NARA | GOAL TWO

August 2011 - March 2013 Cumulative Report

VALUE-ADDED POLYMER
AND CARBON PRODUCTS FROM LIGNIN

Northwest Advance Renewables Alliance

NARA is led by Washington State University and supported by the Agriculture and Food Research Initiative Competitive Grant no. 2011-68005-30416 from the USDA National Institute of Food and Agriculture.

Goal Two: 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.

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 (Table 1; Task C-CP-2 each task progress is detailed in progress reports following this summary). The most common strategy for dealing with these residual solids is to recover their fuel value to assist in powering the plant. While this strategy remains as a potential, NARA researchers are developing new lignin-based products that provide a higher value than current commercial lignin use. Creating high-value products from the lignin-rich byproduct is essential to establishing a value-chain to improve profitability of the bio-refinery.

To meet this challenge, NARA's co-product residual research has progressed on multiple fronts. First, hydrolysis residuals were collected from the four pretreatment processes (SPORL, mild bisulfite (CLE), wet oxidation, and dilute acid), and evaluated for the lignin, carbohydrate and ash contents (Table 1; Task C-CP-2). Three methods were developed to isolate the lignin from spent sulfite liquors (SSL) — amine extraction, ultra-filtration, and calcium precipitation — and the lignin molecular weight was determined. (Table 2; Task C-CP-2)

Two promising applications are currently targeted for near-term use of the hydrolysis residuals. First, we are developing lignin-based activated carbon with a very high surface area. Laboratory procedures were developed to produce activated carbons (AC) with different surface areas and different types of porosity from hydrolysis residuals. The second application is for use as a viscosity modifier for concrete. Initial analyses have been completed for other applications include modifying the hydrolysis residuals to serve as a replacement for carbon black and use as an anti-oxidant for asphalt binder for roads. (Task C-CP-2)

A more long-term directive is to evaluate the use of co-product residuals as a component in bioplastics. The domestic U.S. market for foamed commodity thermoplastics is projected to reach 4 billion kg in 2013. Unfortunately, our initial attempts to form bioplastics using the lignin-rich solids generated from pretreated material were unsuccessful. An alternative approach is to use ball milled softwood lignin, which is a relatively purified lignin source. Using this feedstock, which is not produced in our process, miscible polymer blends were produced of methylated ball-milled softwood lignins (MBMLs) at 85% (w/w) levels with low-T_g polymers. This approach has led to formulations for materials that approach 70 MPa in tensile strength. Ongoing work has introduced a wide range of *block*-copolymers with lignins of varied molecular weights to explore blends that lead to commercially valuable bioplastics. Successful approaches here will be transferred later to NARA lignin samples. (C-CP-1)

Our final lignin effort is aimed at partially depolymerizing the high molecular weight and recalcitrant form of lignin that results from the enzymatic hydrolysis process. The goal of producing partially depolymerized lignin (DPL) is to create building blocks for engineering high value polymers. In route to this approach, naturally occurring lignomers were evaluated for their use in epoxy. Eugenol was converted to an epoxy depolymerization. The partially depolymerized lignin was evaluated as a curing agent for epoxies. A third protocol, phenolation liquefaction, has been applied to hydrolysis lignin with the intent to generate lignin-based polyurethanes and phenolics. (C-CP-3)

Significant internal outputs to date for this team are listed below. Additional outputs are listed at the end of each progress report.

- Analysis shows that the lignin produced from the various pretreatments and post hydrolysis is significantly different from the traditional Kraft and sulfite lignin currently in the marketplace. The NARA lignins derived from various pretreatment protocols exhibit unique characteristics. Although analysis is ongoing, these unique lignin types present an exciting opportunity for use as feedstocks to generate novel lignin-based products with high potential economic return (Table 1; Task C-CP-2).

- A high porosity activated carbon can be made from NARA fermentation residual lignin. The techno-economic analysis of NARA activated carbon (AC) indicates a positive potential for this material. Using a conventional steam activation method, it predicts that the cost of producing AC will be $0.57/lb, including a transfer price of $0.145/lb to the iso-paraffinic kerosene (IPK) plant. Given an activated carbon selling price of $0.75/lb for mercury-emissions-control-grade and given a total capital cost estimated at $168,000,000, the internal rate of return (IRR) is calculated to be 22.5%. Furthermore, the market for such a grade is growing rapidly and would consume a major portion of the output of hydrolyzed residues from the IPK plant. CLE-HydR-derived carbon samples had significant elemental mercury adsorption capacities as shown in the Table 3. Task C-CP-3). The mercury adsorption capacity values were 95 and 88% of the adsorption capacity measured for a commercial standard carbon used for mercury adsorption, Norit Darco-Hg. The most significant result was that the carbonized/washed CLE-HydR materials were capable of performing nearly as well as the commercial carbon and the KOH-activated carbon without any physical or chemical activation, which may significantly reduce the cost of activated carbon production compared to competing products (Task C-CP-2).

- Lignin separated from the spent sulfite liquor of the SPORL and CLE (Mild Bisulfite) pretreatment methods display excellent concrete dispersion properties. Initial results show a two-fold increase in effectiveness over commercially available dispersants (Table 3; Task C-CP-2).

- Formulations for lignin-based thermoplastics have been achieved with suitable block copolymers when using model lignin compounds (Figures 1-3, Task C-CP-1).

