. Since measuring the elastic modulus of thermoset in rubbery state is a very tedious experiment, it is a convenient custom to use E′ in the rubbery state, e.g., at Tg + 50 °C, to substitute E in the calculation. The cured PDL-epoxy resins had higher E′ at room temperature than that of the cured DER332 resin. This was probably because PDL-epoxy had more bulky structures than DER332, therefore resulted in more rigid resins at room temperature. In Table C-CP-3.3, it is noted that the Tg and crosslinking density of PDL-epoxy resins were higher than that of the DER332 resin. It is understood that higher crosslink density and more rigid chain segment lead to a higher Tg.

Figure C-CP-3.5 shows the TGA results of the cured resins, and Table C-CP-3.2 summarizes the char yield at 585 °C and temperatures at which 5% weight loss (T5%) and 10% weight loss (T10%) were incurred. PDL-epoxy-117 °C/TMA had higher T5% and T10% values than that of DER332/TMA. On the other hand, the char yield of PDL-epoxy-117 °C/TMA at 585 °C was obviously higher than DER332/TMA because of the presence of more rigid molecular structure in lignin. These results indicated that the thermal stability of PDL-epoxy resin was almost as good as that of epoxy resins based on bisphenol A.

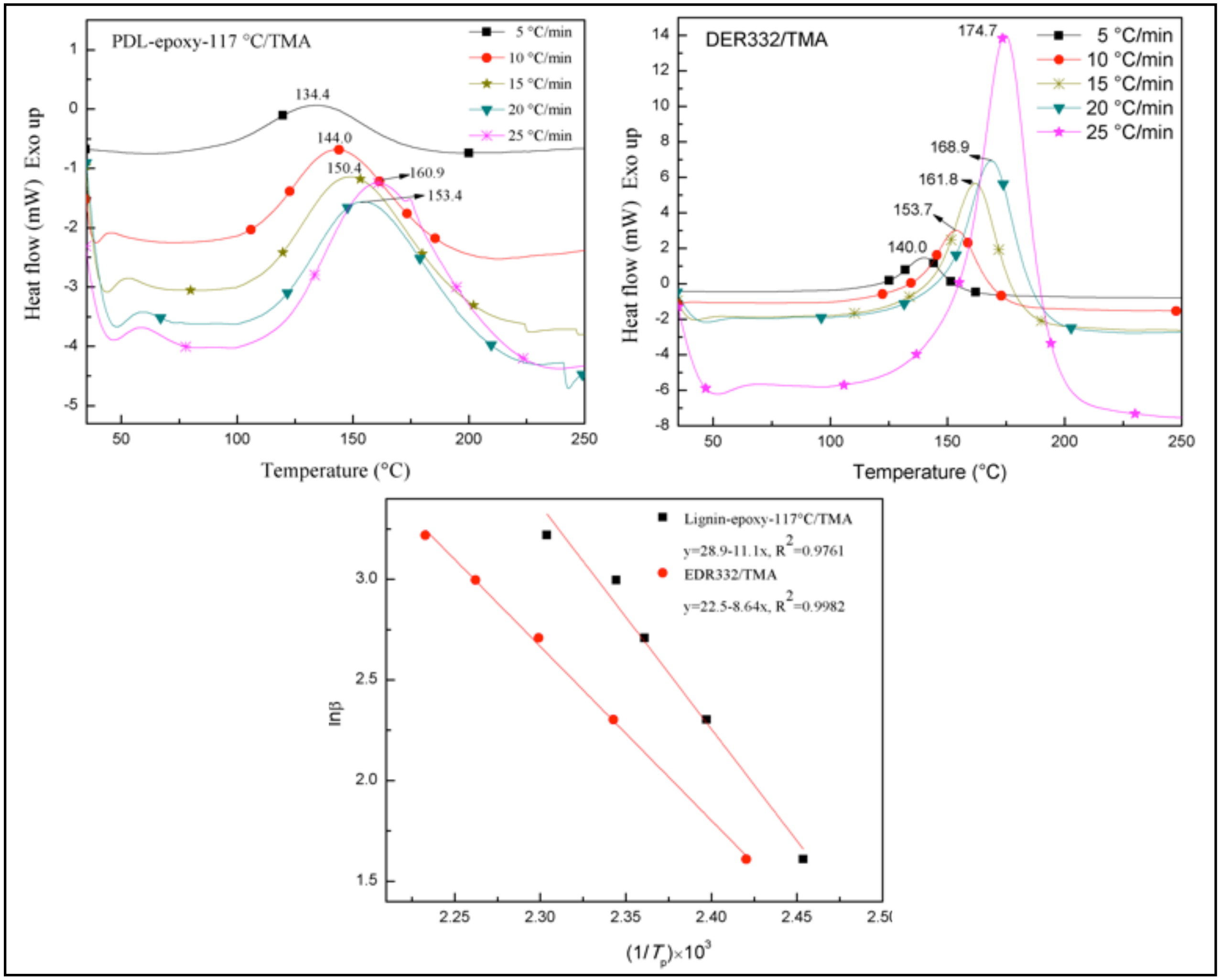


Figure C-CP-3.3. The representative DSC thermograms of non-isothermal curing of the epoxies at different heating rates and the plots of 1/(Tp) versus ln(ϕ)

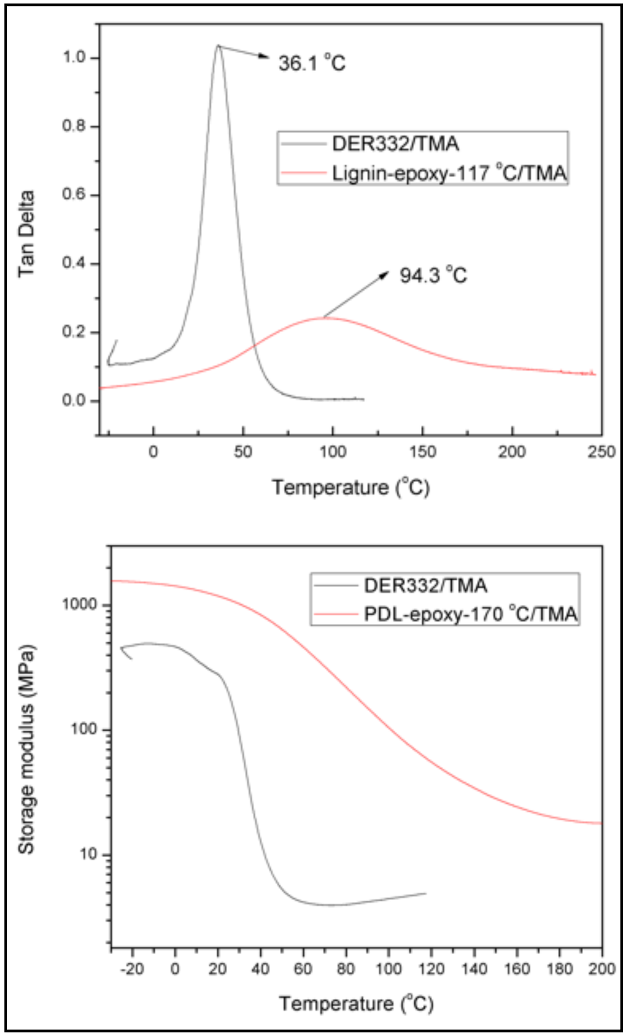


Figure C-CP-3.4. Storage modulus and tan δ versus temperature for DER332 and PDL-epoxy-170 ºC cured with TMA.

