NARA Goal Two

2nd Cumulative Report

April 2013 - March 2014

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.

TABLE OF CONTENTS

SUMMARY

Based on current estimates, for every bone-dry ton of forest residue converted to isobutanol, three quarters remain as residual material called co-product residuals (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 from the residual solids that provide a higher value than current use for energy. Creating high-value products from the residual solids is essential to establish a value-chain for improved bio-refinery profitability.

RESIDUAL SOLIDS AS MATERIAL FOR ACTIVATED CARBON AND SUPERCAPACITORS

To meet this challenge, NARA's co-product residual research has progressed on multiple fronts. In the first cumulative report spanning 2011-March 2013, residual solids generated from enzymatic hydrolysis on FS-03 samples were collected from the four pretreatment processes evaluated (SPORL, mild bisulfite, wet oxidation, and dilute acid), and characterized for lignin, carbohydrate and ash content. Experiments to generate activated carbon from the residual solids remaining after fermentation were initiated.

For this reporting period, hydrolysis residual solids (HRS) and fermentation residual solids (FRS) were characterized (carbohydrate and lignin analysis) from Douglas-fir FS-10 samples pretreated by optimized wet oxidation (WOX) and mild bisulfite (MBS) protocols. In addition, methods have been developed to extract high purity lignin from these samples to test how lignin chemistry is affected by the WOX and MBS pretreatment protocols (Task C-CP-2.1.1).

Powdered activated carbon (PAC) was prepared from the FRS derived from the MBS and WOX pretreatment processes and is being evaluated as a material used for vapor phase mercury capture from coal power plant flue gas and for electrodes in supercapacitors (Task C-CP-2.2). The porous structure of the activated carbon samples was investigated by gas physisorption using two absoptives, nitrogen and carbon dioxide. Experiments show that the activated carbon derived from MBS and WOX pretreatment samples differs in porosity. Activated carbon derived from MBS has a larger pore size than WOX derived activated carbon. A larger pore size may allow for enhanced absorbance and ion conductivity. To test the mercury absorbance capacity, PAC samples generated from the MBS and WOX pretreated material were sent to the URS Corporation for analysis. Results from this analysis are being evaluated, and additional partners are being sought for further testing and pilot scale evaluation. The revenue potential from the activated carbon could be substantial and contribute significantly towards the biorefinery profitability.

Initial supercapacitor performance tests suggest that MBS carbons demonstrate a more capacitive behavior compared to WOX carbons.

LIGNIN USE AS THERMOPLASTIC MATERIAL

A more long-term directive is to evaluate the use of co-product residuals as a component in thermoplastics used for residential insulation and food and beverage packaging. Initial attempts to form thermoplastics using the lignin-rich solids generated from pretreated material were unsuccessful. The lignin-rich material generated from dilute-acid pretreatment contained relatively high carbohydrate content combined with low molecular weight lignin. These conditions prevented favorable cohesion. Methylated ligninsulfonates obtained from sulfite pretreatment processes, on the other hand, readily formed cohesive materials, but the casting conditions employed generated voids within the materials produced. Methylated ball-milled softwood lignin (MBML), which is a relatively purified lignin source and not produced by available pretreatment processes, does produce polymeric material exhibiting ~50% tensile strength and elongations at break around 8%. Work this year focused on improving MBML polymer characteristics by introducing blend components (Task C-CP-1.3). Perhaps the most promising methylated ball-milled lignin-based blend was one containing only 5% w/w (400 molecular weight) poly(ethylene glycol) that exhibited a 65 MPa tensile strength with an elongation at break near 10%. It is intended that once optimal blend components and casting conditions for MBML are established and characterized, that this understanding will be adapted to generate polymers from the lignin rich material generated through the pretreatment process (C-CP-1).

PARTIALLY DEPOLYMERIZED LIGNIN AS A BUILDING BLOCK FOR CHEMICAL SYNTHESIS

Our final co-products effort is aimed at partially depolymerizing the high molecular weight and recalcitrant form of lignin that results from the enzymatic hydrolysis and fermentation process. The goal of producing partially depolymerized lignin (PDL) is to create building blocks used to engineer high value polymers. In the previous cumulative report, two depolymerization protocols, mild hydrogenolysis and base-catalyzed depolymerization (BCD), were evaluated on their ability to depolymerize Kraft lignin and the lignin derived from dilute acid (DA) pretreated residual solids after enzymatic hydrolysis. For this reporting period, the mild hydrogenolysis and BCD depolymerization protocols were also applied to the lignin derived from forest residuals pretreated by the mild bisulfite

(MBS) and wet oxidation (WOX) processes. Depolymerization yields from the BCD treatments ranged from 55.2% to 88.8% depending on temperature and pretreatment sample with the highest yield and hydroxyl value resulting from the DA sample. Yield of conversion to PDL using the mild hydrogenolysis protocol ranged from 70 to 82% with a temperature optimum of 180ºC. Hydroxyl values ranged from 3.58 (DA pretreatment) to 4.68 (WOX pretreatment). The mild hydrogenolysis treatment relies on less chemicals and is performed at lower temperature that the BCD, which makes it a more attractive PDL treatment in terms of energy use and chemical cost. PDL solubility in organic solvent is an important consideration for chemical modification. The lignin subjected to hydrogenolysis dispersed well in organic solvents whereas non-depolymerized lignin was insoluble. Taken together, these results suggest that partial depolymerization methods tested produce high yields of depolymerized lignin from all pretreatment sources and that the depolymerized lignin is soluble in organic solution.

A PDL-epoxy was made from lignin derived from DA and MBS pretreated samples. These resins show promising properties with the PDL-epoxy derived from MBS material demonstrating superior mechanical properties over the PDL-epoxy derived from DA pretreated material (Task C-CP-3.2)

In addition to the PDL work, preliminary experiments to modify lignin in solid states, i.e., performing the reaction in a ball mill, have been initiated. Fatty acids were successfully introduced onto lignin to modify the lignin characteristics with the intent of producing lignin-based materials suitable as a blend in thermoplastics.

LIGNIN CONVERSION TO INDUSTRIAL CHEMICALS

During this project period, a new pathway was discovered to selectively covert biorefinery lignin to dicarboxylic acids (DCA), including muconic, maleic, and succinic acids. These DCAs are highly valuable industrial chemicals and platform intermediates used in many areas including biopolymer, pharmaceutical, and food additives industries (Task C-P-2.1). Conversion optimization and a techno-economic analysis for this pathway is in progress. In addition, an alkaline peroxide pretreatment protocol has been developed. When applied to Douglas-fir samples, the treatment converts hemicellulose simple sugars into valuable organic acids, such as lactic acid and succinic acid (Task C-P-2.3).

Significant outputs to date from the teams involved with co-product development are listed below.

- Published partial depolymerization results of lignin (Task C-CP-3.2). http://www.sciencedirect.com/science/article/pii/S0960852413019329
- A new pathway was discovered to selectively convert biorefinery lignin to dicarboxylic acids (DCA), including muconic, maleic, and succinic acids. These DCAs are highly valuable industrial chemicals and platform intermediates used in many areas including biopolymer, pharmaceutical, and food additives industries (Task C-P-2.1). http://onlinelibrary.wiley.com/doi/10.1002/cssc.201300964/abstract

Training

Name	Affiliation	Role	Contribution
Yi-ru Chen	Univ of Minnesota	Res. Assoc.	Lignin isolation and characterization
Yun-Yan Wang	Univ of Minnesota	Grad. Stud.	Lignin-based plastic formulations
Jianglei Qin	WSU, CMEC	Post-doc	Lignin depolymerization and epoxies
Junna Xin	WSU, CMEC	Post-doc	Lignin depolymerization and epoxies
Daniel Leong	Olin College of Engr.	NARA SURE Student	Lignin depolymerization
Xiaojie Guo	WSU, CMEC	PhD Student	Lignin modifications and blends
Mei Li	WSU, CMEC	Visiting PhD Student	Lignin modification and epoxies
Chanel Casayuran	Cornell	NARA SURE Intern	Development of data relating lignin feedstock to resultant activated carbon properties
Stephen Cline	Penn State	NARA SURE Intern	Development of separation procedure for lignin from hydrolysis residuals

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

The scale of biofuels production from lignocellulosic biomass to be implemented by 2030 will give rise to more than 200 million tons of lignin derivatives. Here, systematically reliable means are being developed for converting such co-product lignins into thermoplastics that are much like polystyrene mechanically; the most suitable of these are to be transformed into foams for the thermal insulation of residential buildings. Sources of co-product lignins will ultimately be from our NARA partners at the scales needed. Apart from reducing the heating/cooling costs for buildings, the value added to the co-product lignins will improve the economic viability of biorefining processes. The advantage of designating thermally insulating foams as early applications of lignin-based plastics is that the mechanical properties of such materials will not have to meet demands as stringent as, for example, engineering plastics. The domestic U.S. market for foamed plastic is projected to reach 4 billion kg in 2013.

It is certainly possible to plasticize simple lignin derivatives by, for example, blending them with miscible low-Tg polymers. It has been demonstrated at the University of Minnesota that methylated and ethylated softwood kraft lignins (which themselves can be similar to polystyrene in tensile behavior) are readily plasticized when blended at 25%–35% levels with poly(ethylene glycol) or certain main-chain aliphatic polyesters. In a preliminary demonstration, it has proven possible to convert homogeneous blends of methylated softwood kraft lignins with 20% (w/w) low-Tg aliphatic polyesters into uniform 0.10 g cm-3 foams using chemical blowing agents at temperatures approaching 160 °C.

The ultimate goal of the present project is to convert co-product lignosulfonates and dilute-acid lignins from softwood pretreatment processes into useful thermoplastic polymer blends with high (75 – 85% w/w) lignin contents. The lignosulfonates have to be methylated prior to incorporation into suitable blend formulations, while the dilute-acid lignins will be analogously employed with and without derivatization. It is anticipated that the latter will lead to the creation of the first generation of 85% w/w dilute-acid lignin-based plastics.

Attempts to convert co-product dilute-acid lignins and ligninsulfonates to thermoplastics have not succeeded. The dilute-acid lignins provided have either been of too low molecular weight or possessed too high carbohydrate contents. The methylated ligninsulfonates, on the other hand, readily form cohesive materials, but the casting conditions employed have generated voids within the materials produced for reasons that remain to be elucidated. Thus, attention has been preliminarily focused upon blends of methylated native ball-milled softwood lignins for the purposes of establishing realistic expectations for the mechanical properties of plastics based on such starting materials. These experiments have shown considerable promise, and the new blend formulations will be translated to co-product dilute-acid lignins and ligninsulfonates once the boundaries of these next-generation native lignin-based plastics have been delineated.

Activities and Results

As a prelude to transforming NARA co-product lignins into plastics, Simo Sarkanen's group at the University of Minnesota has been examining polymeric materials with the highest attainable methylated native softwood lignin contents. It is necessary to approach the conversion of the co-product lignins in this way because NARA lignin-derivative structures are more complicated (in terms of the functional groups present) than the native biopolymers from which they have been formed. Actually, the mechanical properties of certain polymeric materials with 85% – 100% w/w methylated ball-milled lignin contents are very promising in exhibiting tensile strengths between 50 and 70 MPa with 7% – 14% elongations at break. These are unprecedented findings; they clearly refute the traditional working hypothesis (developed over 40 years ago) that the hydrodynamic compactness of lignin macromolecules arises from crosslinking of the polymer chains. To the contrary, the compactness of macromolecular lignin species arises from the strong non-covalent forces that prevail between substructures in lignin polymer chains. The result is found in the configurations of the domains in lignin-based polymer materials that are composed of associated complexes interacting with one another through their peripheral chain segments. Consequently, the compositions of polymeric materials embodying the highest attainable lignin contents are formulated in recognition of the need for a balance between the lignin–lignin and lignin–blend-component interactions. When these conditions are met, the tensile properties of the resulting lignin-based polymer blends can supersede those of polystyrene or poly(methyl methacrylate).

A few remarkable but, in context, typical examples are worth mentioning; all are based on methylated ball-milled softwood lignin preparations that are representative of the softwood lignin overall. In the absence of any additional blend components, the methylated ball-milled lignin can form a material exhibiting a tensile strength of 50 MPa with an 8% elongation at break. In the presence of 15% w/w poly(ethylene oxide-b-1,2-butadiene-b-ethylene oxide), the resulting blend can display a 68 MPa tensile strength with an elongation at break of 7%. Even a multiphase blend containing 15% poly(ε-caprolactone) can reveal a tensile strength of 61 MPa with a 7% elongation at break. Perhaps the most promising methylated ball-milled lignin-based blend was one containing only 5% w/w (400 molecular weight) poly(ethylene glycol) that exhibited a 65 MPa tensile strength with an elongation at break near 10%. Increases of 40 – 100% in these elongations at break are not difficult to achieve. Such unprecedented results provide a firm foundation for developing promising polymeric materials from NARA co-product lignin derivatives.