- Experimental results validated our hypothesis that partially depolymerized lignin (PDL) with good solubility and dispersion characteristics can be converted into effective building blocks for engineering polymers (Task C-CP-3).

Outcomes/Impacts

Events that cause a change of knowledge, actions or conditions for stakeholders and society.

- None to report

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	Eugenol –derived epoxies, developing BCD methods, developing lignin epoxies and curing agent
Junna Xin	WSU, CMEC	Post-doc	Developing hydrogenolysis method
Kun Huang	WSU, CMEC	Visiting Student	developing lignin epoxies and curing agent
Jinwu Wang	WSU, CMEC	Research Asst Professor	Investigating potential resin applications

Resource Leveraging

None to report

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 annually 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-T_g 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-T_g 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 the conversion of 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.

At the time of writing, 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 content. 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.

Task C-CP-1.1 Biorefinery coproduct lignins

This project is dedicated to developing reliable means for converting biorefinery lignins into homogeneous thermoplastic polymer blends with mechanical properties similar to those of polystyrene. The co-product lignins isolated as a result of pretreating softwoods for saccharification purposes need to be purified, fractionated and derivatized prior to blending with low-T_g polymers to produce plastics. The most appropriate candidates in the present context are those formed as a result of bisulfite or dilute-acid pretreatment. It is essential that any samples to be investigated for thermoplastic formulation development be polymeric rather than oligomeric. A reference point has been created for comparing the raw materials from any particular lignocellulosic source upon which different lignin-based plastics are to be based. Accordingly, three contrasting lignin preparations have been methylated to develop blend formulations for next-generation lignin-based plastics. The lignin derivatives included a Jack-pine native ball-milled lignin, a high (>10 k) molecular weight fraction from a commercially available ligninsulfonate, and a Douglas fir lignin sample alkali-extracted after dilute-acid pretreatment and cellulase-catalyzed saccharification of steam-exploded wood.

Task C-CP-1.2 Plasticizers for lignin-based polymeric materials

In this study, the most promising formulations will be converted into foams capable of acting as efficient insulation materials. 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. For this purpose, all three kinds of methylated lignin derivatives will be plasticized with miscible low-T_g polymers analogous to those previously employed.

This information is potentially proprietary and has been omitted. Please contact members of the NARA Executive Committee for further information.

Task C-CP-1.3 Processability of lignin-based plastics

We have carried out mechanical testing and thermal analysis of several lignin-based thermoplastic blends. As described in Task Progress, the mechanical properties of the thermoplastics that have been produced are extremely promising. As far as thermoplastic processability is concerned, strain-hardening is considered to be an important feature, especially in regard to reducing foam density. The extensional viscosimetric behavior of each series of methylated lignin-based blends will be examined as a function of low-T_g plasticizing polymer content between 0 and 35% (w/w). These studies will be focused on how strain-hardening varies with the relative strengths of the intermolecular interactions between the blend components. It is anticipated that strain-hardening will be enhanced when these interactions are stronger: the associated lignin complexes are partially dismantled under such circumstances so that there should be a greater incidence of chain entanglement between the peripheral components in the huge supramacromolecular assemblies that make up these materials. To the best of our knowledge, this would be the first time that any extensional viscosimetric studies are carried out with lignin-based polymer melts.

Most commercial foams are produced through continuous extrusion processes. Nevertheless, batch processing offers several advantages. It requires only small quantities of material and allows operating conditions such as temperature and pressure to be more flexibly controlled. For example, the saturation pressure and temperature affect the amount of blowing agent dissolved in the polymer matrix and hence these parameters influence the nucleation rate. The growth of nucleated cells is affected by the viscosimetric behavior of the polymer matrix, which in turn can be modulated by the temperature of the foaming medium. In this connection, specimens of precise composition and processing history can be prepared and tested with high reproducibility.

Task Progress

Activities and Results

In its first chapter, the present research project has sought to determine what goals should be set for improvements in the mechanical properties of next-generation lignin-based plastics. In this context, miscible blends of methylated ball-milled softwood lignins (MBMLs) at 85% (w/w) levels with low-T_g polymers have led to formulations for materials that approach 70 MPa in tensile strength. Few polymeric materials in common use can exceed such lignin-based plastics in engineering stress, and thus the frontier of next-generation applications for co-product lignins has been reached.

This information is potentially proprietary and has been omitted. Please contact members of the NARA Executive Committee for further information.

The impact of the lower molecular weight methylated components in these materials can be seen through comparisons between the blends of the parent MBML and higher molecular weight lignin fraction that contain 15 – 20% EBE. Absence of the lower molecular weight lignin components in these blends clearly results in lower tensile strength and greater brittleness. Yet, the respective blends of the parent MBML and higher molecular weight fraction with 25 – 30% (w/w) EBE exhibit very similar tensile behavior (Figure 1) because the predominant lignin species in these materials are associated complexes rather than individual molecular components.

This information is potentially proprietary and has been omitted. Please contact members of the NARA Executive Committee for further information.