Table C-CP-3.3. DSC results of non-isothermal curing and thermal properties of cured epoxies

Epoxy	Tp(°C)a	Ea (KJ/mol)	Tg(°C)^{a}	ve (x103 mol/mm3)	T5%(°C)^{b}	T10%(°C)^{b}	Char yield at 585 °C
PDL-epoxy-117 °C/TungMA	129.9	87.7	94.3	3.02	272.3	311.1	34.7 %
DER332^{c}/ TungMA	134.4	68.3	36.1	0.46	219.8	289.9	6.43 %

a) Linear extrapolation at =0, b) T5% and T10%: temperature of 5% degradation and 10% degradation, c) DER332 epoxy resin (epoxy equivalent weigh (EEW) = 175 g/mol, Dow Chemical Company)

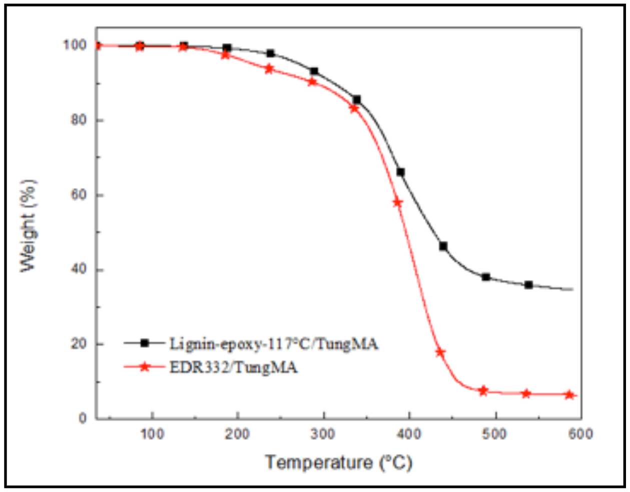
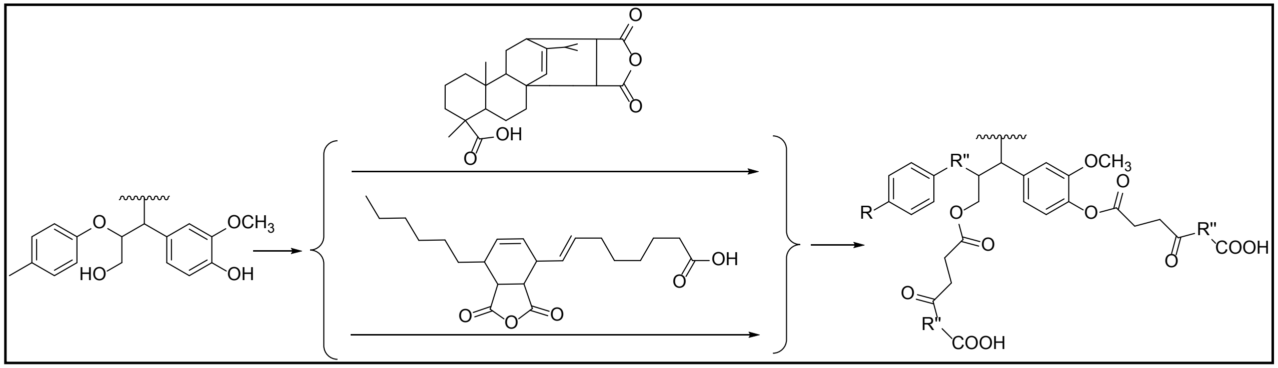


Figure C-CP-3.5. TGA plots of the cured epoxy resin under nitrogen atmosphere.

Task 2.2. Development of partially depolymerized lignin (PDL)-derived curing agents

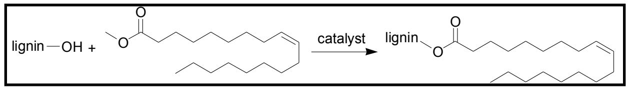
At the same time, two biobased anhydride, maleated rosin and maleated tung acid, were chosen to modify PDL for PDL-based curing agents. As shown in Scheme C-CP-3.2, the resulting PDL curing agents contains two carboxylic acid. The preparation procedure was as follows: PDL, maleated rosin or maleated tung acid, Cat. dimethyl benzylamine and acetone were added into the flask at room temperature. Then the temperature was raised to 70 oC and the reaction was continuously stirred for 18 h. After reaction, acetone was removed by rotatory evaporation. The residue was washed by ethyl ether, acetone and water. The product PDL-MLHSS was obtained from freeze-drying. Yield was calculated by 87.5% (PDL-MLHSS), 81.7% (PDL-MTA) based on PDL, repectively. The characterization and application of these curing agents was in progress.



Scheme C-CP-3.2. The synthesis route of PDL curing agent.

Task 2.3. Explore depolymerization and modification of lignin in solid state reaction

Partial depolymerizations of lignin via both hydrogenolysis and base catalyzed depolymerization (BCD) have proved to be effective in terms of molecular weight reduction, increased hydroxyl value and solubility in organic solvents. However, both processes still require elevated pressure and temperature, though the reaction conditions are moderate compared to conventional hydrogenolysis and BCD. Therefore, we are exploring methods for modification of lignin in a solvent-free and room temperature environment. To this end, reaction under the ball milling condition is a right choice. First, transesterification between lignin and fatty acid ester was studied to introduce fatty acid ester chains onto lignin. Methyl oleate was initially used as the alkylating agent because the characteristic carbon-carbon double bonds are ready identified in the modified products. The oleated lignin was prepared through transesterification using organosolv lignin (OL) reacted with methyl oleate as shown in scheme C-CP-3.3. In Figure C-CP-3.6, two olefinic protons at ~5.3 ppm and three methylic protons at ~3.7 ppm were observed for methyl oleate. After modification and purification, the three methylic protons at ~3.7 ppm disappeared for oleated OL since the unreacted methyl oleated residue were completely removed after purification process. Compared to the spectrum of OL, the new peak at ~5.3 ppm was observed in the spectrum of oleated OL and was attributed to two olefinic protons originated from methyl oleate. This result shows that the fatty acid chains were introduced into the structure of lignin through mechanically activated transesterification between organosolv lignin and methyl oleate in ball mill.



Scheme C-CP-3.3. Transesterification between OL and methyl oleate.