It is generally recognized that the profitability of processing lignocellulose in biorefineries depends on the value added to the co-product lignins generated. Depending on the pretreatment step employed prior to enzymatic saccharification, lignins produced from plant-cell walls are likely to be similar to dilute-acid lignins or even ball-milled (native) lignins. In view of that, the quest for plastics from biorefinery co-product lignins was diverted toward ball-milled softwood lignins (which are representative of softwood lignins as a whole). The research has progressed to the point of a dramatic (and, in some quarters, quite unexpected) breakthrough. Materials made up simply of methylated ball-milled softwood lignins alone can manifest tensile strengths of 50 MPa with ~8% elongations at break. Such lignin-based polymeric materials compare favorably to polystyrene and poly(methyl methacrylate).

There are a number of polymer blends with higher (80 – 85% w/w) methylated softwood ball-milled lignin contents that have been found to exhibit tensile strengths of 60 – 70 MPa. For example, formulations containing 80% and 85% methylated ball-milled lignin in blends with triblock co-poly(ethylene oxide-b-1,2-butadiene-b-ethylene oxide) attain strengths of 63 and 68 MPa, respectively, as the elongations at break reach ~9% and ~7% (Figure C-CP-1.1). These results are quite sensitive to blend-component configuration: analogous materials embodying the corresponding (15% w/w) proportion of diblock co-poly(ethylene oxide-b-1,2-butadiene) exhibit much worse tensile behavior. However, the 85% w/w methylated ball-milled lignin blend with poly(ethylene oxide) exhibits a 52 MPa tensile strength as the elongation at break extends beyond 6% (Figure C-CP-1.1).

Blends of 75% – 85% w/w methylated ball-milled lignin with aliphatic polyesters are also promising, although their tensile behavior does not quite match that of the blends with poly(ethylene oxide-b-1,2-butadiene-b-ethylene oxide). Interestingly, the best results so far have been obtained with multiphase materials containing 15% w/w poly(ε-caprolactone), which can attain strengths of 61 MPa with ~7% elongations at break (Figure C-CP-1.2). On the other hand, homogeneous blends of 75% w/w methylated ball-milled lignin with 25% w/w poly(butylene adipate) may exhibit tensile strengths of only 41 MPa as the elongation at break reaches ~7 % (Figure C-CP-1.2).

There are vagaries in the characterization of methylated ball-milled lignin-based thermoplastic blends that must be regularly taken into account. An incremental rise in the glass transition temperature (Tg), for example, may occur owing to an increase in the degree of association between the lignin components that can take place at elevated temperatures. Such an effect is routinely observed in thermograms during the thermal cycling of uncast methylated ball-milled lignin samples in a differential scanning calorimeter (Figure C-CP-1.3).

On the other hand, miscible blends of methylated ball-milled lignin with, for example, poly(ethylene oxide-b-1,2-butadiene-b-ethylene oxide) or poly(ethylene glycol) exhibit much lower Tg's (Figure C-CP-1.4) than the methylated lignin preparation alone (Figure C-CP-1.3), but the transitions become much broader and more difficult to define.

The results depicted in Figures C-CP-1.1 and C-CP-1.2 stand on an important foundation that has not been understood until now. When properly handled, methylated ball-milled lignin preparations, in the absence of any additional blend components, readily form polymeric materials with ~ 50 MPa tensile strengths and elongations at break around 8% (Figure C-CP-1.5). The low-molecular-weight lignin components in these remarkable materials can actually reduce their brittleness appreciably.

The change in ductility of the methylated ball-milled lignin-based materials caused by miscible low-Tg polymers is sensitive to the balance of intermolecular forces between the lignin and blend components. This is exemplified by the tensile behavior of 85% w/w methylated ball-milled lignin blends with poly(ethylene glycol) and poly(ethylene glycol) methyl ether cast under the same conditions (Figure C-CP-1.6).

In order to ensure that co-product-lignin-based plastics from biorefineries will be commercially attractive from an economic point of view, it should be established at a relatively early stage that the other thermoplastic blend components are reasonably cheap and readily available.

Thermoplastic blends containing the highest attainable methylated ball-milled lignin contents with 5 – 15% w/w poly(ethylene glycol) (PEG) are actually very promising (Figure C-CP-1.7) in regard to their mechanical properties. The blend containing 5 % w/w 400-molecular-weight PEG exhibits a 65 MPa tensile strength with an elongation at break near 10%. In comparison, the corresponding blend with 5% w/w each of 400- molecular-weight PEG and 4,600-molecular-weight PEG possesses a 52 MPa tensile strength beyond the yield point as the elongation-at-break extends past 13% (Figure C-CP-1.7).

The findings presented here are unprecedented in the field of lignin-based polymeric materials. A provisional patent application in regard to these discoveries was filed on March 14, 2014.

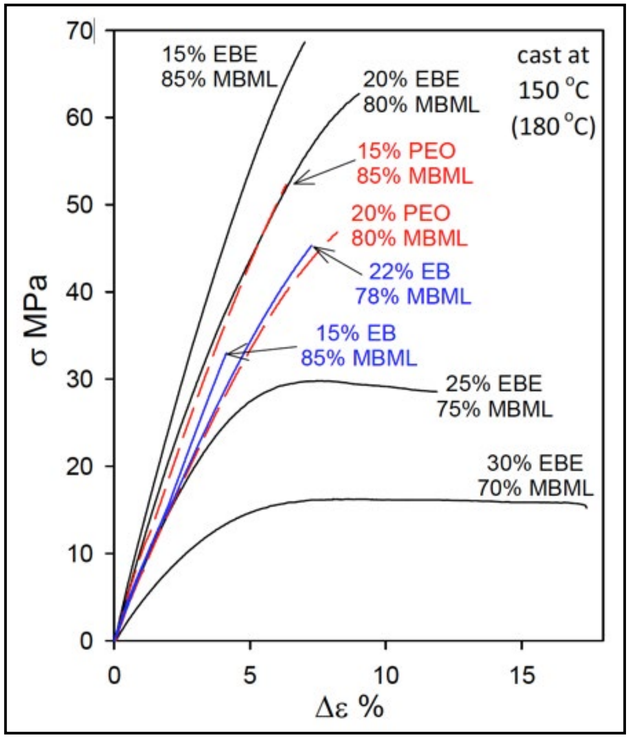


Figure C-CP-1.1. Plasticization of methylated ball-milled softwood lignin (MBML) in blends with poly(ethylene oxide) (PEO), poly(ethylene oxide-b-1,2-butadiene) (EB) and poly(ethylene oxide-b-1,2-butadiene-b-ethylene oxide) (EBE), reflected in the tensile behavior of the corresponding materials.

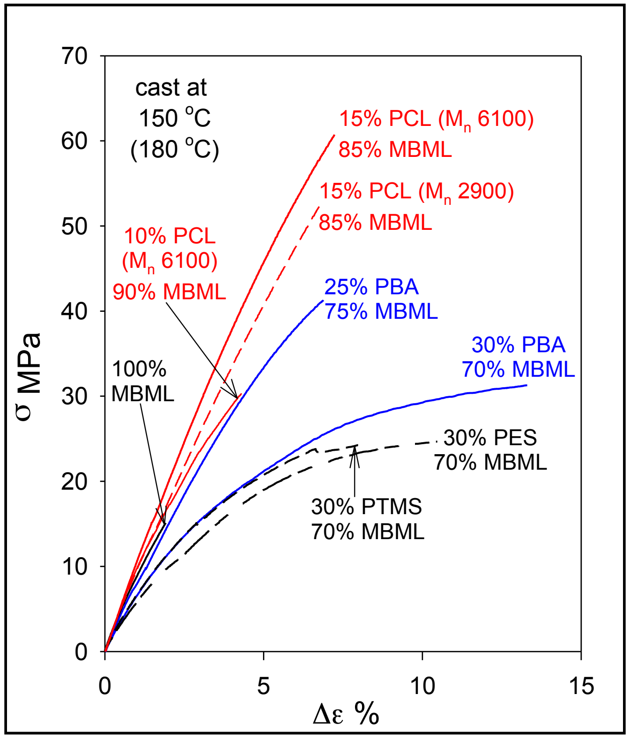


Figure C-CP-1.2. Plasticization of methylated ball-milled softwood lignin (MBML) in blends with poly(ε -caprolactone) (PCL), poly(butylene adipate) (PBA), poly(ethylene succinate) (PES) and poly(trimethylene succinate) (PTMS), reflected in the tensile behavior of the corresponding materials.

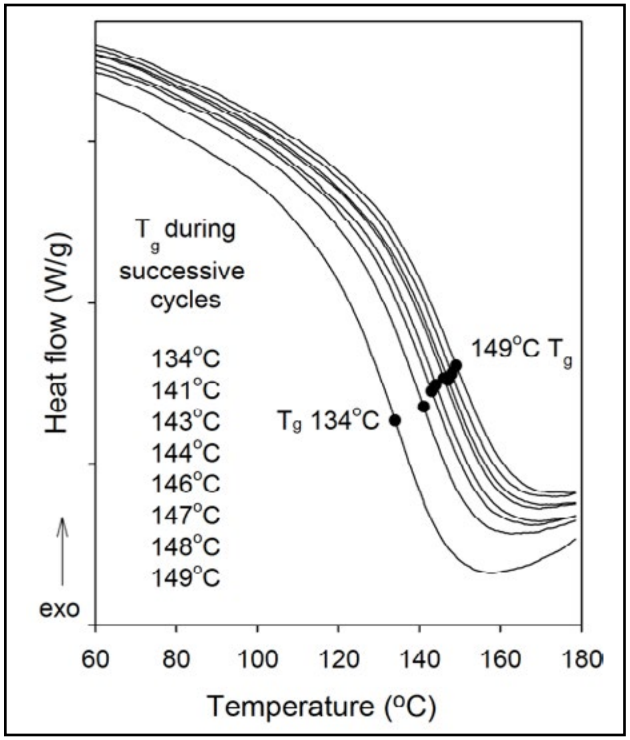


Figure C-CP-1.3. Differential scanning calorimetric (DSC) curves (10°C min-1) characterizing uncast methylated ball-milled softwood lignin during thermal cycling between 40 and 180°C. Symbols • denote rising Tgs

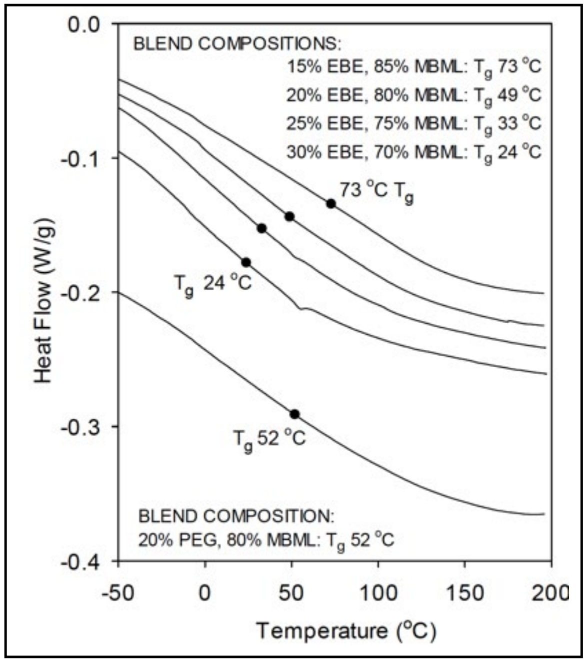


Figure C-CP-1.4. Differential scanning calorimetric (DSC) curves (10°C min-1) characterizing plasticization of methylated ball-milled softwood lignin by EBE and PEG. Symbols • denote the Tgs of these blends.Tgs

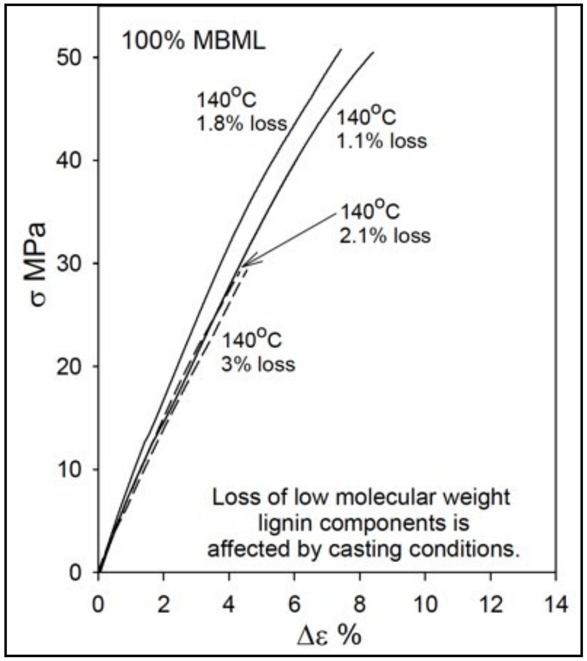


Figure C-CP-1.5. Tensile behavior of methylated ball-milled softwood lignin-based polymeric materials formed by casting for differing periods of time at 140°C.