For comparative purposes, the effects of low-T_g polyesters as blend components in MBML-based plastics were also investigated. Thus, in Figure 3 the consequences of 15% (w/w) levels of poly(ε-caprolactone) (PCL) are compared with those of somewhat higher (25 – 30% (w/w)) proportions of poly(butylene adipate) (PBA), poly(ethylene succinate) (PES) and poly(trimethylene succinate) (PTMS). Remarkably, 15% PCL contents in these materials result in tensile behavior not far removed from that observed with MBML-based blends containing 15% EBE (Figure 1). This is noteworthy because PCL at these levels is not fully miscible with MBML. On the other hand, 30% (w/w) PBA is similar to 25% EBE in its impact on MBML blends. In contrast, 30% (w/w) PES and PTMS produce MBML-based plastics with lower ductility and tensile strength than observed with the corresponding amount of PBA.

This information is potentially proprietary and has been omitted. Please contact members of the NARA Executive Committee for further information. Concomitantly, it should be possible to approach these goals fairly closely through appropriate formulations with homopolymers in binary or ternary blends.

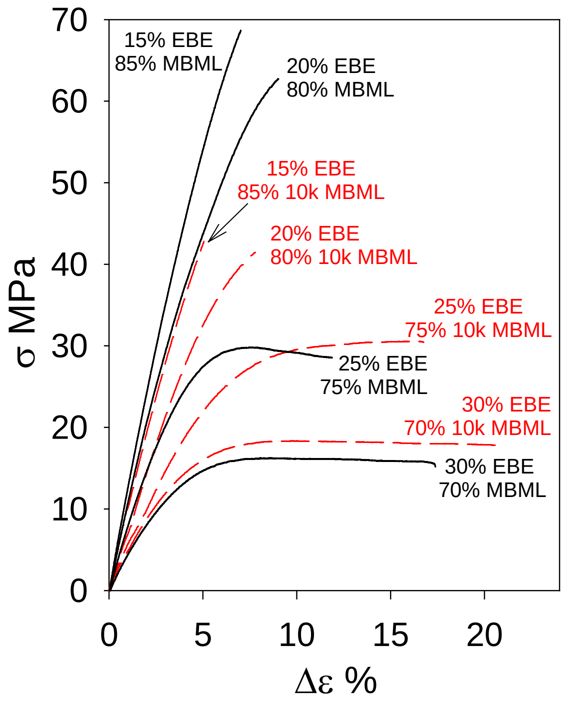

Figure 1. This information is potentially proprietary and has been omitted. Please contact members of the NARA Executive Committee for further information. The 10k MBML in the higher molecular weight lignin-based blends was prepared by extensive ultrafiltration prior to methylation through a 10,000 nominal molecular weight cutoff membrane in aqueous 0.1 M NaOH. (Stress-strain curves were determined with an

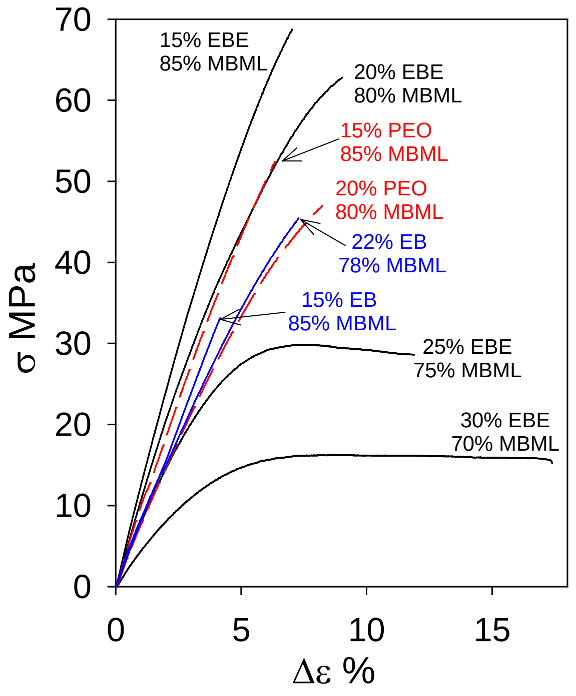

Figure 2. Tensile behavior of parent methylated ball-milled softwood lignin (MBML) in blends with poly(ethylene oxide) (PEO), This information is potentially proprietary and has been omitted. Please contact members of the NARA Executive Committee for further information.

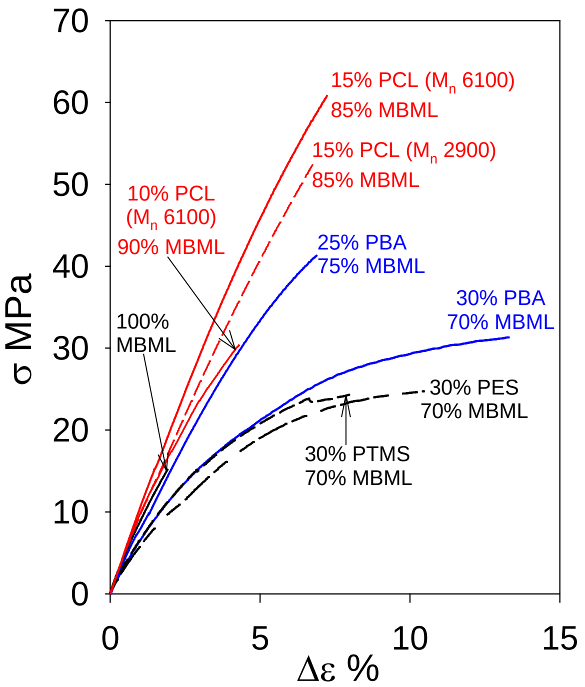

Figure 3. Tensile behavior of parent methylated ball-milled softwood lignin (MBML) in blends with poly(ε-caprolactone) (PCL), poly(butylene adipate) (PBA), poly(ethylene succinate) (PES) and poly(trimethylene succinate) (PTMS).