The hydroxyl values of organosolv lignin and oleated OLs were determined by 31P NMR as shown in Figure C-CP-3.7. The calculated hydroxyl values for OL and oleated OLs samples are summarized in Table C-CP-3.4. Compared to OL (Figure C-CP-3.7), the signal intensity of the aliphatic hydroxyls of oleated OLs in the region of 146-150 ppm significantly decreased and became very weak. On the contrary, the intensity of aromatic and carboxylic hydroxyls with chemical shifts at 133.6-136.6 ppm and 136.6-144.7 ppm remained almost unchanged. As shown in Table C-CP-3.1, the hydroxyl value of the aliphatic OH decreased from 2.57 mmol/g in OL to 0.64 mmol/g in oleated OL#2. Meanwhile, the hydroxyl value of aromatic OH was relatively the same for OL and OL#2 (2.60 and 2.22 ppm). This result means the transesterification mainly took place between the aliphatic hydroxyl groups of lignin and the ester bonds of methyl oleate during ball milling process rather than between the phenolic hydroxyl groups of lignin and the ester bonds of methyl oleate. Compared to that of OL, the total hydroxyl value of oleat-

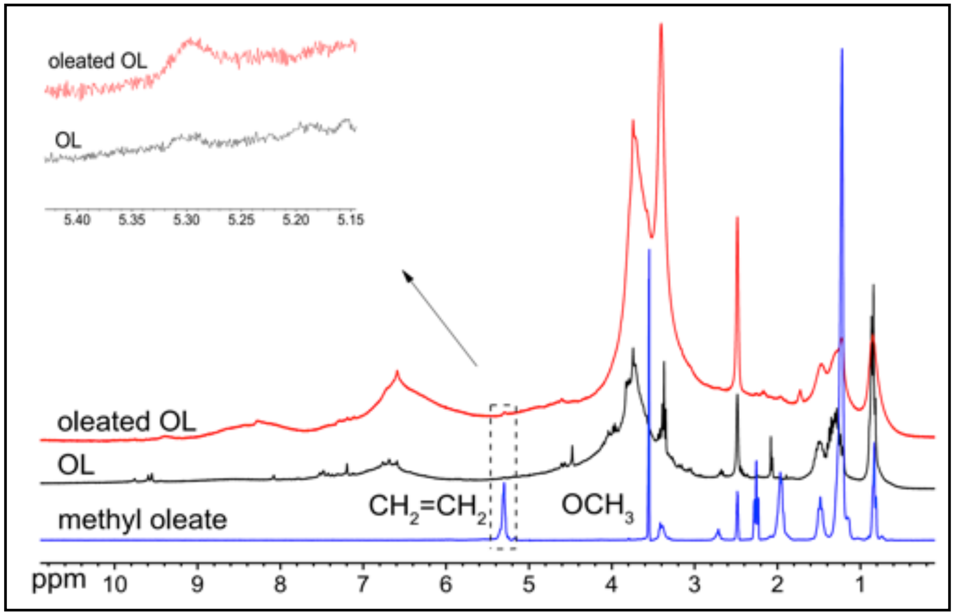


Figure C-CP-3.6. ^{1}H NMR spectra of methyl oleate, organosolv lignin and oleated OL.

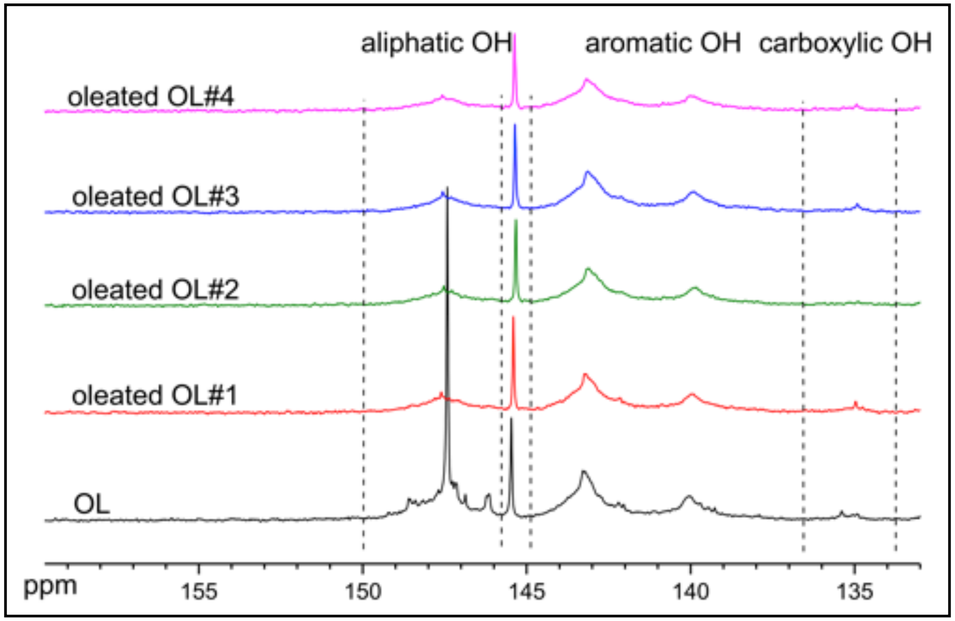


Figure C-CP-3.7. ^{31}P NMR spectra of organosolv lignin and oleated OLs at various compositions.

ed OLs significantly reduced from 5.17 mmol/g to ~2.9 mmol/g. Additionally, the oleated OL#2 (nOL-OH:nMO = 1:0.6) has the lowest hydroxyl value, indicated that this composition might have the optimal reaction conversion and efficiency. The reaction conversion of the transesterification between methyl oleate and organosolv lignin was around 25% at various compositions.

The conversion was calculated through the following equation:

$$x=\frac{(a-b)\times 10^5}{a\times b\times 264+1000\times a}$$

where, x: reaction conversion; a: hydroxyl value of starting lignin (OL), mmol/g; b: hydroxyl value of modified lignin (oleated OL).

Table C-CP-3.4. Hydroxyl value, conversion and particle size of OL and oleated OLs.

Sample	$n_{OL\text{-}OH}$:n_{MO}	Hydroxyl value (mmol/g)			Conversion %
		Aliphatic	Aromatic	Total	
OL	/	2.57	2.60	5.17	/
oleated OL#1	1:0.5	0.70	2.19	2.89	25.02
oleated OL#2	1:0.6	0.64	2.22	2.86	25.46
oleated OL#3	1:0.7	0.59	2.34	2.93	24.43
oleated OL#4	1:0.8	0.72	2.33	3.05	22.72

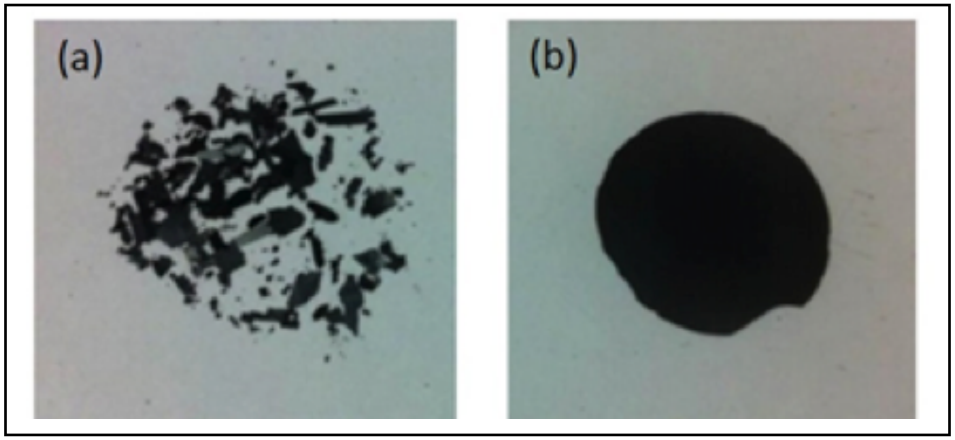


Figure C-CP-3.8. Photographs of (a) untreated OL and (b) oleated OL#2 after hot-pressing at 180 °C.