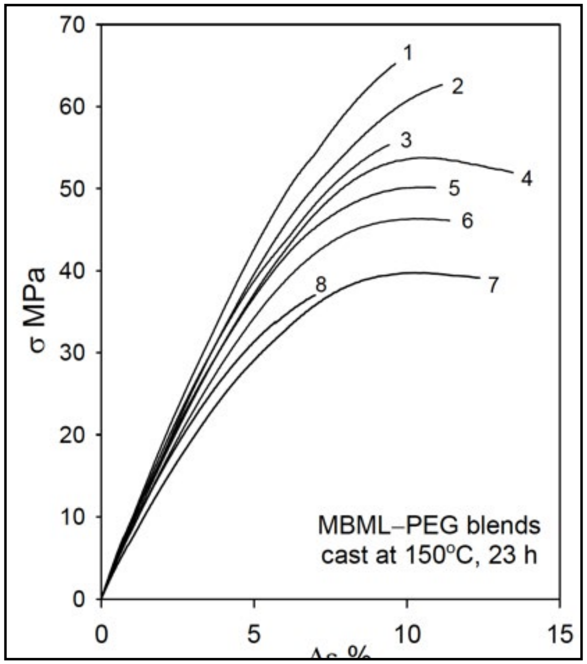


Figure C-CP-1.6. Tensile behavior of methylated ball-milled softwood lignin (MBML) in blends with poly(ethylene glycol) (PEG) and poly(ethylene glycol) methyl ether

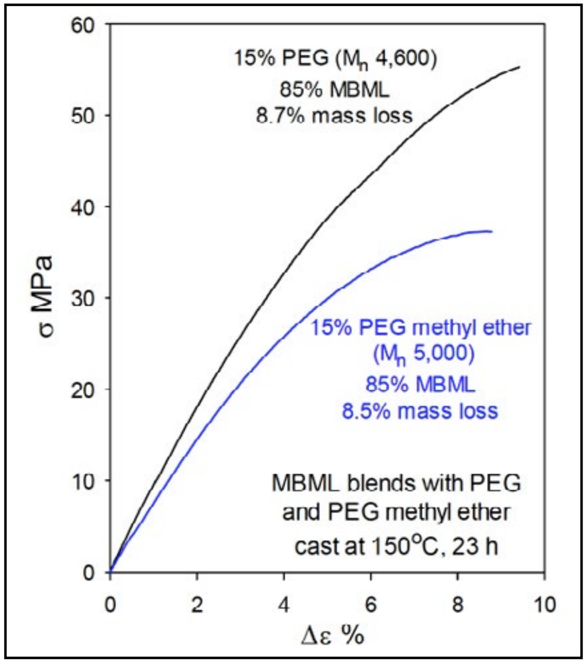


Figure C-CP-1.7. Tensile behavior of methylated ball-milled softwood lignin (MBML) in blends involving poly(ethylene glycol) fractions (PEG) with different molecular weight distributions. [1] 5% PEG (mol. wt. 400); [2] 5% PEG (mw 400), 5 % PEG (mw 10k); [3] 15% PEG (mol. wt. 4.6k); [4] 5% PEG (mw 400), 5% PEG (mw 4.6k); [5] 10% PEG (mw 400); [6] 15 % PEG (mw 2k); [7] 15% PEG (mw 10k); [8] 15 % PEG (mw 35k)

Recommendations | Conclusions

The formulations for methylated ball-milled lignin-based plastics must be further elaborated to achieve 20 – 30% elongations at break without substantially compromising tensile strength. Thereupon, these formulations should be ready for adaptation to NARA co-product lignins.

It is no exaggeration to assert that the foregoing results are the most important to have been reported in the field of lignin-based polymeric materials.

Physical and Intellectual Outputs

CONFERENCE PROCEEDINGS AND ABSTRACTS FROM PROFESSIONAL MEETINGS

"Through Lignin Depolymerase to Native Lignin-based Plastics" by Y.-r. Chen, S. Sarkanen and Y.-Y. Wang, Abstract ID 17515, 247th American Chemical Society National Meeting, Dallas, TX, March 16- 20, 2014.

RESEARCH PRESENTATIONS

Y.-r. Chen, S. Sarkanen, Y.-Y. Wang. Through Lignin Depolymerase to Native Lignin-based Plastics. Oral presentation at 247th American Chemical Society National Meeting, Dallas, TX, March 16-20, 2014.

S. Sarkanen, Y.-r. Chen, Y.-Y. Wang. Formulations for Coproduct Lignin-based Plastics. Oral presentation at NARA Coproducts Team Meeting, Spokane, WA, March 5, 2014.

S. Sarkanen, Y.-r. Chen, Y.-Y. Wang. Formulations for Coproduct Lignin-based Plastics. Oral presentation at NARA Coproducts Team Meeting, Spokane, WA, November 14, 2013.

INTELLECTUAL PROPERTY

Compositions Including Lignin: Chen, Y.-r.; Sarkanen, S.; Wang, Y.-Y. 2014, U.S. Provisional Patent Application No. 61/953,118 filed March, 14.

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

Key Personnel	Affiliation
David Fish	Weyerhauser
Carter Fox	Weyerhauser
Ian Dallmeyer	Weyerhauser

Task Description

Lignin sources for this project will be derived from one or more processes, and from one or more steps in the process, in NARA's conversion process used to supply carbohydrates for fermentation into isobutanol used for fuel production. A key component of the NARA project 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 NARA co-products team. This information is essential to developing suitable end-uses for the various lignins.

At focus are two target products to be produced from the residual lignin: moderately valued activated carbon (AC) with a very high surface area and high value AC for use in supercapacitors and batteries. It was found that with recent EPA requirements, coal-burning facilities must reduce their mercury pollution; consequently, the market for AC designed to clean up flue gas emission has exploded. Our primary goal is to develop an AC that will be effective for mercury clean-up. 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 targeted market is for a sustainable alternative to current materials used in industries where the generation of electricity is variable (wind generators, electric vehicles).
Another more traditional market considered for the lignin sulfonate produced by the mild bisulfite process is use as a viscosity modifier for wet cement.

Activities and Results

The first task was to determine the chemical properties of the hydrolysis residual solids (HRS) and the fermentation residual solids (FRS) from the NARA mild bisulfite (MBS) and wet oxidation (WOX) pretreatment processes. HRS refers to the insoluble material left after wood has undergone pretreatment and enzymatic hydrolysis. FRS refers to the insoluble material remaining after the HRS has been subjected to fermentation. The initial focus is on the FRS materials resulting from processing the NARA FS-10 feedstock since this is the material most representative of what will be used for manufacturing co-products. Table C-CP-2.1 gives the carbohydrate, lignin, and ash contents for the different samples. Washed samples were rinsed three times with deionized water.

Methods have been developed to extract high purity lignin from the FS-10 feedstock, the MBS-FRS, and the WOX-FRS, in order to analyze the effect of the pretreatment methods on lignin chemistry. This analysis is nearly complete, and a full report should be published this year.

The work conducted to date on the development of co-products has focused on the preparation and characterization of powdered activated carbon (PAC) from the FRS obtained from the MBS and WOX pretreatment processes. The goal of this research is to establish conditions by which PAC can be prepared to capture vapor phase mercury from flue gas and for use as electrodes in supercapacitors.

Physical activation with carbon dioxide (CO_2) was selected as the activation process to be studied for producing mercury sorbents. FRS from MBS and WOX were carbonized at different temperatures between 600-1000°C under nitrogen to produce a char. The char was then activated by introducing CO_2 into the furnace. The degree of activation varied according to both the temperature and amount of time that the sample was exposed to CO_2. Figure C-CP-2.1 shows the total yield of AC obtained during activation at 700°C where yield is defined as the weight of carbon remaining after activation for different times ranging from 0-30 minutes (expressed as a percentage of initial oven-dried FRS weight).

Gas physisorption was used to investicate the porous structure of AC samples. Two adsorptives were studied to probe different pore size ranges, namely nitrogen at 77 Kelvin (K) for wide microporosity and mesoporosity characterization and carbon dioxide at 273 K for narrow microporosity characterization. The apparent Brunauer, Emmett and Teller (BET) surface area, pore volume, and pore size distributions were calculated to compare the structures of the different AC samples. Table C-CP-2.2 shows selected data on the porous structure of AC prepared at 700°C. This AC preparation was sent to URS Corporation for vapor phase mercury adsorption evaluation, and their evaluation is being analyzed.

In addition, studies on carbon preparation for supercapacitor electrodes were initiated. Carbons were prepared at 800°C and characterized for their electrochemical properties in tetraethylammonium tetrafluoroborate/propylene carbonate/dimethyl carbonate (TEATFB/PC-DMC) electrolyte system at the laboratory of Professor Guozhong Cao at the University of Washington. Cyclic voltammograms for two cells are shown in Figure C-CP-2.2.

Recommendations | Conclusions

A key discovery from the carbonization and activation work is that the physical activation of the MBS and WOX FRS materials with CO_2 results in different pore size distribution. As can be seen in the bottom two lines of Table C-CP-2.2, the relative amounts of mesoporosity, as a fraction of total pore volume (pores with entrance dimension between 2 – 50 nm) vs. microporosity (pores with entrance dimension less than 2 nm), are higher for MBS carbons, whereas WOX carbons are more microporous at similar degrees of activation. Carbons with more mesoporosity may provide advantages for both of the selected applications (flue gas mercury capture and supercapacitors). For mercury control, larger pore size is needed for rapid transport (gas contact time of 1-2 seconds in a short flue) of mercury to the adsorption sites located in micropores. In supercapacitors, a certain degree of mesoporosity is required to allow rapid ion diffusion during charging and discharging. The importance of balance between meso- and microporosity is already evident as shown in the results obtained in the selected applications, but the appropriate balance for each application is not yet clear. Nevertheless, initial results provide direction for future study.

Using the data obtained from the URS Corporation as a guide, additional samples will be generated to improve the AC's murcury absobance. In addition, other testing partners are being sought to help evaluate the dynamic mercury adsorption capacity as opposed to the equilibrium capacity. So identifying testing parteners has proven difficult; one research group affiliated with ADA-CS, which has developed a new test to evaluate dynamic adsorption of mercury, has been identified. Once the most promising AC samples have been identified, both their equilibrium and dynamic adsorption capacities will be examined.

Initial results from characterizing supercapacitor performance show some very interesting attributes that support our hypothesis that a balance between mesoporosity and microporosity in supercapacitors is important. The shape of the capacitance-voltage (CV) curves in Figure C-CP-2.2 shows that MBS carbons have a more capacitive behavior (indicated by a rectangular CV curve) compared to WOX carbons, which show a more resistive behavior in this initial test. Further testing is required to confirm this observation. It is interesting to note that the WOX carbon has a higher capacitance per unit carbon weight (52.2 F/g for WOX vs. 23.8 F/g for MBS) or volume (54.6 F/cm3 for WOX vs. 32.8 F/cm3), but the apparent BET surface area of the WOX carbon (870 m2/g) is roughly twice that of the MBS carbon (430 m2/g). When capacitance was normalized to apparent BET surface area, the capacitance was similar, albeit still slightly higher in the WOX carbon (0.060 F/m2 vs 0.055 F/m2). This result was expected because micropores act as adsorption sites whereas mesopores act as pathways for ion diffusion, so given sufficient charging time, the total charge storage capacity (energy density) of the WOX carbon should be greater as was observed. However, the advantage of supercapacitors compared to batteries is the power density, or the ability to charge and discharge rapidly without degradation of the cell performance, and the MBS carbon actually showed higher power density (27.5 kW/kg) compared to the WOX carbon (23.4 kW/kg), which hyperthetically, can be attributed to a higher amount of mesoporosity in the MBS carbon.

Given these results, it is recommend that research in both mercury sorbents and capacitor carbons continue as follows:

- For mercury sorbents, it is important to quickly identify an industrial partner or partners to evaluate the technical and economic aspects of scaling up AC production using FRS, because the potential customers (utilities running coal-fired power plants) will require pilot scale evaluation of any AC product proposed for mercury control.
- It is important to determine if the higher production cost (due to lower yield) to increase MBS FRS activationto can be offset by better mercury capture performance. It is assumed that maintaining AC yield above ~30% is desirable, but if a higher activation degree (translating to lower yield) results in a better performing carbon, the higher selling price could justify increasing the activation degree. A higher degree of activation is probably needed to produce a carbon from MBS FRS that performs similar to carbons produced from WOX FRS in mercury capture.
- It is possible that a two-step process, where the FRS is first charred, allowed to cool and then activated in a second step, may offer an alternative way to alter the pore size distribution. Whether this process improves the performance of the carbons in the selected applications is still undertermined. A two step process might also better represent industrial practice, but this point is speculative until an industry partner is identified. The one-step carbonization/activation, used to prepare mercury adsorbents, should be compared to a two-step process in terms of the carbon characteristics and performance. Also, the previously mentioned effect of pre-carbonization and the effect of fermentation on the carbonization characteristics should be studied.
- The supercapacitor work is in initial stages, but the initial results are encouraging even though the tested carbons show only moderate capacitance. Physically activated carbons were tested to establish a baseline electrochemical performance; however, it is known that capacitor carbons are typically much more highly activated, with more stringent purity specifications, compared to mercury sorbents. Published results and previous experiments indicate that chemical activation can dramatically increase the degree of porosity. Published literature has aslo reported that the combination of physical and chemical activation can be used to introduce well-defined mesoporosity into lignocellulosic materials. Additional studies on FRS material activation using different combinations of chemical and physical inputs are recommended.
- The washing conditions used to remove inorganic components on supercapacitor carbons need to be investigated since purity can affect capacitance and cycle life.
- A detailed study should be designed and conducted that covers the range of potential FRS carbon

materials obtained from a combination of physical and chemical activation events and of their electrochemical performance in a variety of different electrolyte systems. Therefore, It would be very interesting to extend our study of capacitor carbons to carbons for batteries and hybrid electrochemical devices.