Recommendations/Conclusions

The methylated ball-milled softwood lignin-based polymeric materials created for reference purposes have confirmed that the kinds of lignin derivatives produced from future biorefineries should be amenable to the development of useful next-generation lignin-based plastics. The tensile properties of the methylated native lignin-based blends with the [This information is potentially proprietary and has been omitted. Please contact members of the NARA Executive Committee for further information.], the PEO homopolymer and the PCL homopolyester are striking in their similarity. Accordingly, there is little doubt that simple softwood lignin derivatives are valuable starting materials for producing renewable biodegradable plastics. A search for new miscible blend components has been initiated to develop native-lignin-based material formulations that are more ductile without incurring reduced strength properties. Routes to the best possible binary and ternary homopolymer formulations will be investigated in attempts to replicate the properties of the most promising MBML-based blends with [This information is potentially proprietary and has been omitted. Please contact members of the NARA Executive Committee for further information.]. Such new plastics will serve as a foundation for developing analogous formulations for NARA co-product dilute-acid lignins and ligninsulfonates.

Physical and Intellectual Outputs

Research Presentations

S.Sarkanen, Y.-r. Chen, Y.-Y. Wang. Formulations for Coproduct Lignin-based Plastics. Oral presentation at NARA Coproducts Team Meeting, Spokane, WA, August 22, 2012.

Y.-Y. Wang, S.Sarkanen, Y.-r. Chen. Formulations for Coproduct Lignin-based Plastics. Oral presentation at NARA 2012 Annual Meeting, Missoula, MT, Sept 13-14, 2012.

Y.-Y. Wang, S.Sarkanen, Y.-r. Chen. Formulations for Coproduct Lignin-based Plastics. Poster presentation at NARA 2012 Annual Meeting, Missoula, MT, Sept 13-14, 2012.

S.Sarkanen, Y.-r. Chen, Y.-Y. Wang. Formulations for Coproduct Lignin-based Plastics. Oral presentation at NARA Coproducts Team February 2013 Quarterly Meeting, Spokane, WA, February 27, 2013.

C-CP-2: Conversion of Lignin to High Value, Large Market Products

Key personnel	Affiliation
John Westland*	Weyerhaeuser
Davis Fish	Weyerhaeuser
Carter Fox	Weyerhaeuser
Ian Dallmeyer	Weyerhaeuser

*retired from Weyerhaeuser

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. These processes are being used to supply the carbohydrates for the fermentation to isobutanol for fuel production. A key component of the 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 Co-Products Team. This information is essential to developing suitable end-uses for the various lignins.

Originally there were only two product areas that were targeted. The first was the conversion of the lignin to a high value activated carbon (AC), with a very high surface area. It was found that with recent EPA requirements that coal burning facilities must reduce their mercury pollution, the market for AC designed to clean up flue gas emission has exploded. Our primary goal has become to develop an AC that will be effective in 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. Additional applications might include some very high-end AC's for uses such as in supercapacitors and batteries. This is a new and emerging market where there is a need for a sustainable alternative to current materials and would be used in industries where the generation of electricity is variable (wind generators, electric vehicles).

The second initially-targeted area was the non-traditional use to convert the lignin to a nano-lignin where it would be substituted for carbon black. However, we have decided to first look at the possibility of replacement or partial substitution of carbon black with conventional lignin in the areas of automotive tires, hoses and belts. Another possibility is the conversion of lignin directly to carbon black.

We are now proposing to also evaluate lignin as an anti-oxidant for asphalt binder for roads and evaluate the effectiveness of the lignin in the traditional area of cement additives.

Activities and Results

The evaluation of hydrolysis residual (HydR) lignins from the pre-treatment processes – Catchlight Energy (CLE), SPORL, wet oxidation (WetOx) and dilute acid (DA) – was completed. Three methods were developed to isolate the lignin from spent sulfite liquors (SSL) – amine extraction, ultra-filtration, and a novel calcium precipitation method. CLE and SPORL SSL's and HydR's had moderate levels of sulfur arising from the pulping chemicals while the WetOx and DA HydR's exhibited background levels of sulfur since there were no sulfur-containing pulping chemicals used.

Table **1** summarizes the HydR results. CLE and SPORL have high ash levels from the residual salts from the pulping chemicals compared to WetOx and DA HydR's levels. The carbohydrate to lignin ratio, which eliminates the dilution effect of the ash for the WetOx and DA residuals is almost double that of the CLE and SPORL. Additional washing of the WetOx residuals had little effect indicating the absence of soluble sugars. Table **2** shows that the molecular weight (MW) for the SPORL HydR is significantly lower than the CLE. Slight differences in the CLE process conditions appear to impact the MW's.