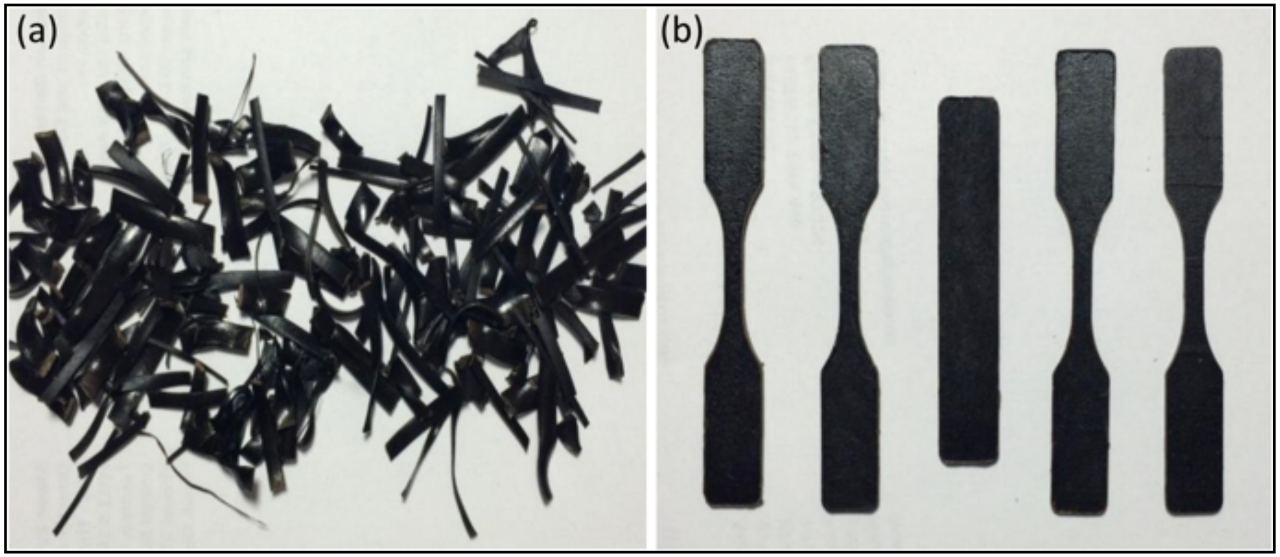


Figure C-CP-3.9. PLA/oleated OL blends: (a) samples through melt extrusion; (b) sample bars from melt molding.

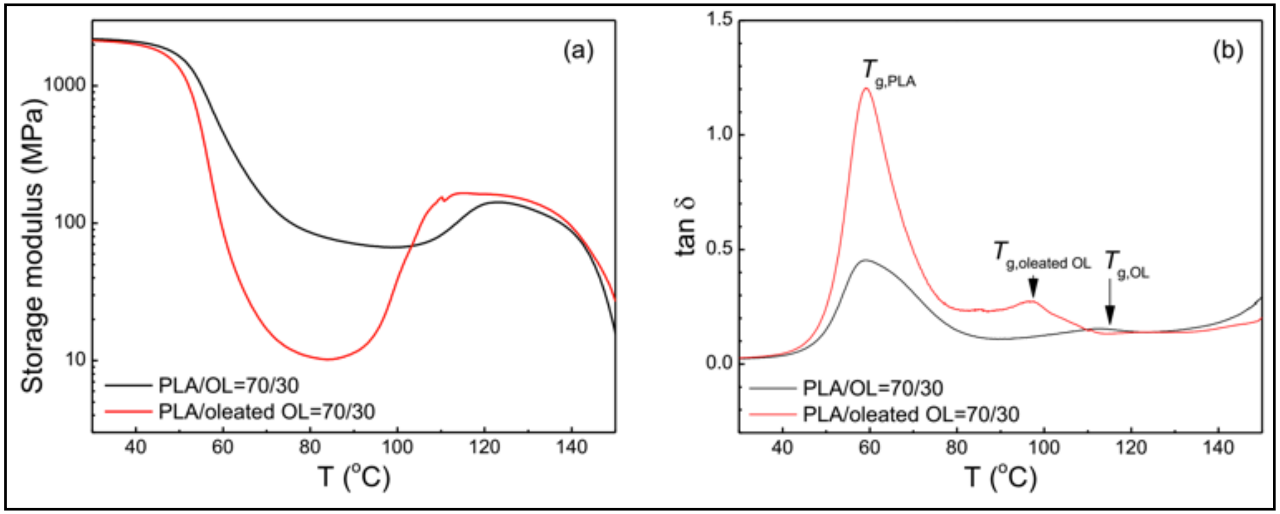


Figure C-CP-3.10. DMA curves of (a) storage modulus and (b) tan δ of the PLA/OL blends with and without mechanochemical modification.

As shown in Figure C-CP-3.8, the oleated OL#2 formed into thin and smooth film after hot pressing at 180 °C while the untreated OL shattered into pieces. The untreated OL showed lack of thermoplasticity when cooled from the melt, while the oleated OL became pliable at 180 °C and reformed into film upon as thermoplastics. Therefore, the thermoplasticity of OL was improved through the mechanically activated transesterification using methyl oleate reacted with OL.

In Figure C-CP-3.9, the PLA/oleated OL blends were successfully prepared through melt extrusion at 180 °C (Figure C-CP-3.9 (a)), the standard tensile and impact specimens were prepared through melt molding (Figure C-CP-3.9 (b)). During melt extrusion, PLA pellets and oleated OL were completely and homogenously mixed at 180 °C, and then the extrudate was cooled under room temperature. The extruding process is fluent and continuous. Moreover, the process of the melt molding is quite smooth as well. Therefore, the PLA/oleated OL blends exhibited pretty good melt processibility.