- Finally, it is known that modifying the surface chemistry of carbons can dramatically alter their electrochemical performance in different types of systems, especially when pseudo-capacitance is introduced, which increase the energy density of supercapacitors and hybrid asymmetric cells. To date, the surface chemistry of the AC obtained from FRS materials has not been studied. It is recommend that the oxygen functionalities on the AC surface be characterized and that methods to dope other types of heteroatoms, (especially nitrogen) into the carbon structure be investigated.

Physical and Intellectual Outputs

Laboratory samples of activated carbon were distributed for outside evaluation.

RESEARCH PRESENTATIONS

Fox, S.C. and D. Fish. Characterization of Lignin from the NARA Project and Conversion to New Products. Oral presentation at the American Chemical Society National Spring Meeting, New Orleans, LA, Apr 11, 2013.

Fox, S.C., S. Cline, and D. Fish. Isolation of Lignin from NARA Hydrolysis Residual Solids. Poster presentation at the NARA Annual Meeting, Corvallis, OR, September 10, 2013.

Dallmeyer, I., C. Fox, and D. Fish. Conversion of NARA Hydrolysis Residuals to Activated Carbons for Mercury Vapor Adsorption. Poster presentation at the NARA Annual Meeting, Corvallis, OR, September 10, 2013.

Casayuran, C., Dallmeyer, J.I., Fish, D. Preparation and Characterization of Porous Carbon Adsorbent Materials from Lignocellulosic Residuals. Poster presentation at the NARA Summer Undergraduate Research Symposium, Pullman, WA, August 2, 2013.

Cline, S., Fox, S.C., Fish, D. Isolation of High Purity Lignin from Bio-Jet Biorefinery Hydrolysis Residue. Poster presentation at the NARA Summer Undergraduate Research Symposium, Pullman, WA, August 2, 2013.

Fox, S.C. and D. Fish. Characterization of Lignin from the NARA Project and Conversion to New Products. Oral presentation at the American Chemical Society National Spring Meeting, New Orleans, LA, Apr 11, 2013.

Fox, S.C. and D. Fish. Isolation and characterization of lignin from co-product streams in biofuel production. Oral presentation at the American Chemical Society National Spring Meeting, Dallas, TX, March 16, 2014.

Table C-CP-2.1. Carbohydrate, lignin and ash content in NARA co-product feedstocks. All values reported as oven dry weight %

		Lignin Analysis			Carbohydrate Analysis				
		Ash Content	Acid-Insol. Lignin	Acid-Sol. Lignin	Glucan	Arabinan	Galactan	Mannan	Xylan
FS-10	Wiley milled*	0.2	32.2	2.7	35.0	1.0	2.6	10.3	5.4
MBS HRS	unwashed	4.5	43.9	6.7	36.5	0.2	0.5	3.1	1.3
MBS FRS	unwashed	8.9	58.4	12.0	15.7	0.1	0.2	2.2	0.7
MBS FRS	washed	4.1	65.3	4.1	21.0	0.1	0.1	2.2	0.5
WOX HRS	unwashed	1.7	53.3	3.9	37.0	0.0	0.1	1.4	1.0
WOX HRS	washed	0.6	56.7	2.5	37.8	0.0	0.1	1.1	1.0
WOX FRS	unwashed	2.0	49.6	3.4	41.9	0.1	0.2	1.1	0.6
WOX FRS	washed	0.5	51.2	2.2	45.4	0.1	0.1	1.0	0.7

Table C-CP-2.2. Porosity characterization data for AC samples prepared at 700°C. (DR = Dubinin-Raduschkevich equation, BET = Brunauer-Emmett-Teller, NLDFT = Nonlocal Density Functional Theory, n/d = not determined

	MBS			WOX		
Activation time (minutes)	5	15	30	5	15	30
Apparent BET surface area (N2 77K, m2/g)	234	314	444	483	581	703
Total pore volume (N2 77K, cm3/g)	n/d	0.18	0.28	0.23	0.28	0.35
DR micropore volume (N2 77K, cm3/g)	0.09	0.13	0.18	0.20	0.24	0.27
DR narrow micropore volume (CO2 273K, cm3/g)	0.20	0.20	0.20	0.22	0.24	0.25
Mesopore volume fraction (NLDFT)	n/d	0.375	0.493	0.215	n/d	0.226
Micropore volume fraction (NLDFT)	n/d	0.625	0.507	0.785	n/d	0.772

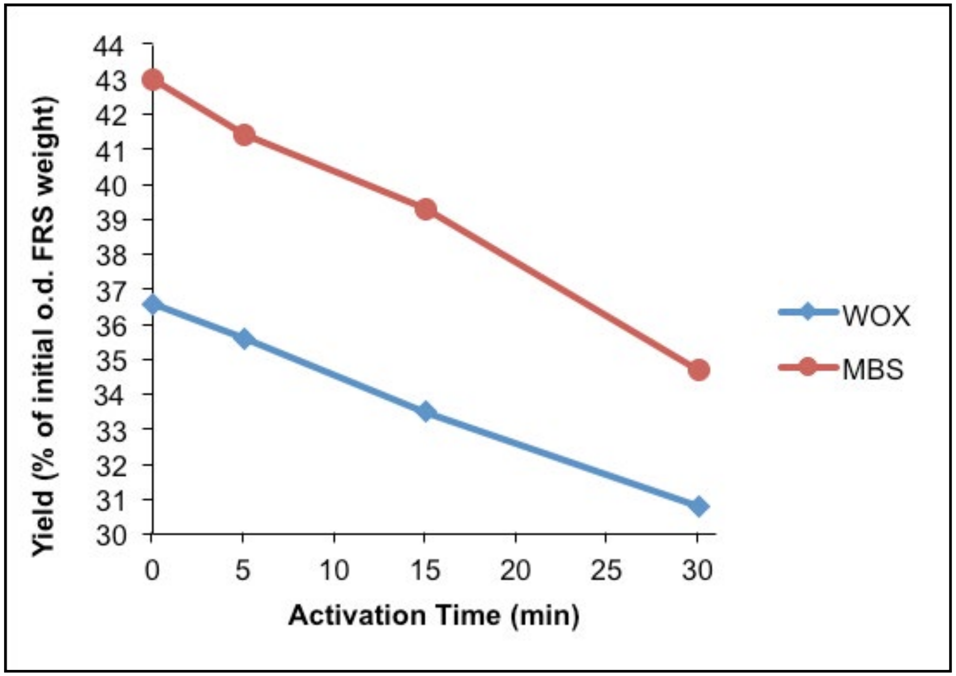


Figure C-CP-2.1. Yield of activated carbon (o.d. FRS basis) as a function of activation time at 700°C

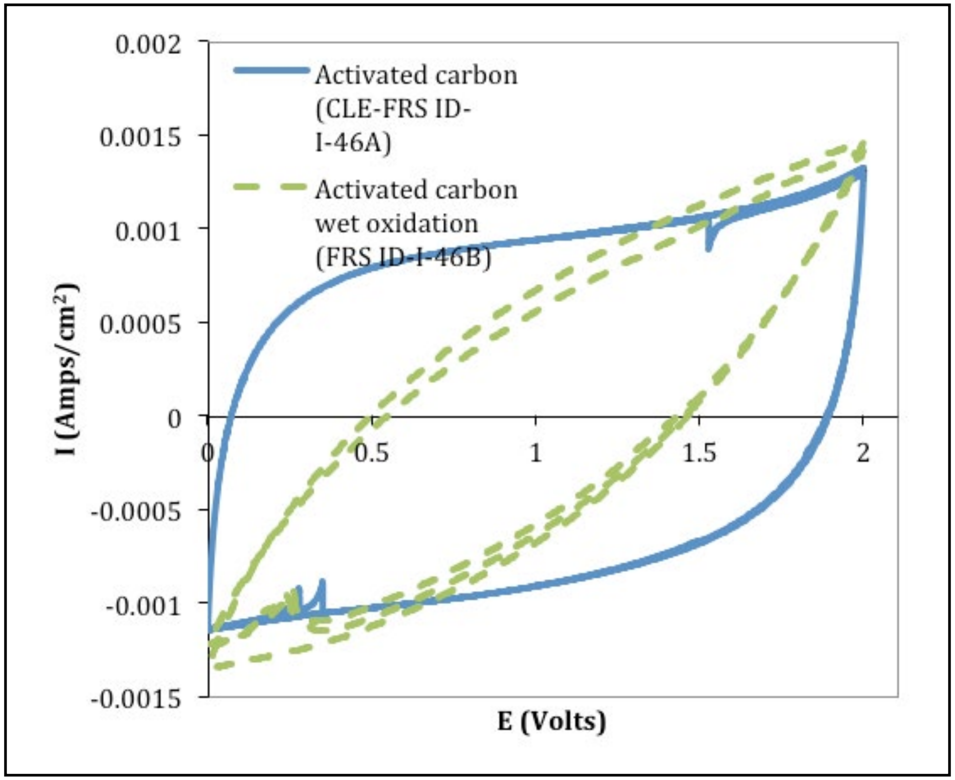


Figure C-CP-2.2. Cyclic voltammograms taken at 10 mV/s of two-electrode cells in TEATFB/PC-DMC using carbons prepared from MBS (blue curve) and WOX (green curve) FRS.

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 produce polymer materials has received extensive investigations from academia and industry. However, neither the direct use of lignin as a 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 associated with lignocellulosic biorefineries, a huge amount of hydrolysis lignin is expected to be available.

Lignin-to-chemical conversion is a highly desirable approach for lignin utilization and could potentially produce many important aromatic chemicals including intermediate monomeric feedstocks. Scientists are exploring various technologies to selectively cleave lignin for use as 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 other chamicals 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 of depolymerization, increasing the use of and adding value to the lignin polymer that nature has already provided is a more attractive option for the chemical industry. In this project, new technologies are proposed 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 hydroxyl access for modification reactions. As previously indicated, to completely disintegrate the lignin structure and use the resulting monomeric chemicals for construction of new polymers is, so 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 the current effort, but it will not be the only application interest in the 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 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. Eugenol was selected as the model compound for epoxy synthesis. 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. In an earlier task, it was demonstrated 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 NARA's first cumulative report. A manuscript has also been submitted recently for publication.

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

First, a thorough review of lignin depolymerization was conducted. Based on the review, two methods were selected for examination: (1) base catalyzed depolymerization (BCD) in supercritical solvent and

(2) hydrogenolysis under catalysis of Raney nickel. To achieve oligomeric compounds rather than the more commonly targeted monomeric compounds, cracking methods were examined 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. The resulting PDL will be converted to building block chemicals, which are to used to synthesize various potential engineering polymers. 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, the application of PDL-based epoxies in an underexplored but increasingly important product, i.e., epoxy asphalt, will be explored. To this application, the designs of PDL-based epoxies and curing agents will be customized to meet the specific requirements for asphalt application, formulation and preparation of the epoxy asphalt. 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) to explore the application development using the lignin-derived polymers.

Activities and Results

Task C-CP-3.1 has been successfully accomplished. If eugenol or similarly lignin-derived chemicals can be obtained with high purity and reasonable cost, quality alternative epoxies can be made. Nonetheless, such a lignin-to-chemical technology is not likely any time soon.

Task C-CP-3.2 is currently ongoing. Two depolymerization methods, base catalyzed depolymerization (BCD) and hydrogenolysis under mild conditions, proved to be successful in partially depolymerizing lignin. Besides kraft lignin, NARA lignin was also partially depolymerized by BCD. As shown in Table C-CP-3.1, three NARA lignins derived from different pretreatments were partially depolymerized at different temperatures using 1N NaOH solution. The highest achieved yield of partially depolymerized lignin (PDL) was ~80% at 200 °C. The hydroxyl value of PDL was greatly improved. Compared to the other two lignins, NARA dilute acid (DA) lignin showed higher yield and hydroxyl value.

Hydrogenolysis under mild conditions proved to be a more effective method to achieve PDL and resulted in high yield. Partial hydrogenolysis of lignin samples derived from dilute acid (DA), mild bisulfite (labeled as CLE (A) and CLE (B)) and wet oxidation (WO) pretreated wood residual biomass were investigated. All the hydrogenation reactions were conducted under the catalysis of Raney Ni at mild conditions in a 3% NaOH solution in dioxane/H_2O (1/1, v/v). Reaction temperature effects on conversion yield was fully studied as shown in Figure C-CP-3.1. The PDL yield increased continuously with temperature from 120 to 180 °C. For the reaction performed at 180 °C, the yield of conversion was 70 ~ 82%; however, the yield decreased to ~70% when the temperature was further increased to. The decrease in yield at 200 ºC was likely due to the formation of more monomeric chemicals at high temperature which remained soluble in the mixture of dioxane/H_2O after lignin was precipitated. Lignin hydroxyl groups can be categorized into three groups, aliphatic, aromatic and carboxylic. The calculated hydroxyl values for all four depolymerized lignin samples are summarized in Table C-CP-3.2. With hydrogenolysis temperature increasing from 160 to 180 ºC, the hydroxyl value of the resulting products increased continuously. The increase was mainly seen in the aromatic hydroxyls, which suggests that the cleavage of ether bonds in lignin occurred effectively. This process was essentially due to the cleavage of α- and β-O-4 bonds which was predominant during the hydrogenation in the alkaline medium and produced para-OH-Ø and guaiacyl.