Laboratory procedures were developed to produce activated carbons (AC) from hydrolysis residuals with different surface areas and different types of porosity. The CLE HydR's (as is) were heated to 800 °C under a nitrogen atmosphere. The surface area was 250 m^2/g with a microporous structure. The same material was also acid-washed and the surface area was 450 m^2/g and showed mesoporosity. Adding between 1 and 3 parts potassium hydroxide to 1 part HydR, the surface area generated varied from 1330 to 2200 m^2/g with a highly microporous structure. CLE-HydR-derived carbon samples had significant elemental mercury adsorption capacities as shown in the Table 3. The mercury adsorption capacity values were 95 and 88% of the adsorption capacity measured for a commercial standard carbon used for mercury adsorption, Norit Darco-Hg. The most significant result was that the carbonized/washed CLE-HydR materials were capable of performing nearly as well as the commercial carbon and the KOH-activated carbon ***without any physical or chemical activation***, which may significantly reduce the cost of activated carbon production compared to competing products. A TEA was developed for production of AC from HydR. Using a conventional steam activation method, it predicts that the cost of producing AC will be $0.57/lb, including a transfer price of $0.145/lb to the iso-paraffinic kerosene (IPK) plant. Given an activated carbon selling price of $0.75/lb for mercury emissions control grade and given a total capital cost estimated at $168,000,000, the internal rate of return (IRR) is calculated to be 22.5%. Furthermore, the market for such a grade is growing rapidly and would consume a major portion of the output of HydR from the IPK plant.

Using commercially available lignosulfate salts and Kraft lignin, we evaluated partial substitution of these salts for carbon black in rubber. Total replacement of all the carbon black gave very poor results while partial substitution did have some positive effects – especially the rubber modulus with the sodium salt. The cure times increased with the addition of the Kraft lignin and the calcium salt. However, the addition of sodium salt seemed to have little effect on the cure time or may have actually reduced it slightly.

A positive effect was seen from the addition of 3% CLE-HydR to asphalt with regards to offering protection against oxidation. (See Figure 1.) Also, the CLE-SSL lignin was shown to be superior to other commercially available lignosulfonate salts as a viscosity modifier for cement (See Table 4).

Table 1: Summary of Results for Hydrolysis Residual Lignins

	Total Carbohydrate wt. %	Total Klason Lignin wt. %	Ash wt. %	Total wt. %	Carb: Lignin Ratio
CLE-A	20.6	69.8	7.80	98.2	0.295
CLE-B	19.4	70.1	7.35	96.8	0.277
SPORL	22.5	70.6	5.73	98.9	0.319
SPORL- Washed	19.6	70.2	5.89	95.7	0.279
Wet Ox	39.0	56.8	2.02	97.8	0.687
Wet Ox - Washed	38.1	58.3	1.93	98.3	0.653
Dilute Acid	33.4	66.2	1.99	101.6	0.505

Table 2 Molecular Weights of SSL Lignins as Measured by SEC-MALS

Sample	M_n (kDa)	M_w (kDa)	PDI (M_w/M_n)
CLE A	16.6 ± 0.3	24.1 ± 0.4	1.4 ± 0.1
CLE B	29.7 ± 0.7	43.0 ± 1.0	1.5 ± 0.1
SPORL	3.0 ± 0.2	4.2 ± 0.3	1.4 ± 0.2