Figure C-CP-3.10 shows storage moduli (E') and tan δ of the PLA/OL blends. With increasing temperature, both blends experienced rapid drop in E' in the glass transition region (~60 °C) of PLA phase. The PLA/oleated OL blends exhibits lower E' than the PLA/OL blend in rubbery state, one possible reason is the introduction of long fatty chains of methyl oleate onto OL which improved the molecular mobility of the blends. As temperature further increased, E' started to increase at ~100 °C for the blends, this recovery of E' is believed to result from the cold crystallization of PLA. Due to the enhanced molecular mobility of plasticized PLA, an early cold crystallization was noted for PLA/oleated OL blend. In Figure C-CP-3.10b, two distinct peaks at 60 and 105 °C corresponded to Tgs of PLA and lignin phases. Compared with PLA/OL blends, Tg of PLA phase in oleated blends exhibited a slight increase, while Tg of OL phase greatly decreased. The shift of Tgs suggests the compatibility of PLA and OL was improved for the PLA/oleated OL blends. Therefore, the mechanically activated transesterification between OL and methyl oleate OL resulted in the increased compatibility between PLA and OL. The height of tan δ, also known as damping, represents the ability of accomplishing energy absorption and diepersal. The PLA/oleated OL blends exhibited higher damping value when compared with the PLA/OL blends in the temperature region from 40 to 110 °C. One reason for the increased damping value of the PLA/oleated OL blends is that the introduction of long fatty acid chains onto OL increased the mobility among molecular chains, which resulted in the improved flexibility and led to the higher damping value. Another possible reason is that the introduction of fatty acid chain acted as a soft portion, which decreased the rigidity and increased the elasticity of the PLA/oleated OL blends. Therefore, the PLA/oleated OL blends had better damping properties than the PLA/OL blends.

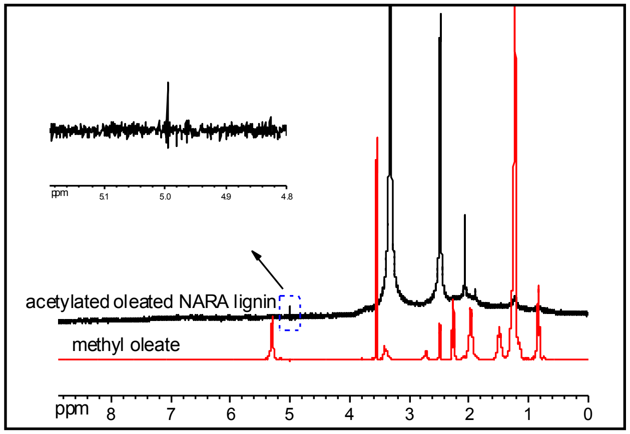


Figure C-CP-3.11. ^{1}H-NMR spectra of oleated NARA lignin and methyl oleate.

After the preliminary exploration of using organosolv lignin (which has a better solubility), NARA lignin was used to react with methyl oleate through ball milling. In order to increase the solubility of oleated NARA lignin in DMS-d6, the samples was first acetylated then purified to remove unreacted methyl oleate. The acetylated oleated NARA lignin was used for 1H-NMR analysis as shown in Figure C-CP-3.11. The three methylic protons from methyl oleate at ~3.7 ppm disappeared for the oleated NARA lignin since the residue methyl oleated were completely removed after purification, while the two olefinic protons (C=C) at ~5.3 ppm appeared and a little shifted to ~5 ppm for the oleated NARA lignin. Therefore, the transesterification between NARA lignin and methyl oleate was initially proved to occur during ball milling process.

Task C-CP-3.3. Application Development for PDL-Based Epoxy Asphalt

The asphalt was successfully modified by adding different amount of PDL-based epoxy/TMA mixture. As summarized from above discussion, the epoxy resin derived from PDL-epoxy/TMA show comparable properties comparing to commercial one. Because of the bulk structure in lignin, that will result in high Tg and good mechanical and thermal performance of the final epoxy resin. So the addition of PDL based epoxy resin into the asphalt was supposed to improve the temperature resistance and whole performance grade of the asphalt.

The preparation process of epoxy asphalt was as follows: Asphalt was heated to 90 ±5 °C in an oven for 30 min. The liquid mixture of PDL-epoxy/TMA (no curing) was added into the asphalt in a mortar and blend the mixture till the mixture became completely homogenous. Epoxy-asphalts modified with 7.5, 15.0, 22.5 and 30.0 wt % epoxy resin were prepared, respectively. The mixture of epoxy asphalt was transferred into teflon mold. The curing process was performed at 150 °C for 2 h and then at 200 °C for 1 h. Then the samples were cut into dimensions of 30 mm×18 mm and used for dynamic mechanical analysis. The characterization results of epoxy asphalt will be reported in next report.

Recommendations | Conclusions

Partial hydrogenolysis of NARA lignin was conducted in a 2-L reactor with a decent conversion and showed good reproducibility. An efficient and simple preparation method of PDL-epoxy was developed through direct-glycidylation reaction with epichlorohydrin using DMSO as co-solvent. The epoxy resins based on PDL epoxy showed competitive properties, suggesting the PDL-epoxy is a potential alternative to petroleum based epoxy for certain applications. The preparation of PDL based curing agents was also successfully conducted via two biobased maleated anhydrides. The resulting PDL curing agents have multifunctional groups and displays competitive advantage in application of epoxy resin. The further characterization of epoxy asphalt will be carried out by DMA, Reometer, DSC, etc. Structure characterization of PDL curing agents and cuing behavior of PDL curing agent with commercial DER332 will be further investigated.

Esterification of lignin through transesterification between organosolv lignin and methyl oleate was successfully achieved by mechanochemical reaction ball milling. The hydroxyl value decreased from 5.17 mmol/g of untreated OL to ~2.9 mmol/g of oleated OLs, the transesterification was mainly occurred between the aliphatic hydroxyls of OL and the ester bonds of methyl oleate. After mechanochemical modification, the oleated lignin exhibited improved thermoplasticity. Furthermore, the oleated OL was melt blended with PLA through twin-screw extrusion, the PLA/oleated OL blends exhibited good processibilty. Compared to the PLA/OL blends, the PLA/oleated OL blends exhibited better compatibility between PLA and lignin, which supported by the obvious shift of glass transition temperature of oleated lignin.

Next, the effects of milling conditions (such as milling time, types and content of catalyst, types of ball mills, etc.) on the transesterification between lignin and methyl oleate will be investigated. Characterization of oleated NARA lignin will be carried out by 31P-NMR, FT-IR, etc., and the oleated NARA lignin will be melt blened with PLA. Other alkylating agent such as soybean oil will be used to modify lignin through mechanochemical grinding, and other reaction types concerning lignin through ball milling will be continuously explored.

Physical and Intellectual Outputs

REFEREED PUBLICATIONS

Xin, J., Zhang, P., Wolcott, M.P., Zhang, J., Hiscox, W.C., & Zhang, X. (2014). A novel and formaldehyde-free preparation method for lignin amine and its enhancement for soy protein adhesive, Industrial Crops and Products, under review.

Li, M., Xina, J., Zhanga, J. and Xia, J. (2015). Application development of partially depolymerized lignin epoxy resin in epoxy asphalt, completed.

Guo, X., Xin, J. & Zhang, J. (2015). Mechanochemical synthesis of oleated lignin and properties of its blends with PLA, completed.

CONVERSION

PRETREATMENT TEAM

TASK C-P-2: DILUTE ACID PRETREATMENT OF SOFTWOOD AND LIGNIN PRODUCTS DEVELOPMENT

Key Personnel	Affiliation
Xiao Zhang	Washington State University

Task Description

Task C-P-2.1: Assist in optimizing large scale pretreatment and lignin product development

The termination of the diluted acid pretreatment activity allowed us to focus on developing new pathway/ technology for biorefinery lignin conversion and product development. This activity was initially scheduled to start in the second half of the third year. Significant progress has been made this year as shown in the task progress. This conversion technology will be investigated on NARA lignin samples.