PDL solubility in organic solvent is very important for modifications like acetylation, methylolation, glyoxalation, epoxidization, etc. The dissolutions of NARA DA lignin before and after hydrogenolysis at 180 ºC in tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), pyridine and 3% NaOH dioxane/H_2O were compared. In Figure C-CP 3.2a, the original lignin in all the solvents selected apparently accumulated to the center of the halomarks (upper row), suggesting insolubility. On the contrary, the hydrogenolyzed lignin in all four solvents left well diffused halomarks, indicating the lignin was soluble, or at least was finely dispersed, in the solvents. After overnight incubation, the mixtures of the original lignin in all four solvents apparently stratified (Figure C-CP 3.2); in contrast, the hydrogenolyzed lignin still appeared as a stable solution.

The resulting PDL was converted into glycidyl ether type epoxies (PDL-epoxy). PDL-epoxy was prepared using PDL directly reacted with epichlorohydrin. This proved to be a highly efficient method because it avoided using propylene oxide as a chain extender. Two biobased anhydrides: dipentene-maleic anhydride (DPMA) and tung-maleic anhydride (TMA) were used for curing agents. Two kinds of PDLs, based on different batches (DA and CLE (62A)) of NARA lignins, were chosen to prepare the PDL-epoxy. The resins based on PDL exhibited some promising results. The mechanical and physical properties of the cured epoxy resins are shown in Figure C-CP-3.2. PDL-epoxies cured with TMA showed higher Tgs than those cured with DPMA; PDL-epoxy based on CLE (62A) demonstrated better mechanical properties. In general, further work on cured resin properties could be explored.

Meanwhile, preliminary experiments on modifying lignin in solid state, i.e., performing the reaction in ball mill, has been performed. At this point, only esterification modification via transesterification has been studied. Our aim is to introduce fatty chain moieties to the lignin structure so that the modified lignin will exhibit improved compatibility as a major blending component with various thermoplastics. Both fatty acid methyl esters and soybean oil were used as the acylating agents. The results indicate that the hydroxyl value of lignin decreased after the reaction and that fatty chains were introduced to the lignin structure as verified by FTIR and NMR experiments. The results suggest that this solid reaction approach presents an important viable method for lignin modifications. Currently, blending the esterified lignin with polylactic acid (PLA) and other biodegradable polyesters is in process. In the future, the reaction in ball mill will be expanded to partial depolymerization, oxidation and various other modification reactions.

Work on Task C-CP-3.3 has not begun.

Recommendations | Conclusions

In summary, two depolymerization methods, BCD and hydrogenolysis, partially depolymerize NARA lignin effectively. The BCD method produced a PDL with more hydroxyl value and high yield, especially for NARA DA lignin, but this method used a higher NaOH concentration and higher reaction temperature than the hydrogenolysis method. Partial hydrogenolysis of NARA lignins successfully performed under the catalysis of Raney Ni in lower NaOH solution concentration under mild conditions. The hydrogenolysis of NARA DA gave a higher yield but lower hydroxyl value for the resulting PDL compared to the hydrogenolysis of NARA WO. The PDL prepared by hydrogenolysis exhibited good solubility/dispersability in THF, dioxane, pyridine and 3% NaOH solution. Good solubility/dispersibility in organic solvent is very helpful for further modifications to NARA lignin like epoxidation, ammoxidation or oxidation which convert lignin into effective building blocks used for engineering polymers.

In addition, lignin-based epoxy was developed by directly reacting PDL with epichlorohydrin. PDL-epoxies cured with biobased curing agents (DPMA and TMA) displayed better mechanical and physical properties. Traditional diglycidyl ether of bisphenol A (DGEBA) type epoxies are prepared by using excessive epichlorohydrin as the solvent for the reaction. However, this is not applicable to the synthesis of PDL-based epoxies because epichlorohydrin could not dissolve PDL. Therefore, the epoxies obtained did not have high enough epoxy values, resulting in insufficient mechanical performance for the cured resins. More work will be made to investigate synthesis of PDL-based epoxies, such as using solvent or finely ground DPL for improving reaction efficiency.

The exploration of reacting lignin in solid state is highly attractive and promising. It eliminates the need for solvent and heating during the reaction. This approach will likely result in some breakthrough in lignin reaction technology and make lignin-based polymer materials viable.

Physical and Intellectual Outputs

Refereed Publications (accepted or completed)

Qin, J., H. Liu, P. Zhang, M.P. Wolcott and J. Zhang. 2013. Use of eugenol and rosin as feedstock for biobased epoxy resins and study of curing and performance properties, Polymer International, DOI: 10.1002/pi.4588

Qin, J., M. Wolcott and J. Zhang. 2014. Use of polycarboxylic acid derived from partially depolymerized lignin as curing agent for epoxy application, ACS Sustainable Chemistry & Engineering, DOI: dx.doi.org/10.1021/sc400227v. 2(2):188-193.

Xin, J., P. Zhang, M.P. Wolcott, X. Zhang, and J. Zhang. 2014. Partial depolymerization of enzymolysis lignin via mild hydrogenolysis over Raney Nickel. Bioresource Technology. DOI: http://dx.doi.org/10.1016/j.biortech.2013.12.092.

CONFERENCE PROCEEDINGS AND ABSTRACTS FROM PROFESSIONAL MEETINGS

Jinwen Zhang. Diversifying Biobased Polymers and Expanding the Window of Properties via Manipulating the Structures of Building Blocks, 2013 First International Biobased Macromolecule Material Forum, Nov 13 – 14, 2013, NingBo, China

Jinwen Zhang. Improving the performance of biobased polymers via manipulating the structures of building blocks, the 13th International Symposium on Bioplastics, Biocomposites and Biorefining, May 19 – 24, 2014, Guelph, Ontario, Canada.

RESEARCH PRESENTATIONS

Xin, J., J. Qin, D. Leong, M. Wolcott, and J. Zhang. Exploration of lignin partial depolymerization and development of polymer materials applications. Poster presentation at the NARA Annual Meeting, Corvallis, OR, September 10, 2013.

Leong, D., J. Xin and J. Zhang. Partial Depolymerization of Lignin Using Hydrogenolysis over Raney Nickel. Poster presentation at the NARA Summer Undergraduate Research Symposium, August 2, 2013, Pullman WA.

Table C-CP-3.1. Depolymerized lignins by BCD

Samples	Hydrogenolysis Temp.	Yield (%)	OH value (mmol/g)
DA	175 °C	87.8	-
	200 °C	88.8	4.4
	250 °C	75.4	-
CLE (A)	175 °C	66.8	-
	200 °C	80.8	3.8
	250 °C	55.2	-
WO	175 °C	88.0	-
	200 °C	86.0	4.1
	250 °C	61.0	-

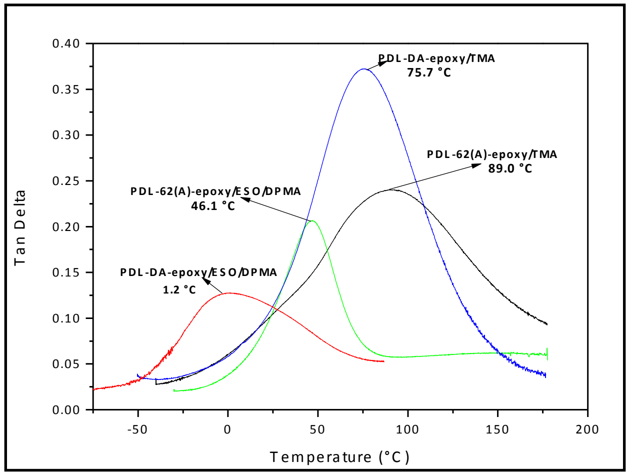


Figure C-CP-3.2. Tan Ŏ versus temperature for PDL-epoxy cured with DPMA and TMA

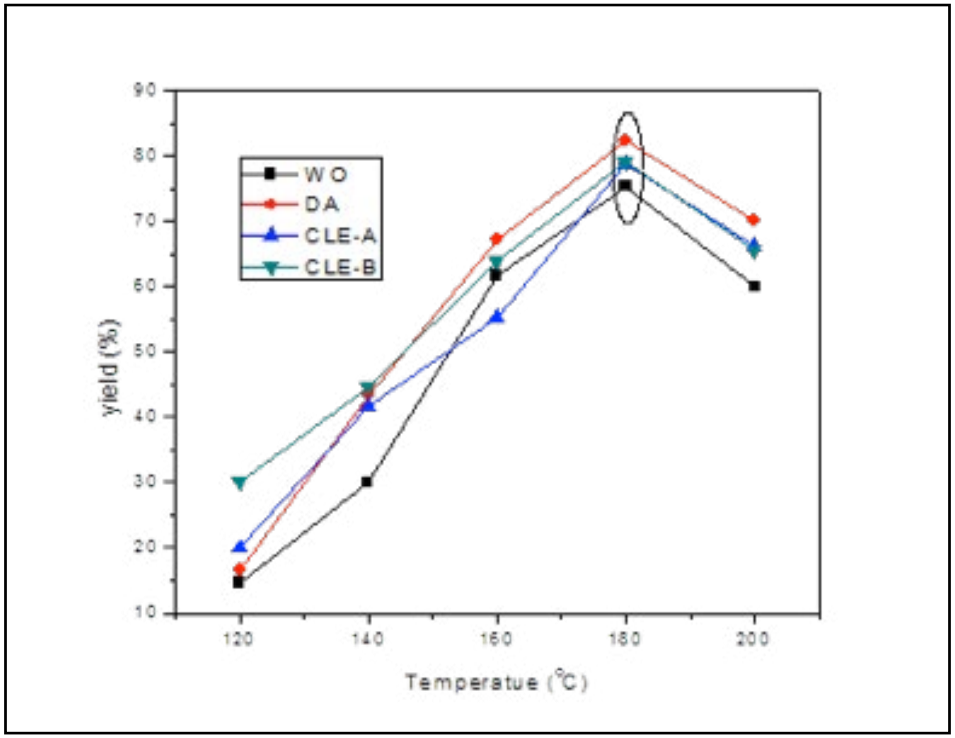
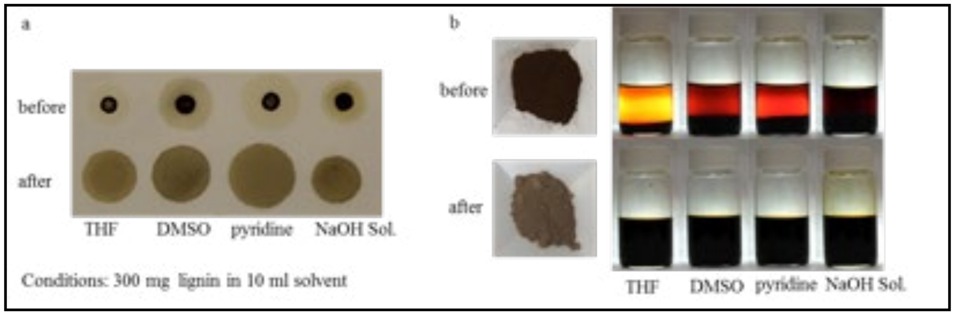


Figure C-CP-3.1.Effects of temperature on yield of hydrogenation of NARA lignin



Conditions: 300 mg lignin in 10 ml solvent

Figure C-CP-3.3. Comparisons of solubility of lignins between before (a) and after hydrogenolysis (b)

Table C-CP-3.2. 31P NMR results of hydroxyl values of depolymerized lignins hydrogenolyzed at different temperatures

Lignins	Temp.	Aliphatic OH (mmol/g)	Aromatic OH (mmol/g)	Carboxylic acid OH (mmol/g)	Total
DA	160 °C	0.81	2.40	0.37	3.58
	180 °C	0.71	2.68	0.44	3.83
CLE (A)	160 °C	0.63	2.72	0.54	3.89
	180 °C	0.56	3.02	0.42	4.00
CLE (B)	160 °C	0.80	2.76	0.32	3.88
	180 °C	0.78	3.10	0.43	4.31
WO	160 °C	1.00	2.83	0.60	4.22
	180 °C	0.93	3.08	0.67	4.68

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

Task C-P-2.1: Lignin product development

During this project period, a new pathway (Figure C-P-2.1) to selectively covert biorefinery lignin into dicarboxylic acids (DCA), including muconic, maleic, and succinic acids is reported. These DCAs are highly valuable industrial chemicals and platform intermediates used in many areas including biopolymer, pharmaceutical, and food additives industries [1]. The detailed findings for this pathway are published in February issue of ChemSusChem, DOI: 10.1002/cssc.201300964. Further investigation of the reaction mechanism has elucidated that the conversion of biorefinery lignin to DCA is a two-step reaction process (Figure C-P-2.2) involving 1) lignin depolymerization to monolignols and 2) aromatic ring cleavage to DCA. As a result, the low molecular weight aromatic compounds (LMWAC) and DCA are expected to reach their optimal yield under different reaction conditions. InnovaTek has been asked to design and test a two-step reaction system to maximize the selectivity for each step to reach a high DCA yield.