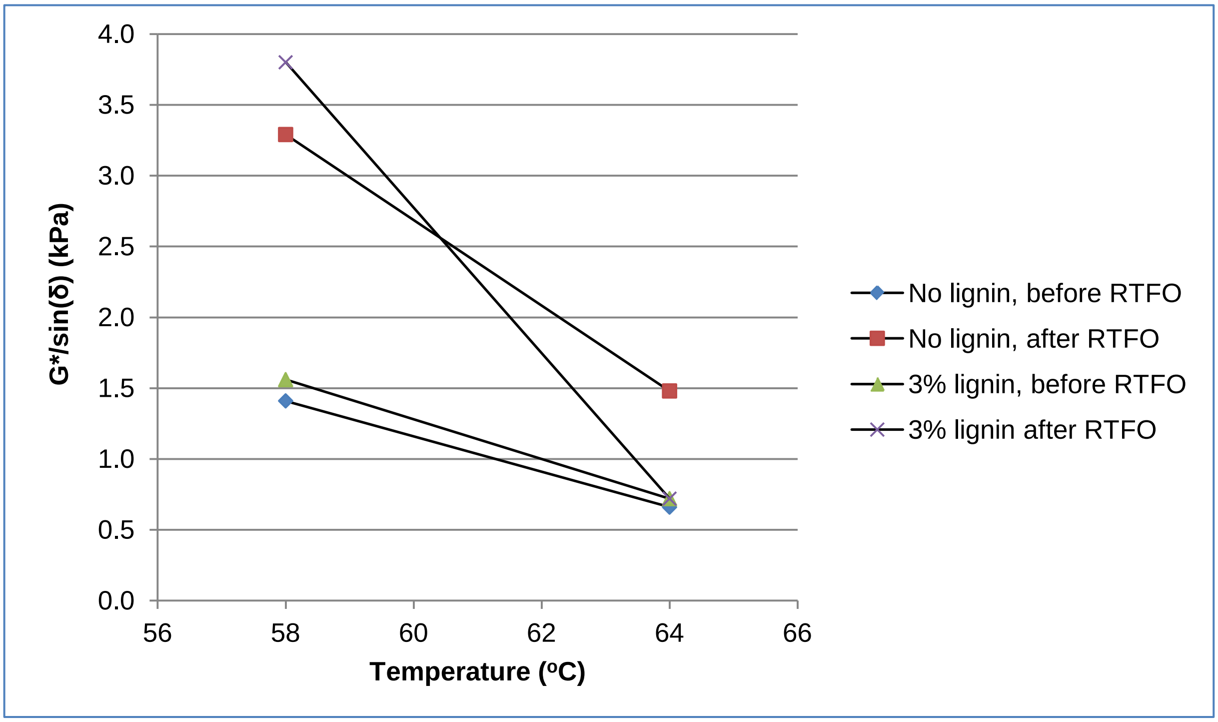

Figure 1: Mechanical Properties of Asphalt Containing 3% Lignin as a Function of Temperature (G* is the complex dynamic shear and δ is the phase lag between stress and strain.)

Table 3: Equilibrium vapor phase elemental mercury adsorption capacities of CLE-HydR-derived carbons prepared at 800°C, with (KOH:CLE-HydR, 1:1) and without KOH activation (CLE-HydR).

Sample	Equilibrium adsorption capacity μg Hg/g carbon (@ 50 μg/Nm^3)
CLE-HydR, 800°C	1415
KOH:CLE-HydR, 1:1, 800°C	1605
Darco-Hg	1680

Table 4: Effect of Various Lignosulfonates on Freshly Mixed Cement Viscosity as Measured by ASTM C 1437-07," *Standard Test Method for Flow of Hydraulic Cement Mortar".*

Lignosulfonate Sample	Measured Flow (%)
Control	68.1
Control	65.2
CLE A	123.3
CLE B	125.6
Ultrafiltered CLE A	120.7
Ultrafiltered CLE B	120.6
SPORL SSL	120.9
Control	69.0
Georgia Pacific L - CN	84.4
Georgia Pacific L - 100	78.3
Georgia Pacific L - 458	88.0

Recommendations/Conclusions

I. Evaluation of Lignins from the Pre-Treatment Processes

All the analyses show there are significant differences among lignins from different pretreatment processes – some expected, some unexpected. Sulfur may have a beneficial effect on mercury adsorption from flue gas and this hypothesis will have to be studied more. When taking into account the level of sulfur on the total analysis, nothing remarkable is seen regarding the carbon, hydrogen, and nitrogen levels.

From an end-use perspective, we don't have sufficient data to say whether these high levels of carbohydrates will have a negative impact on the end-uses being investigated by Weyerhaeuser. This point needs to be evaluated next. However, it is clear that high carbohydrate levels remaining after pretreatment will have a significant impact on the economics of the biofuel production. The differences in molecular weights among CLE and SPORL SSL lignins show that choice of pretreatment affects lignin molecular weight. Interestingly, even subtle differences between batches using CLE pretreatment produced lignosulfonates with different molecular weights. More research on the relationship between pretreatment conditions and lignin molecular weight is needed. Furthermore, NMR analyses showed major differences between the SSL's. More analysis will have to be done to verify these findings.

II. Evaluation of End-Uses for Lignins

Production of activated carbons is technically feasible and represents a promising opportunity for valorization of the lignin-rich residual stream from the NARA biorefinery. Since market studies show world consumption of activated carbon is expected to increase from 1.2 million metric tons (Mt) in 2012 to 2.3Mt in 2017, and there will be coal precursor shortages in China, we intend to strongly pursue this use for lignin. Chemical activation with alkali metal hydroxides can produce carbons with a high degree of adsorptive capacity, but may be too expensive to implement at the scale envisioned for the NARA biorefinery. A reasonable alternative to chemical activation would be to use a standard steam activation method – the most common method for producing activated carbon on an industrial scale. It is expected that steam activation would produce an activated carbon that would be cost effective and match current market needs. We will be looking at this method next.

The next step in proving the potential of profitable activated carbon production is to obtain more detailed information on the range of AC products that can be produced from NARA residual streams and compare the cost of production at the relevant scale with the potential selling prices for different applications. Mercury emissions and water treatment are the largest scale applications for activated carbon and require a low-to-medium grade product with moderate selling price. To address these markets we propose to first thoroughly investigate the properties of carbonized lignin residuals without any additional activation to determine whether an inexpensive process can produce AC materials with suitable performance. Concurrently, steam activation of carbonized chars will be investigated to generate medium grade activated carbons for these large markets. Furthermore, emerging markets in energy storage (electrochemical capacitors, batteries, gas storage) also offer exciting opportunities for higher grade carbons which will likely be more costly to produce, but may also bring a higher selling price.

More work is needed to confirm any beneficial effect of lignin addition to asphalt binder, although Figure **1** does show a positive effect on the oxidative aging of the binder from the addition of the CLE-HydR. The binder exhibited a greater degree of thermal softening when the temperature was increased from 58-64°C with the addition of CLE-HydR, indicates a lower degree of oxidative degradation of the binder during simulated aging in the RTFO. More testing is being planned for year 3, but will have a lower priority than our activated carbon. The same goes for the lignin in rubber work.