Task C-P-2.2: Diluted acid pretreatment of Douglas-fir wood and forest residues

This activity has been terminated. However, the Ph.D student Carlos Alvarez, a Fulbright scholar, has started to work on an alternative pretreatment method with a focus to maximize hemicellulose recovery. This activity is mainly funded by Carlos Alvarez's Fulbright scholarship. Carlos presented his results at The American Institute of Chemical Engineers annual meeting (AICHE).

Task C-P-2.3: Identify new approach to selective conversion of softwood hemicellulose to fuel precursors and/or value chemical in high yield

It has been a great challenge to develop an economically viable pretreatment method to deconstruct softwood to produce fermentable sugars for biofuel production. One of the factors contributing to this challenge is the low recovery of carbohydrates, especially hemicellulose, to monosaccharides. The objective of this task is to identify new approach to incorporate catalysts to softwood pretreatments to improve hemicellulose conversion to platform chemicals. This is an unfunded research activity which will be conducted by a PhD student funded by a Fulbright scholarship.

Activities and Results

This project is not currently funded by NARA. The research activity is leveraged by a Fulbright Scholarship to a PhD student Carlos Alvarez's and Sungrant project which support another PhD student Ruoshui Ma.

We have made significant progress toward lignin depolymerization and application as well as identifying new approach for biomass hemicellulose utilization. Four papers have been published in ChemSusChem (2), Bioresearch Technology and Bioenergy Research. The paper entitled "*Catalytic Oxidation of Biorefinery Lignin to Value-added Chemicals to Support Sustainable Biofuel Production*" ChemSusChem 2015, vol. 8, p. 24 has been listed as one of the most accessed paper in ChemSusChem (http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1864-564X/homepage/2476_mostaccessed.html).

WE have demonstrated new pathways to selectively depolymerization of biorefinery lignin to monomeric phenolic compounds and dicarboxylic acids (Figure C-P-2.1).

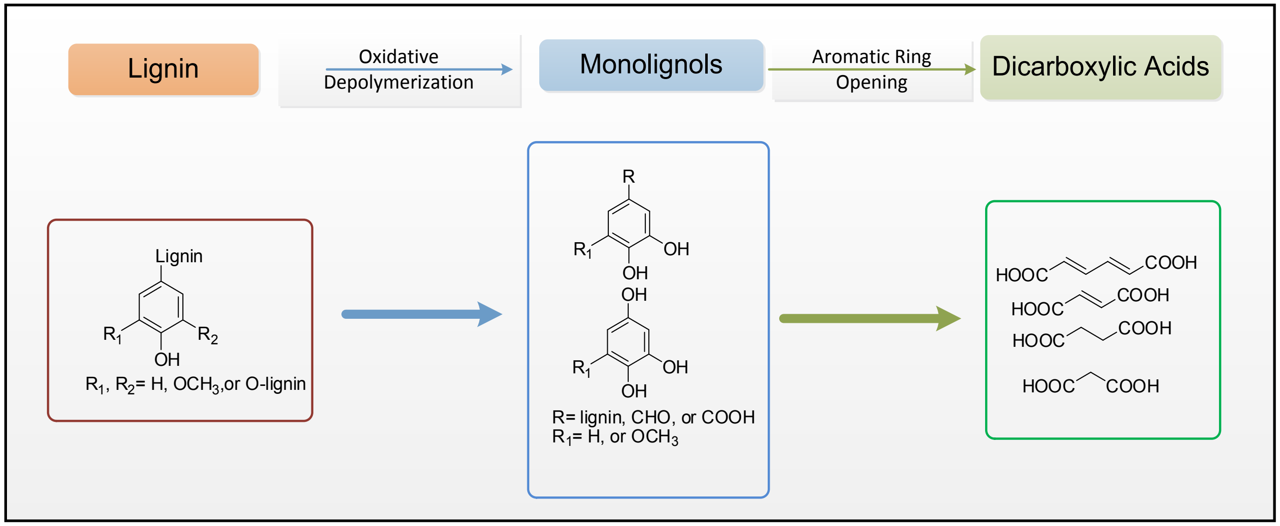


Figure C-P-2.1. Selective conversion of biorefinery lignin to monomeric phenolic compounds and dicarboxylic acids

Recommendations | Conclusions

Our recent work on lignin depolymerization and conversion to monomeric phenolic compounds and dicarboxylic has opened new avenues toward lignin conversion and utilization will attract considerable amounts of interest. Dr. Xiao Zhang visited Solvay Chemical Headquarter in Houston in October 2014 and learned that chemical companies are looking into similar chemistries we applied on lignin for phenolic chemicals production. Therefore further investigation to gain detail understanding of these pathways will be of great commercial and scientific interest. We have not systematic investigated these conversions on NARA lignin (sulfite lignin and milled wood lignin) yet. We hope to have finical support from NARA in the next year to allow us to focus on evaluating these conversion technologies on both sulfite lignin and milled wood lignin from sugar depot.

Physical and Intellectual Outputs

REFEREED PUBLICATIONS (ACCEPTED OR COMPLETED)

1. Ma, R.S., Xu, Y. & Zhang, X. (2015). Catalytic Oxidation of Biorefinery Lignin to Value-added Chemicals to Support Sustainable Biofuel Production. ChemSusChem, 8(1), 24-51.

2. Alvarez-Vasco, C. & Zhang, X. (2014). Alkaline hydrogen peroxide (AHP) pretreatment of softwood: The effect of pretreatment conditions and hemicellulolytic enzymes addition on sugar yields, Bioresource Technology. In preparation.

3. Ma, R.S., Yan, X. & Zhang X. (2014). Catalytic oxidation of biorefinery lignin to value-added chemicals to support sustainable biofuel production. ChemSusChem. Accepted.

4. Alvarez-Vasco, C., Guo, M. & Zhang, X. (2015). Dilute acid pretreatment of Douglas fir forest residues: pretreatment yield, hemicellulose degradation, and enzymatic hydrolysability. BioEnergy Research, 8(1), 42-52. doi:10.1007/s12155-014-9496-7.

RESEARCH PRESENTATIONS

1. Oral presentation: "Catalytic Oxidation of Biorefinery Lignin to Value---Added Chemicals to Support Sustainable Biofuel Production From Lignocellulosic Biomass" Frontier in Biorefinery, Oct.21-24, 2014 ST Simons Island GA.

2. Oral presentation: Chemical Conversion of Biorefinery Lignin to Value Added Platform Chemicals, American Institute of Chemical Engineers (AICHE) Meeting, Altlanta GA, Nov. 17-20, 2014, presented by PhD student Ruoshui Ma

3. Oral presentation: Selective Conversion of Biorefinery Lignin to Dicarboxylic Acids, American Institute of Chemical Engineers (AICHE) Meeting, Altlanta GA, Nov. 17-20, 2014, presented by PhD student Ruoshui Ma

4. Oral presentation: "Potential of Alkaline Hydrogen Peroxide (AHP) As Softwood Forest Residue Pretreatment Method: Hemicellulose and Cellulose Conversion to Sugars and Chemicals", American Institute of Chemical Engineers (AICHE) Meeting, Atlanta, GA. November 18, 2014. presented by PhD student C. Alvarez-Vasco.