It is well recognized that economic feasibility is a key component to a successful biorefinery operation. In addition to experimental work, a techno-economic analysis (TEA) model, to specifically evaluate the lignin to DCAs conversion unit, has been initiated. SuperPro software will be used in this task. SuperPro integrates both process and economic analyses and has the strength to identify specific economic bottleneck(s) in the process. A SuperPro based process model will be delveloped with updated research results along the project's progress inputted. This information will help evaluate progress and will help identify areas for conversion improvement.

[1] a) S. Y. Lee, S. H. Hong, S. H. Lee, S. J. Park, Macromol Biosci 2004, 4, 157-164; b) K. Sato, M. Aoki, R. Noyori, Science 1998, 281, 1646-1647; c) M. Dugal, G. Sankar, R. Raja, J. M. Thomas, Angew Chem Int Edit 2000, 39, 2310-2313; d) H. Yu, F. Peng, J. Tan, X. W. Hu, H. J. Wang, J. A. Yang, W. X. Zheng, Angew Chem Int Edit 2011, 50, 3978-3982.

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

In this project year, it was discovered that alkaline peroxide pretreatment (AHP) on Douglas-fir can convert softwood hemicellulose to valuable organic acids, such as lactic acid and succinic acid (Figure C-P-2.3). Applying AHP on NARA feedstock samples FS-01 and FS-10 to produce fermentable sugar has been evaluated and a draft manuscript was prepared. Forest residuals typically contain a high amount of inorganic substances, the effects of metal ions on carbohydrate degradation was investigated using Avicel, beech xylan and konjac glucomannan as model substrates. As shown in Figure C-P-2.4, the addition of a metal ion in a 5mM concentration can significantly increase the carbohydrate conversion to organic acids by more than two fold. This initial finding is encouraging and suggests AHP may be suitable for forest residual pretreatment since the presence of inorganic substances can potentially improve hemicellulose conversion yield. The potential mechanism of metal ion-promoted carbohydrate conversion to organic acids is being investigated.

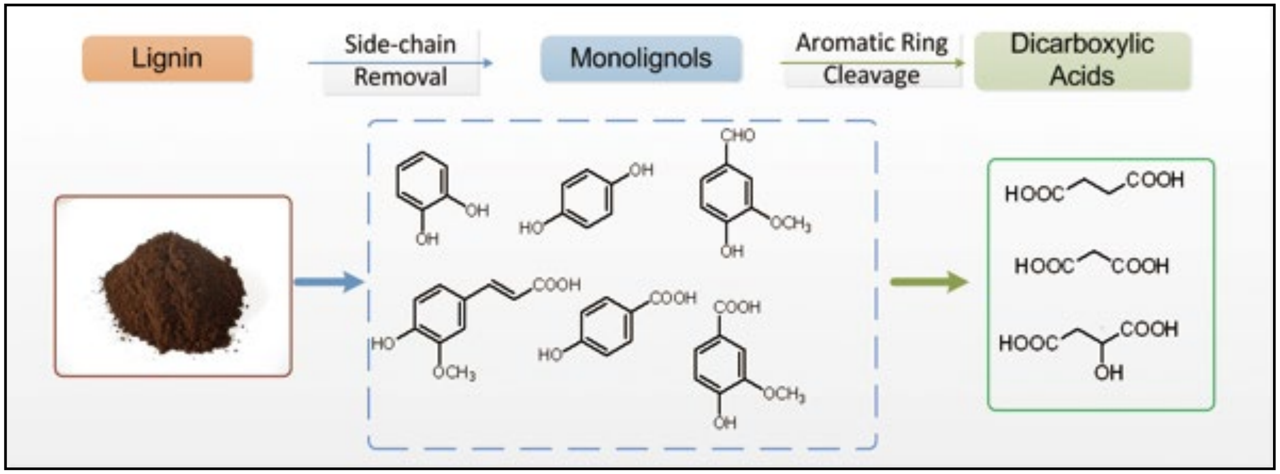


Figure CP-2.1. A new pathway to conversion lignin to diacarboxylic acid (Ma et al, ChemSusChem 7:412, 2014).

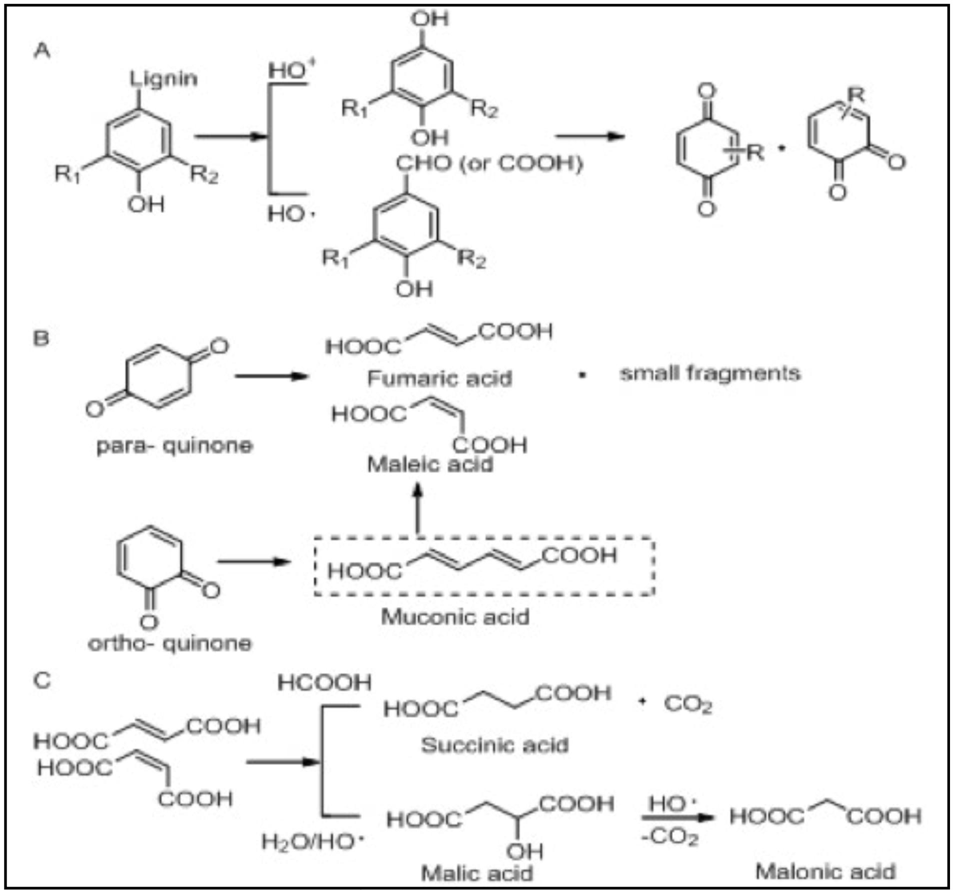


Figure CP-2.2. Proposed mechanisms for (A) lignin depolymerization and aromatic nuclei oxidation; (B) aromatic ring cleavage; and (C) formation of final products.

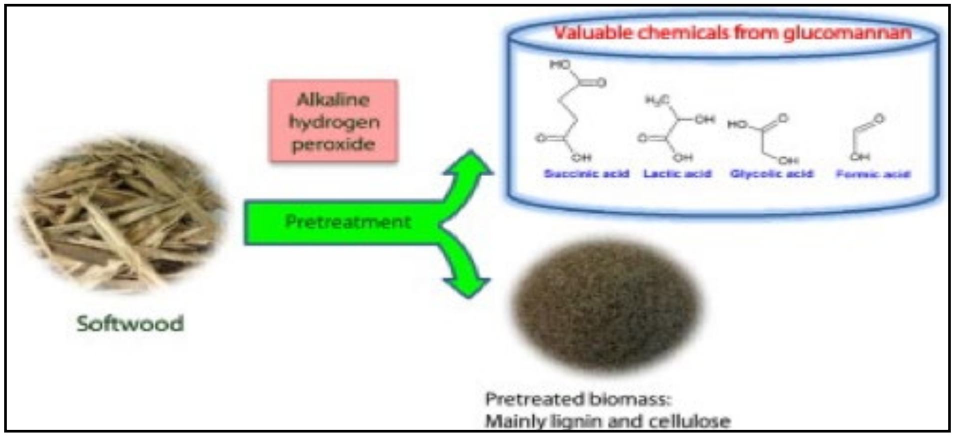
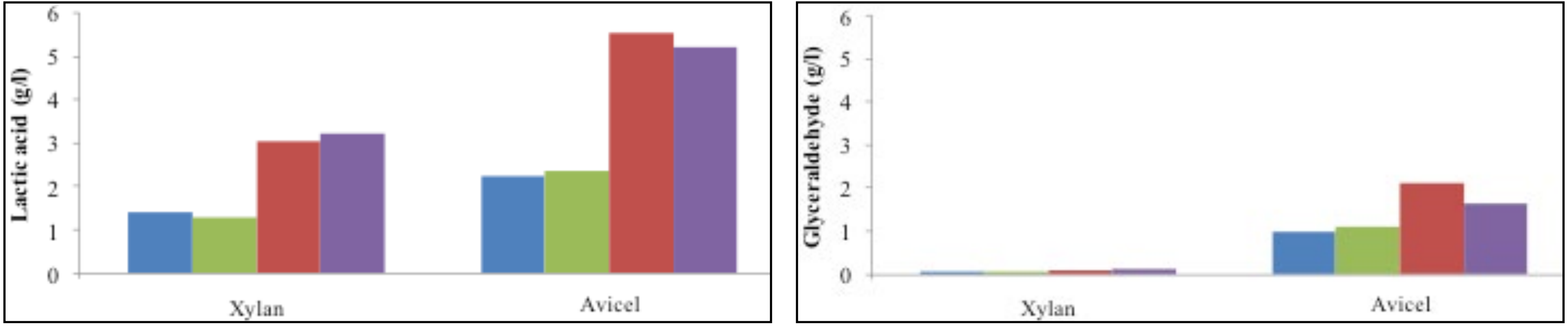
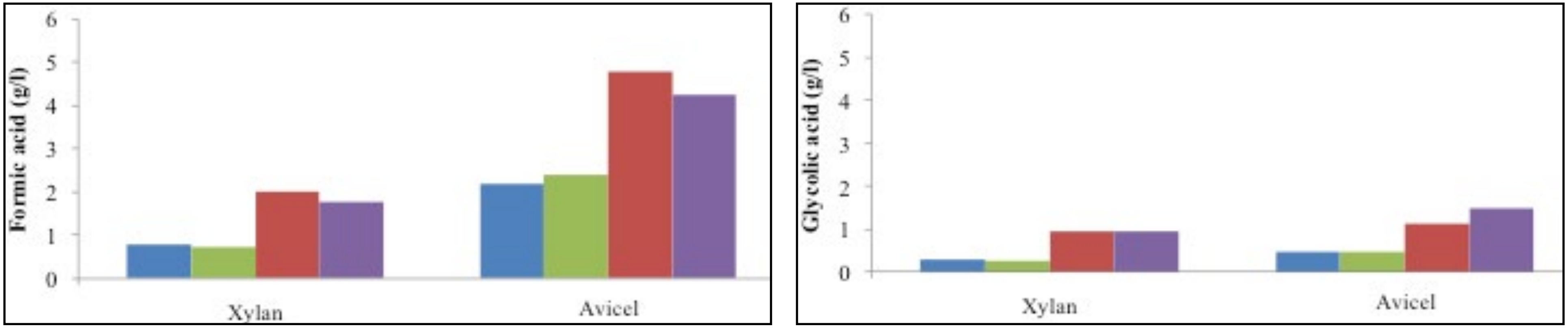


Figure CP-2.3. Conversion of hemicelluloses to organic acids during alkaline hydrogen peroxide pretreatment (Alaverze et al, Bioresource Technology, 150: 321, 2013).


A) Lactic Acid

A) Glyceraldehyde


B) Formic Acid

A) Glycolic Acid

Figure CP-2.4. Concentrations of sugar and decomposition products in water soluble fractions (WSF) during AHP pretreatment of Avicel and beechwood xylan at pH=11.6 and T=180°C.

Recommendations | Conclusions

Lignin-to-DCA conversion presents a new concept and opens a new pathway for lignin utilization. This new technology has attracted significant interest from several industrial companies including Solvay Chemicals, Agrivida, Optafuel, InnovaTek, PNNL etc. This research effort will lead to a significant impact on lignin product development. A close collaboration with these industrial partners will be established to evaluate and develop this technology toward commercial application.

Physical and Intellectual Outputs

REFEREED PUBLICATIONS (ACCEPTED OR COMPLETED)

Alvarez Vasco, C., Zhang, X. 2013. Alkaline hydrogen peroxide pretreatment of softwood: Hemicellulose degradation pathways, Bioresource Technology, 150C: 321-327.