The largest current market application for lignosulfonates is as an ingredient in concrete admixtures to help improve concrete workability before setting. The large difference between the CLE SSL lignin and the commercial grades, require further investigation. Combined with using the HydR for AC and the SSL for cement should present a high value for these by-products of the bio-fuel production.

Physical and Intellectual Outputs

Physical

- NARA pretreatment lignins have been characterized.
- A preliminary techno-economic analysis for activated carbon production from lignin has been accomplished.
- Preliminary data on the porosity and effectiveness of activated carbon derived from NARA residuals has been generated.

Research Presentations

Fox, S.C., and D. Fish. 2012. Isolation and characterization of NARA lignins. Poster presentation at NARA 2012 Annual Meeting, Missoula, MT, Sept 13-14, 2012.

Fox, S.C. and D. Fish. Isolation and characterization of NARA lignins. Poster presentation at the Northwest Bioenergy Research Symposium, Seattle, WA, Nov 13, 2012.

Fox, S.C. and D. Fish. Isolation and characterization of NARA lignins. Poster presentation at Weyerhaeuser Technology Poster Session, Federal Way, WA, Dec 19, 2012.

Fox, S.C. Jet Fuel – And Other Products – From the Forest with NARA. Oral presentation at Oregon State University Dept. of Wood Science and Engineering Graduate Seminar, Corvallis, OR, Mar 6, 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.

Task C-CP-3: Novel Engineering Polymers from Lignin-Derived Building Blocks

<u>Key personnel</u>	<u>Affiliation</u>
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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, i*ncreasing 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, so far, not practical and may not be economically advantageous. In this project, *<u>our hypothesis</u>* 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 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 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 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. The resulting PDL will be converted to building block chemicals, which are to be used for synthesis of 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, 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) 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 a similar 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. To investigate preparation of partial depolymerization of lignin (PDL) for epoxy synthesis, we initiated our investigation with Kraft lignin (KL) as a model lignin because of its easy availability, relatively low molecular weight and high hydroxyl content. Both base-catalyzed depolymerization (BCD) and hydrogenolysis in mild conditions proved to be successful in partially depolymerizing lignin. The conversion of KL to a soluble compound was successful with a yield ≥70 wt%. In general, BCD performed with NaOH as catalyst at ~250 °C for 90 minutes can result in 70% or higher soluble PDL. The resulting PDL was converted to glycidyl ether type epoxies (LEP) and polycarboxylic acid (LPCA) type curing agents. LEP and LPCA are black viscous liquid or paste-like solid and soluble in many organic solvents. Methods for synthesizing LEPs with high epoxy values are still under investigation. However, curing commercial Bisphenol A (BPA) type epoxies using LPCAs resulted in some promising results. The moderate mechanical and physical properties of the cured resins suggest LPCAs are worth further exploration for curing agent application (Figure 1). Furthermore, the properties of the cured resin could be greatly regulated by using mixed curing agents. Hydrogenolysis under mild conditions proved to be a more effective method to achieve PDL and resulted in ~85% or higher soluble PDL. Compared to the original KL, the hydroxyl value of the hydrogenated KL was increased by 0.85 mmol/g, being 7.19 mmol/g. We studied effects of temperature, solvent and reaction stoichiometry and concentration of reagent on yield of conversion and hydroxyl content.

Partial depolymerization of *NARA lignin* (hydrolysis lignin) was subsequently studied based on the experience learned using the KL. Surprisingly, under various reaction conditions, use of the BCD method generally resulted in low yield for the lignin-to-soluble conversion (<45%). This result was probably due to the high initial molecular weight (MW) of the NARA lignin, which largely resembles the lignin in its native intact state. This reasoning is supported by the fact that there has not been an effective solvent identified to dissolve the NARA lignin for molecular weight (MW) determination.

Mild hydrogenolysis, however, still proves to be an effective approach to partially depolymerizing NARA lignin. In a preliminary experiment, hydrogenolysis of the DA lignin in 10% NaOH aqueous solution exhibited a much high conversion than in 10% NaOH methanol solution (73% vs. 23%). This result might be attributed to the higher solubility of the resulting PDL in water. More hydrogenolysis has been performed in 3% NaOH solution in dioxane/water (1:1) mixture. Hydroxyl content is measured using ^{31}P NMR. Figure 2 shows the ^{31}P NMR spectra of NARA dilute acid (DA) lignin before and after hydrogenolysis at different temperatures, while Table 1 shows the hydroxyl content of the resulting PDLs increased continuously with temperature up to 200 °C. Figure 3 shows effects of temperature on conversion of PDL, indicating the conversion peaked at 180 °C. Catalyst concentration and reaction time are also found to significantly influence the conversion.

Task C-CP-3.3 has not started yet.