5. Oral presentation: " Metal Catalyzed Conversion of Biomass to Maximize Hemicellulose Sugar Conversion to Valuable Organic Acids", American Institute of Chemical Engineers (AICHE) Meeting Atlanta, GA. November 17, 2014. presented by PhD student C. Alvarez-Vasco.

Conversion-CP_Sarkanen

	Task Name	
1	C-CP-1. Formulations for Coproduct Lignin-based Plastics	48%
2	Task C-CP-1.1. Biorefinery coproduct lignins	65%
6	Task C-CP-1.2. Plasticizers for lignin-based polymeric materials	85%
9	Task C-CP-1.3. Processability of lignin-based plastics	42%
17	Task C-CP-1.4. NARA ligninsulfonate-based polymeric materials	28%
18	Ligninsulfonate derivatization	50%
19	X-ray and AFM characterization	35%
20	Flame retardants and foams	0%
21	Molecular-weight dependence of properties	0%
22	Task C-CP-1.5. Translation to industrial processing	0%
23	Incomplete derivatization, industrial conditions	0%
24	Basic blend components and polysaccharides	0%
25	Use of foaming agents (tentative)	0%
26	Estimated production costs	0%
27	Task C-CP-1.6. Final Report	0%

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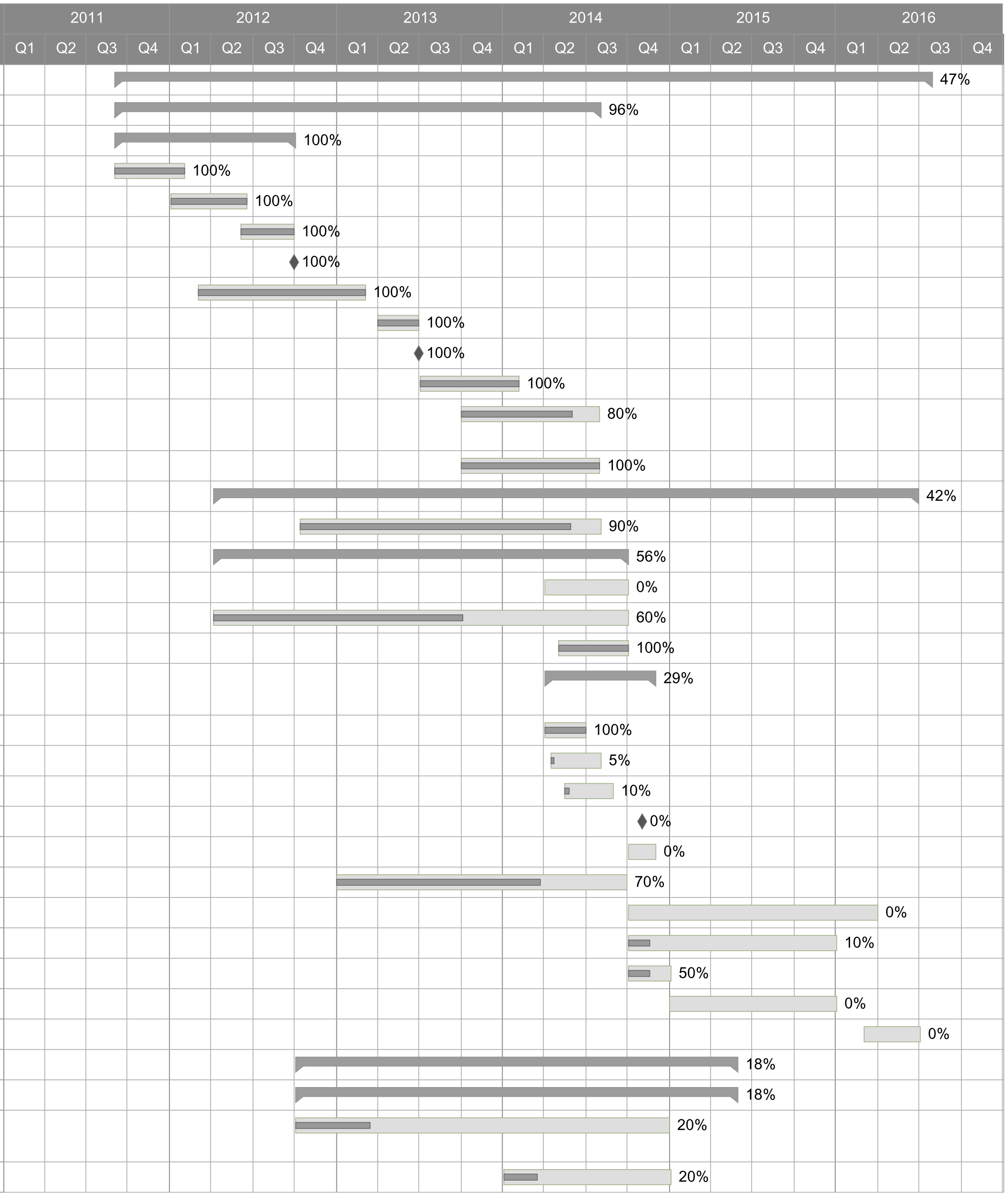
Conversion-CP_Garcia-Perez

	Task Name	
1	C-CP-2. Conversion of Lignin to High Value, Large Market Products	47%
2	Task C-CP-2.1. Characterization of NARA Lignin	96%
3	Task C-CP-2.1.1. Develop Initial Isolation Methods & Test Lignins	100%
4	Determine purity of lignin as delivered	100%
5	Develop best method for isolation/purification	100%
6	Complete chemical and structural analysis	100%
7	Isolation procedure developed & lignin characterization completed	100%
8	Evaluate the 6 lignins produced from the 4 current processes	100%
9	Analyze and Compile Results	100%
10	Report on isolation procedure and structural analysis of lignin	100%
11	Evaluate methods to isolate lignin from hydrolysis residuals	100%
12	Write and submit paper(s) for publication on the properties of the NARA lignin and the activated carbons made from NARA lignins	80%
13	Analyze the lignin produced on a larger scale by the 3 current processes	100%
14	Task C-CP-2.2. Convert lignin to high surface area activated carbon	42%
15	Develop lab carbonization/activation process	90%
16	Task C-CP-2.2.1. Refine lab carbonization/activation process	56%
17	Develop yield-performance-economics curve	0%
18	Determine whether one- or two- activation process on product performance	60%
19	Develop initial commercial scale production model	100%
20	Task C-CP-2.2.2. Search and obtain an industrial partner to help with commercial development	29%
21	Develop an intellectual property plan for protection of activated carbon IP	100%
22	Make initial contact with potential partners	5%
23	Develop criteria for partner selection	10%
24	Selection of partner	0%
25	Develop and have signed appropriate agreements with partner	0%
26	Evaluate product economics	70%
27	Conduct Customer Trials	0%
28	Develop plan and process for scale to pilot	10%
29	Locate facility for pilot scale production	50%
30	Product pilot scale quantities of AC	0%
31	Summary report on customer trials (activated carbon)	0%
32	Task C-CP-2.5. Study other potential uses of NARA lignin	18%
33	Task C-CP-2.5.1. Evaluate lignin or derivatives for use in super capacitors	18%
34	Evaluate physically activated carbons developed for mercury adsorption for use in supercapacitors	20%
35	Develop criteria for improved supercapacitor performance.	20%