Ma, R.S., Guo, M., Zhang, X., Selective conversion of biorefinery lignin to dicarboxylic acids, ChemSusChem, 7(2) 412-415.

RESEARCH PRESENTATIONS

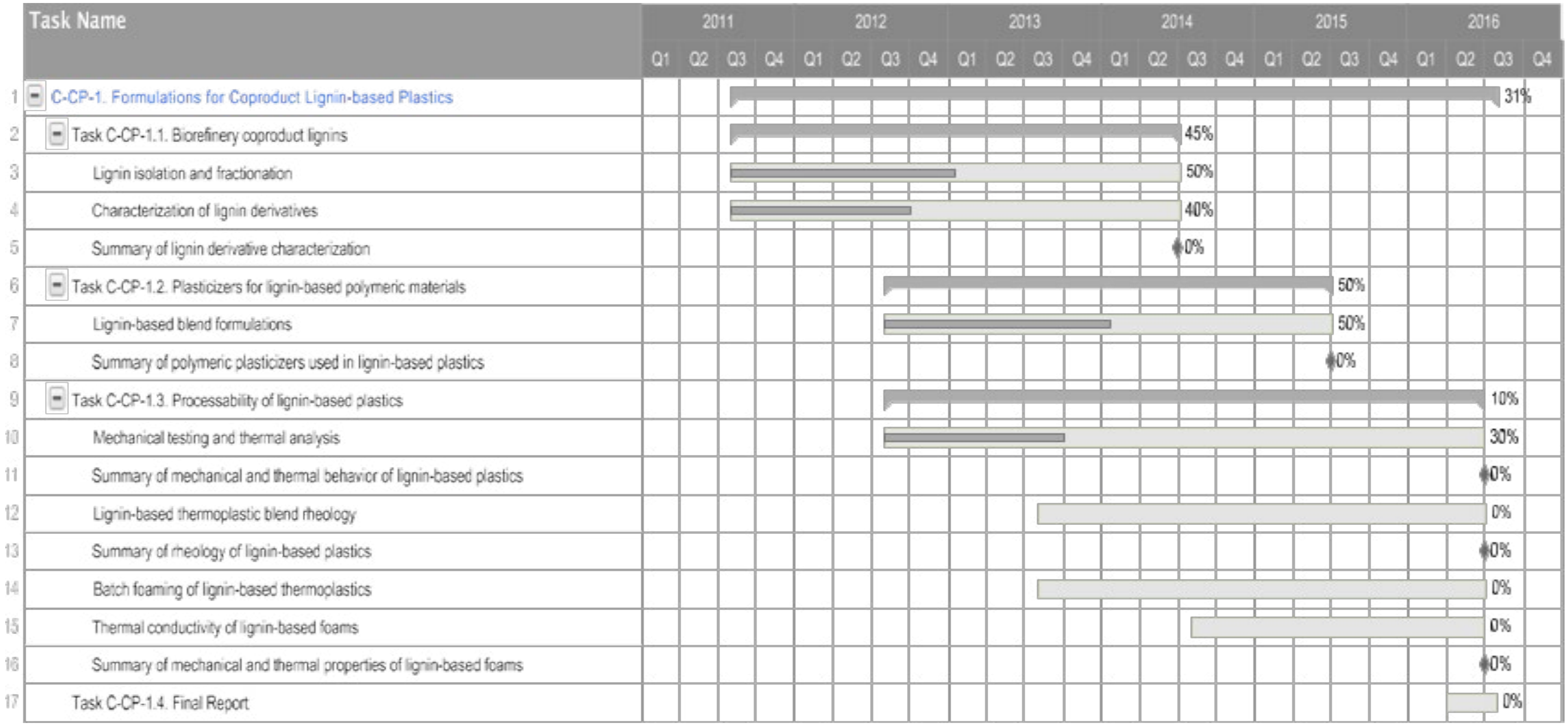
Alvarez Vasco, C., Potential of AHP to maximize hemicellulose and cellulose conversion to Fuels and Chemicals, WSU Showcase, Pullman, WA.
Ma, Ruoshui, "Selective conversion of biorefinery lignin to dicarboxylic acids" oral presentation at 2013 AICHE annual conference, San Francisco, CA, Oct. 7, 2013.

Alvarez Vasco, C., "Alkaline hydrogen peroxide pretreatment of softwood: Hemicellulose degradation pathways" at 2013 AICHE annual conference, San Francisco, CA, Oct. 8, 2013.

INTELLECTUAL PROPERTY

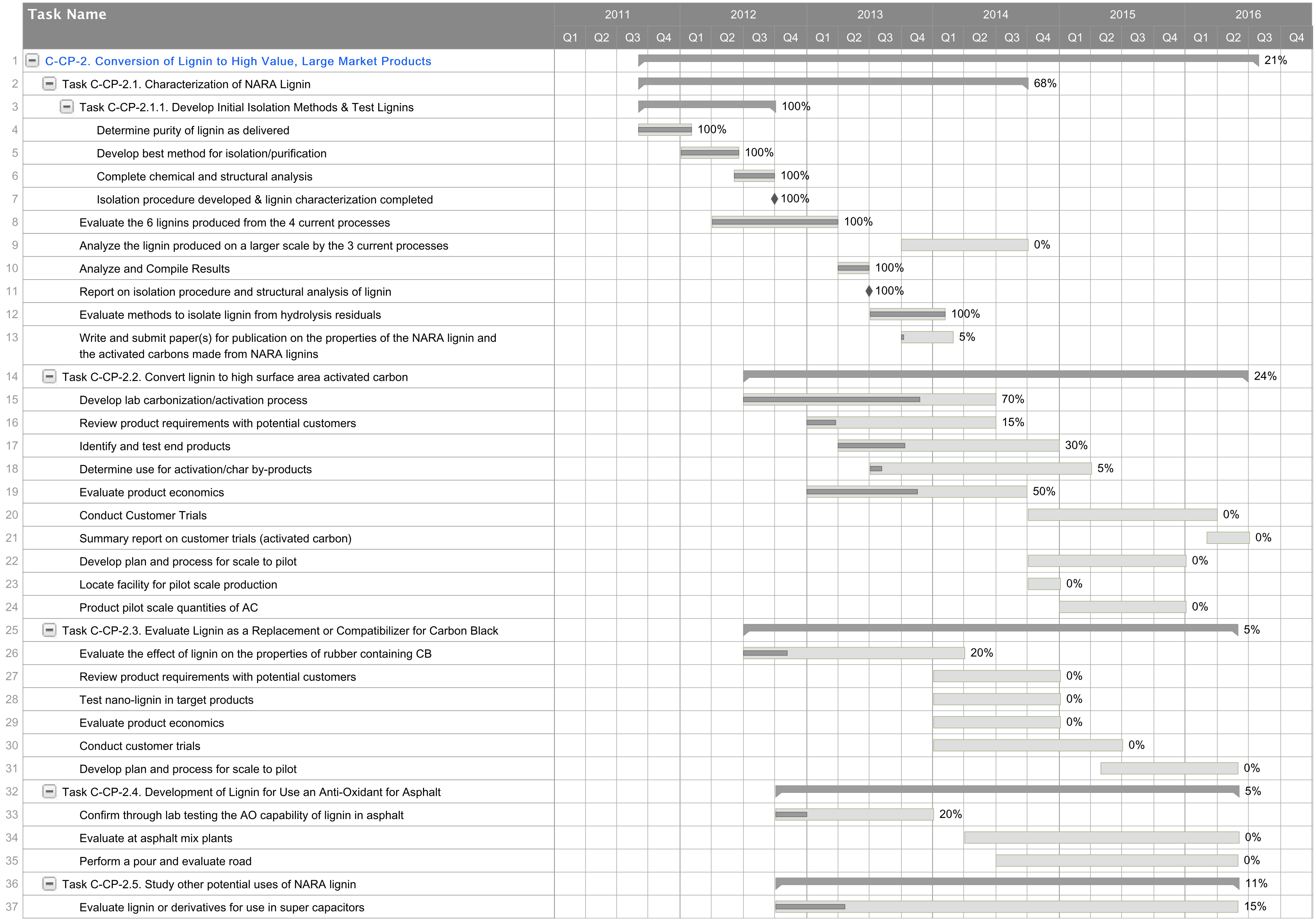
US patent application: Zhang, X. METHODS TO CONVERT LIGNIN TO PHENOLIC AND CARBOXYLATE COMPOUNDS, US-842432-01-US-PCT. 2013

Conversion-CP_Sarkanen



	Task Name	
1	C-CP-1. Formulations for Coproduct Lignin-based Plastics	31%
2	Task C-CP-1.1. Biorefinery coproduct lignins	45%
3	Lignin isolation and fractionation	50%
4	Characterization of lignin derivatives	40%
5	Summary of lignin derivative characterization	0%
6	Task C-CP-1.2. Plasticizers for lignin-based polymeric materials	50%
7	Lignin-based blend formulations	50%
8	Summary of polymeric plasticizers used in lignin-based plastics	0%
9	Task C-CP-1.3. Processability of lignin-based plastics	10%
10	Mechanical testing and thermal analysis	30%
11	Summary of mechanical and thermal behavior of lignin-based plastics	0%
12	Lignin-based thermoplastic blend rheology	0%
13	Summary of rheology of lignin-based plastics	0%
14	Batch foaming of lignin-based thermoplastics	0%
15	Thermal conductivity of lignin-based foams	0%
16	Summary of mechanical and thermal properties of lignin-based foams	0%
17	Task C-CP-1.4. Final Report	0%

Conversion-CP_Fish



	Task Name	%
1	C-CP-2. Conversion of Lignin to High Value, Large Market Products	21%
2	Task C-CP-2.1. Characterization of NARA Lignin	68%
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 the lignin produced on a larger scale by the 3 current processes	0%
10	Analyze and Compile Results	100%
11	Report on isolation procedure and structural analysis of lignin	♦ 100%
12	Evaluate methods to isolate lignin from hydrolysis residuals	100%
13	Write and submit paper(s) for publication on the properties of the NARA lignin and the activated carbons made from NARA lignins	5%
14	Task C-CP-2.2. Convert lignin to high surface area activated carbon	24%
15	Develop lab carbonization/activation process	70%
16	Review product requirements with potential customers	15%
17	Identify and test end products	30%
18	Determine use for activation/char by-products	5%
19	Evaluate product economics	50%
20	Conduct Customer Trials	0%
21	Summary report on customer trials (activated carbon)	0%
22	Develop plan and process for scale to pilot	0%
23	Locate facility for pilot scale production	0%
24	Product pilot scale quantities of AC	0%
25	Task C-CP-2.3. Evaluate Lignin as a Replacement or Compatibilizer for Carbon Black	5%
26	Evaluate the effect of lignin on the properties of rubber containing CB	20%
27	Review product requirements with potential customers	0%
28	Test nano-lignin in target products	0%
29	Evaluate product economics	0%
30	Conduct customer trials	0%
31	Develop plan and process for scale to pilot	0%
32	Task C-CP-2.4. Development of Lignin for Use an Anti-Oxidant for Asphalt	5%
33	Confirm through lab testing the AO capability of lignin in asphalt	20%
34	Evaluate at asphalt mix plants	0%
35	Perform a pour and evaluate road	0%
36	Task C-CP-2.5. Study other potential uses of NARA lignin	11%
37	Evaluate lignin or derivatives for use in super capacitors	15%