	Task Name	
36	Modify carbonization/activation and post-treatments to include chemical activation and surface chemistry conrtol for electrochemnical applications	15%
37	Evaluate effect of washing on supercapitor performance	10%
38	Task C-CP-2.6. Evaluate effects of NARA spent sulfite liquor on fresh cement properties	30%
39	Task C-CP-2.7. Write Final Report	0%

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Conversion-CP_Zhang_Wolcott

	Task Name	
1	C-CP-3. Novel Engineering Polymers from Lignin-Derived Building Blocks	60%
2	Task C-CP-3.1. Preparation of epoxies using lignomers	100%
11	Task C-CP-3.2. Development of partially depolymerized lignin (PDL) epoxies and lignin modification	80%
12	Task C-CP-3.2.1. Preparation of epoxies and curing agents from lignin fragments	89%
13	Initial preparation of epoxies and curing using commercial Kraft lignin as a model	100%
14	Report on feasibility of preparation methods using Kraft lignin	100%
15	**Viability of preparation methods assesssed**	100%
16	Assess various PDL products for MW, hydroxy number, solubility	95%
17	Develop synthesis methods for PDL derived epoxy and curing agent	97%
18	Characterize curing behavior and physical performance of DPL derived materials	70%
19	Report PDL epoxy development and performance	67%
20	**Viability of PDL epoxy determined**	50%
21	Task C-CP-3.2.2. Explore deploymerization of lignin and preparation epoxies and curing agents using partially depolymerized lignin (PDL)	74%
22	Conduct thorough review of lignin depolymerization using various methods	100%
23	**Delineate methods and conditions to produce partially depolymerized lignin (PDL)**	100%
24	Preliminary assessment for liquefaction of NARA lignin in supercritical solvents	100%
25	Preliminary assessment for hydrogenolysis of NARA lignin using Reney Ni	100%
26	Assess performance producing PDL using both method: Target >70% yield	100%
27	Refine assessment for liquefaction of NARA lignin in supercritical solvents	100%
28	Refine assessment for hydrogenolysis of NARA lignin using Reney Ni	100%
29	Explore methods for enhancing the efficiency of lignin depolymerization	87%
30	Explore depolymerization and modification of lignin in solid state reaction	40%
31	Prepare articles and presentation for the efficacy of liquefaction and hydrogenolysis depolymerization of NARA lignin	65%

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	Task Name	
32	**Performance of liquifaction and hydrogenolysis methods have been assessed on NARA lignin**	75%
33	Task C-CP-3.3. Application Development for PDL-Based Epoxy Asphalt	23%
34	Preliminary development of epoxy asphalts formulations using commercial components	45%
35	Preliminary development of epoxy asphalts formulations using Kraft epoxy	100%
36	Develop PDL-derived epoxy asphalt	20%
37	Evaluate performance and application for PDL-derived epoxy asphalt	20%
38	**Structure-Property Relationships in Epoxy-Asphalt Assessed**	0%
39	Refine PDL-derived epoxy and asphalt performance for commercial application	0%
40	**Commercial viability and value assessed**	0%
41	Task C-CP-3.4. Final Report	0%

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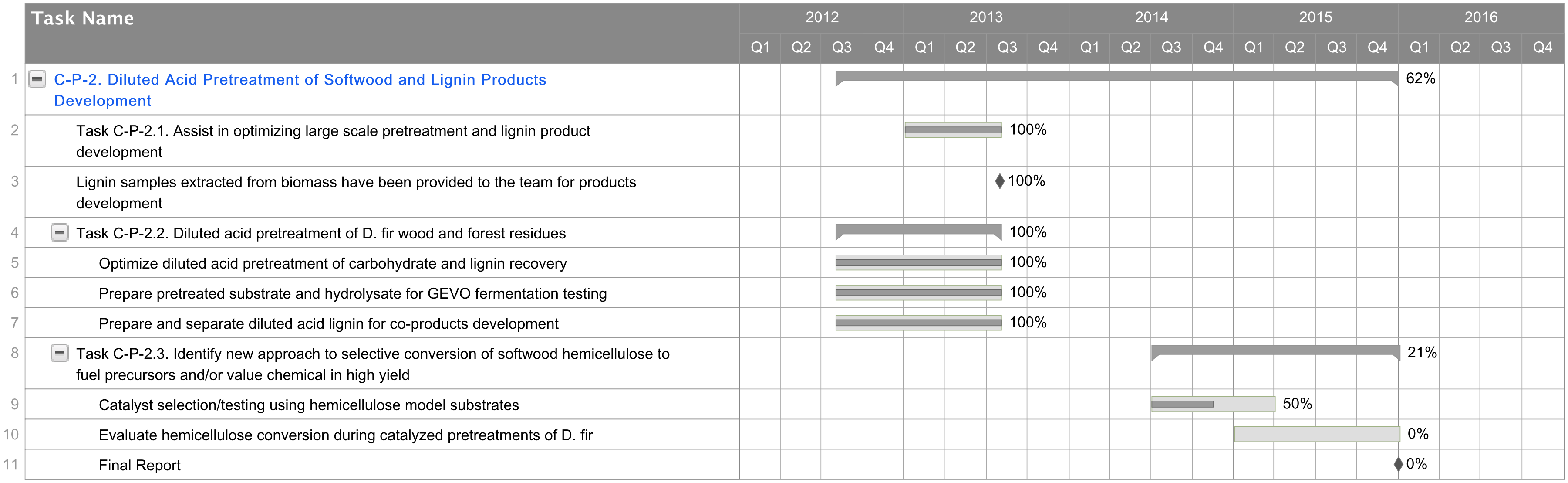
Pretreatment_XZhang



	Task Name	%
1	C-P-2. Diluted Acid Pretreatment of Softwood and Lignin Products Development	62%
2	Task C-P-2.1. Assist in optimizing large scale pretreatment and lignin product development	100%
3	Lignin samples extracted from biomass have been provided to the team for products development	100%
4	Task C-P-2.2. Diluted acid pretreatment of D. fir wood and forest residues	100%
5	Optimize diluted acid pretreatment of carbohydrate and lignin recovery	100%
6	Prepare pretreated substrate and hydrolysate for GEVO fermentation testing	100%
7	Prepare and separate diluted acid lignin for co-products development	100%
8	Task C-P-2.3. Identify new approach to selective conversion of softwood hemicellulose to fuel precursors and/or value chemical in high yield	21%
9	Catalyst selection/testing using hemicellulose model substrates	50%
10	Evaluate hemicellulose conversion during catalyzed pretreatments of D. fir	0%
11	Final Report	0%

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