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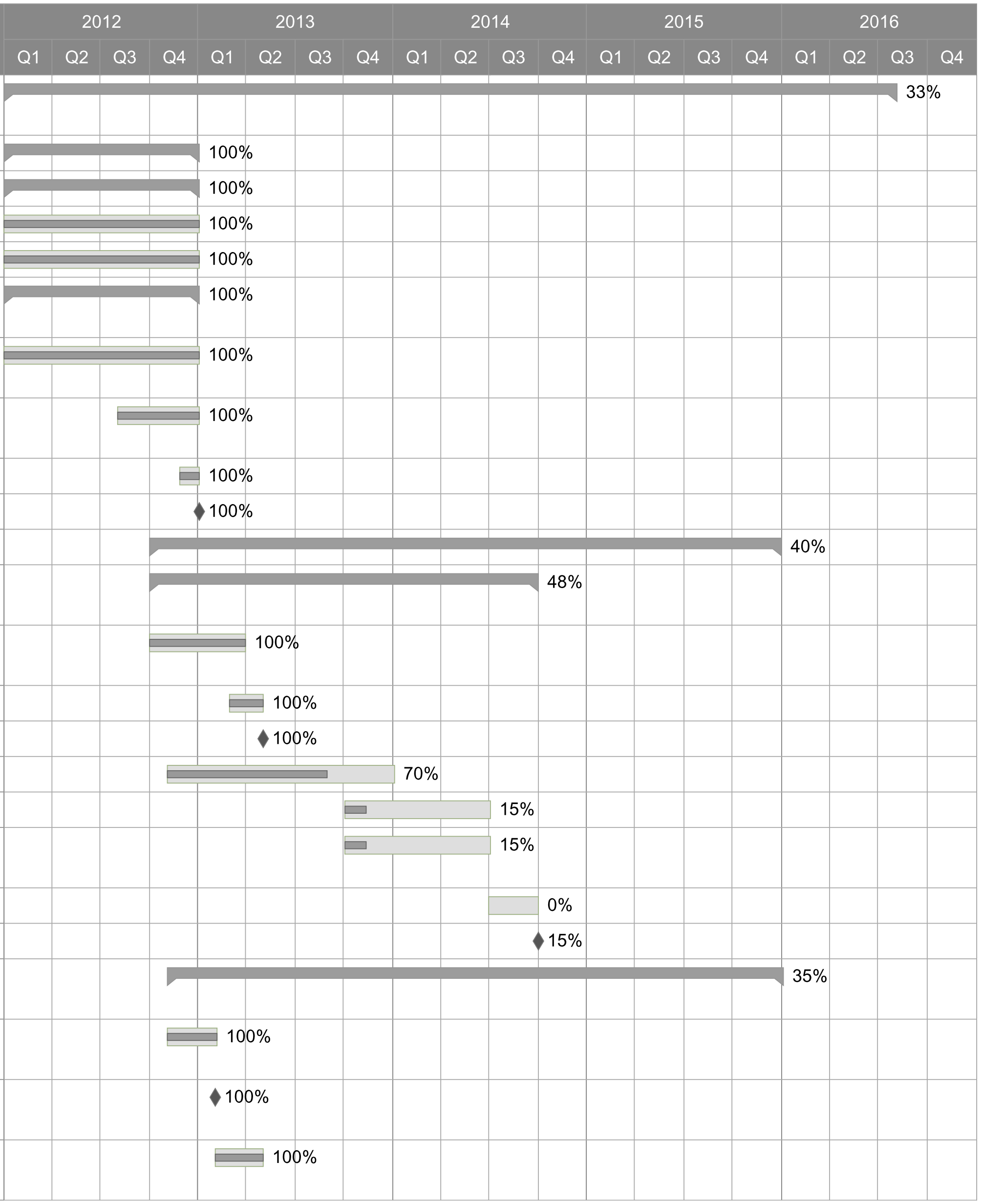
Page 1 of 2

	Task Name
38	Evaluate lignin as a pre-cursor for carbon black
39	Task C-CP-2.6. Evaluate effects of NARA spent sulfite liquor on fresh cement properties
40	Task C-CP-2.7. Write Final Report

Conversion-CP_Zhang_Wolcott

	Task Name	%
1	C-CP-3. Novel Engineering Polymers from Lignin-Derived Building Blocks	33%
2	Task C-CP-3.1. Preparation of epoxies using lignomers	100%
3	Task C-CP-3.1.1 Investigate synthesis method leading to high yield of epoxy	100%
4	Explore the synthesis methods of epoxies using the lignomer analogs	100%
5	Prepare epoxies using lignomers	100%
6	Task C-CP-3.1.2 Study curing-structure-property relationship of the resulting epoxies	100%
7	Investigate and optimize curing conditions including curing temperature, steps, time; and catalyst	100%
8	Study curing kinetics of the prepared epoxies including comparison with commercial products	100%
9	Report on lignomer derived expoxy	100%
10	Viability of synthesis methods of lignomer derived epoxies assessed	100%
11	Task C-CP-3.2. Development of partially depolymerized lignin (PDL) epoxies	40%
12	Task C-CP-3.2.1. Preparation of epoxies and curing agents from lignin fragments	48%
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	70%
17	Develop synthesis methods for PDL derived epoxy and curing agent	15%
18	Characterize curing behavior and physical performance of DPL derived materials	15%
19	Report PDL epoxy development and performance	0%
20	**Viability of PDL epoxy determined**	15%
21	Task C-CP-3.2.2. Explore deploymerization of lignin and preparation epoxies and curing agents using partially depolymerized lignin (PDL)	35%
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%



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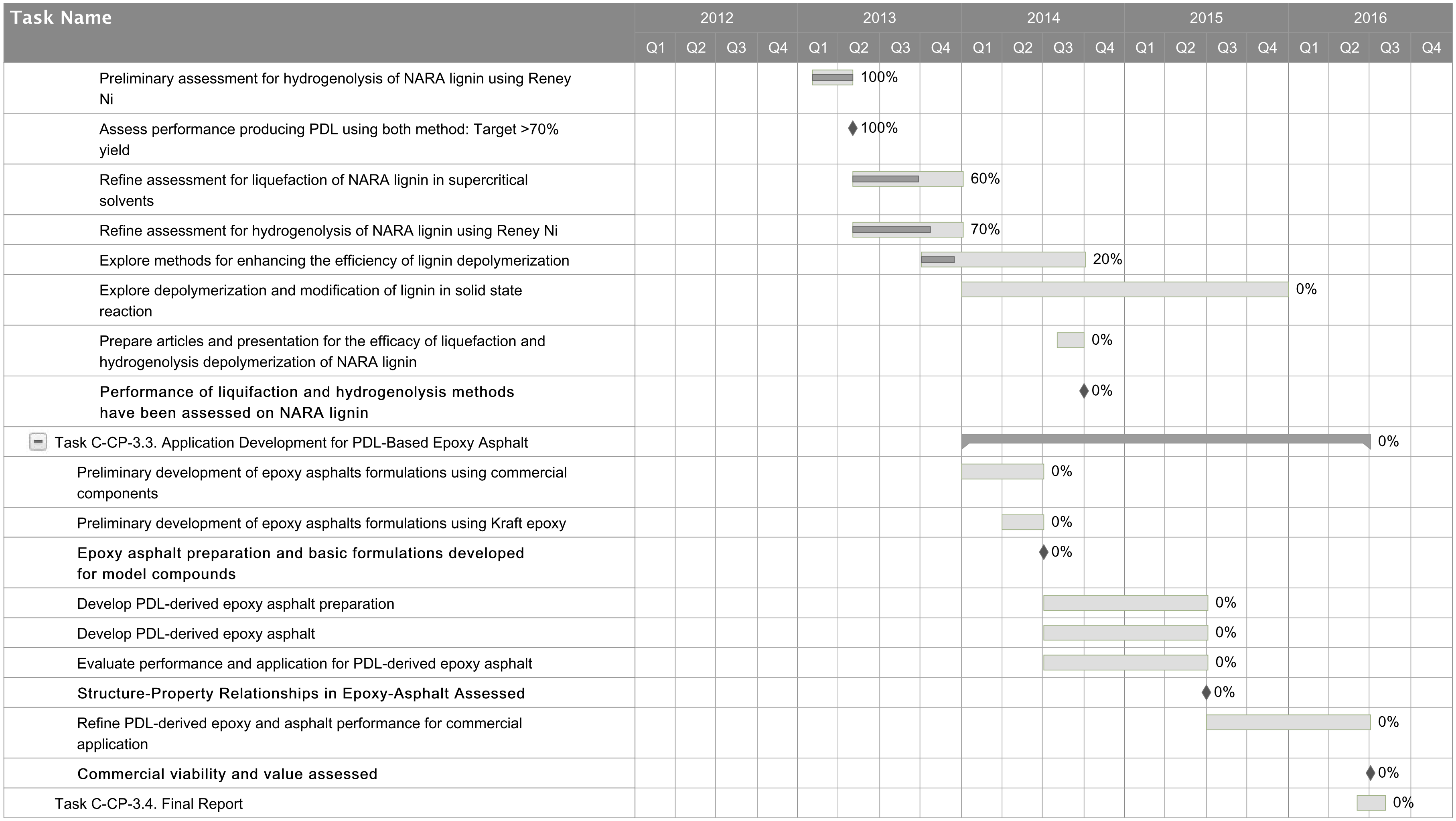
Page 1 of 2



	Task Name	% Complete
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	60%
28	Refine assessment for hydrogenolysis of NARA lignin using Reney Ni	70%
29	Explore methods for enhancing the efficiency of lignin depolymerization	20%
30	Explore depolymerization and modification of lignin in solid state reaction	0%
31	Prepare articles and presentation for the efficacy of liquefaction and hydrogenolysis depolymerization of NARA lignin	0%
32	**Performance of liquifaction and hydrogenolysis methods have been assessed on NARA lignin**	0%
33	⊟ Task C-CP-3.3. Application Development for PDL-Based Epoxy Asphalt	0%
34	Preliminary development of epoxy asphalts formulations using commercial components	0%
35	Preliminary development of epoxy asphalts formulations using Kraft epoxy	0%
36	**Epoxy asphalt preparation and basic formulations developed for model compounds**	0%
37	Develop PDL-derived epoxy asphalt preparation	0%
38	Develop PDL-derived epoxy asphalt	0%
39	Evaluate performance and application for PDL-derived epoxy asphalt	0%
40	**Structure-Property Relationships in Epoxy-Asphalt Assessed**	0%
41	Refine PDL-derived epoxy and asphalt performance for commercial application	0%
42	**Commercial viability and value assessed**	0%
43	Task C-CP-3.4. Final Report	0%

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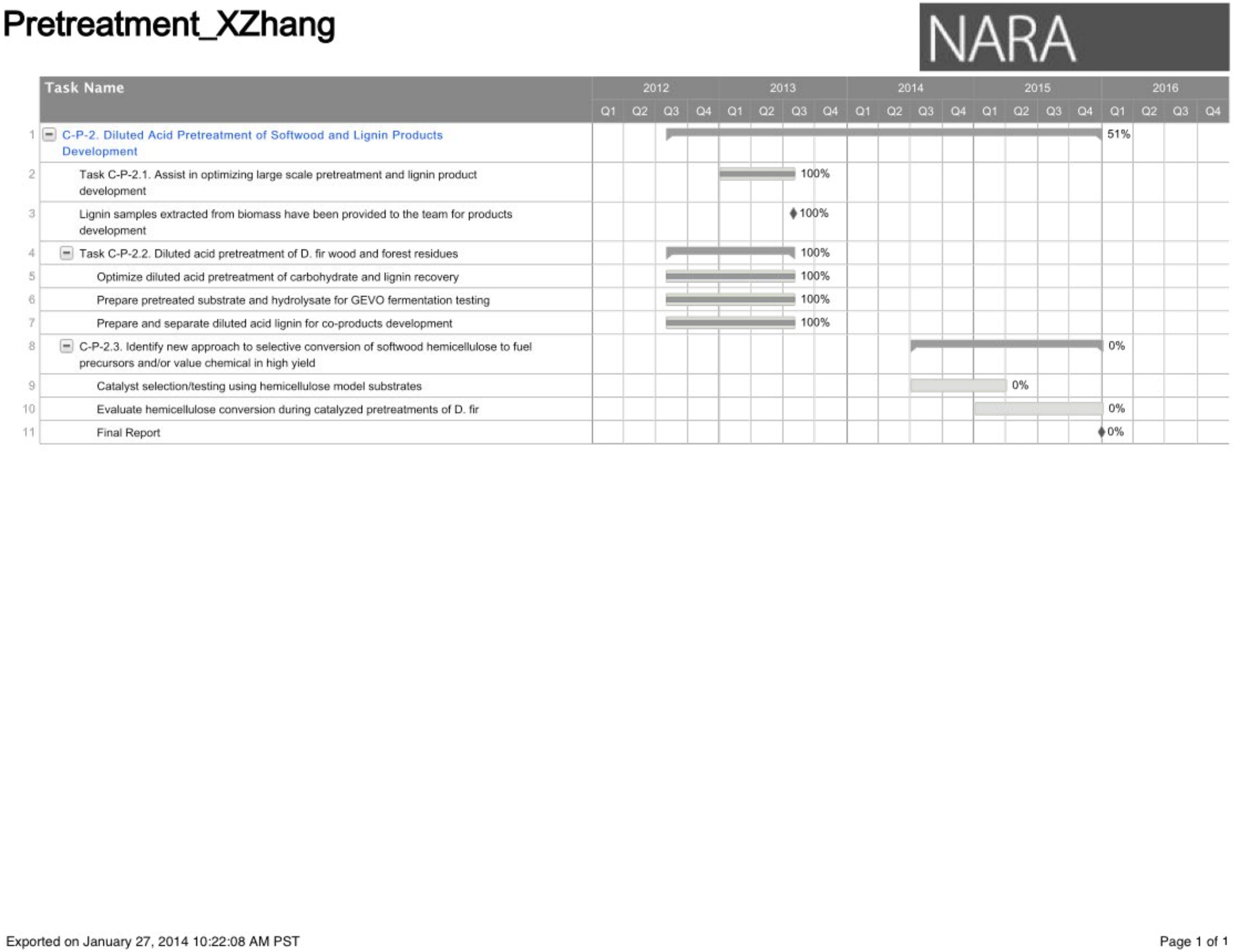
Page 2 of 2



Pretreatment_XZhang

	Task Name	
1	C-P-2. Diluted Acid Pretreatment of Softwood and Lignin Products Development	51%
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	C-P-2.3. Identify new approach to selective conversion of softwood hemicellulose to fuel precursors and/or value chemical in high yield	0%
9	Catalyst selection/testing using hemicellulose model substrates	0%
10	Evaluate hemicellulose conversion during catalyzed pretreatments of D. fir	0%
11	Final Report	◆0%

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Page 1 of 1