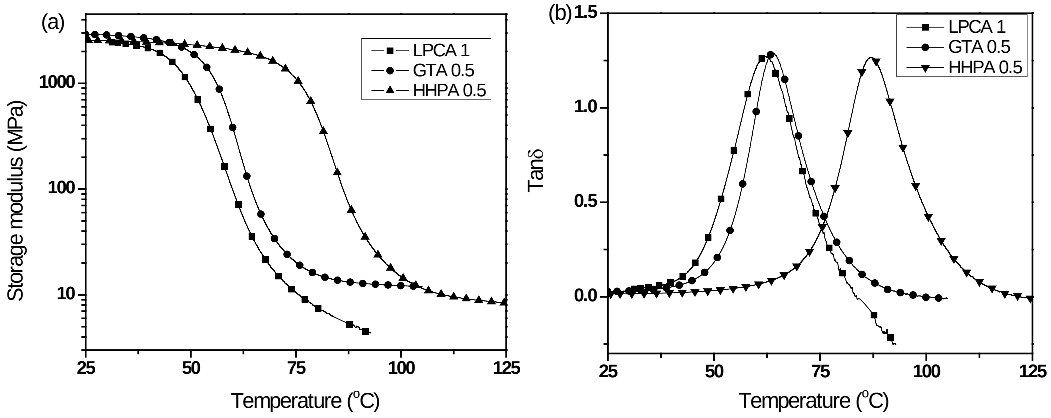

Figure 1. Storage modulus (a) and tan δ (b) versus temperature for the DER 353 cured by LPCA co-curing agents.

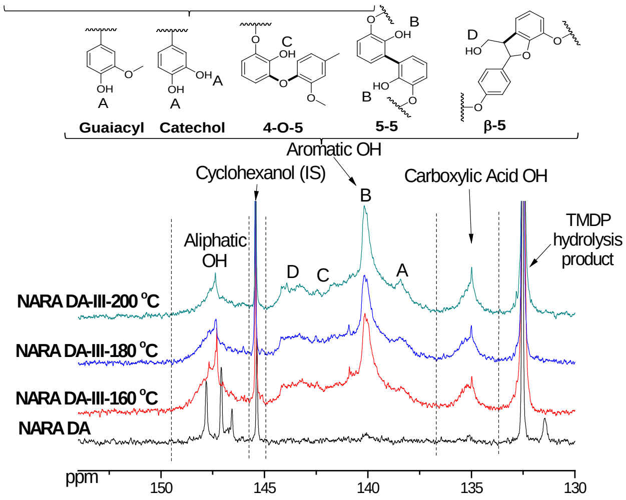

Figure 2. ^{31}P NMR spectra of NARA DA lignin before and after hydrogenolysis at different temperatures.

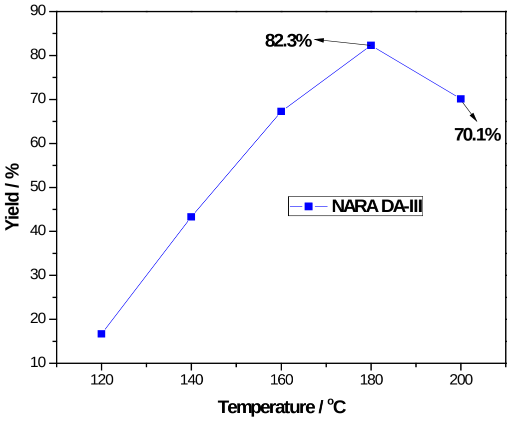

Figure 3. Effect of temperature on conversion of partial depolymeriztion of NARA DA lignin by hydrogenolysis.

Table 1. Hydroxyl content NARA DA lignin hydrogenolyzed at different temperatures using ^{31}P NMR

Structure	δ ^{31}P NMR	OH value (mmol / g)		
		160 °C	180 °C	200 °C
Aliphatic OH	145.5-150.0	0.81	0.71	0.66
Aromatic OH	136.6-144.7	2.4	2.68	3.22
Carboxylic acid OH	133.6-136.6	0.37	0.44	0.50
Total		3.58	3.83	4.38

Recommendations/Conclusions

In summary**,** the results obtained to date have largely validated our *hypothesis* that the partially depolymerized lignin (PDL) with good solubility/dispersability can be converted into effective building blocks for engineering polymers. Epoxies cured with PDL-based curing agents display promising mechanical and physical properties. Though PDL-based epoxies have not achieved the anticipated performance, the result is more likely due to the methodological approach in the synthesis of glycidyl ether of PDL. In the future, more effort will be made to investigate synthesis of PDL-based epoxies.

Mild hydrogenolysis under the catalysis of Raney Ni can effectively depolymerize both Kraft lignin (KL) and various NARA lignins to produce PDLs. However, the base-catalyzed depolymerization (BCD) approach is only effective on KL. The results obtained suggest that catalyst content, temperature, and reaction medium all greatly influence the conversion, hydroxyl content and molecular weight of the resulting PDLs. Additional efforts are needed to refine individual and combined parameters before the optimum reaction conditions can be identified. This will be one of the prime focus areas for the coming year of research.

In addition, recently preliminary results indicate that phenolation liquefaction is an effective approach to depolymerize (i.e. liquefy) NARA lignin. Interpretation of this result suggests that NARA lignin may also play a role in polyurethanes and phenolic resins in the future. We recommend exploring phenolation liquefaction using lignin-derived total phenol as liquefying agent. If this attempt is proved feasible, a novel and new approach for preparation of lignin-based polyurethanes and phenolics will be introduced.

Physical and Intellectual Outputs

Refereed Publications (accepted or completed)

Qin, J., H. Liu, P. Zhang, M. Wolcott, and J. Zhang. Preparation of biobased epoxy resin from eugenol and rosin and study of curing and performance properties (submitted)

Conference Proceedings and Abstracts from Professional Meetings

Qin, J., J. Xin, M. Wolcott and J. Zhang. 2013. Use of Lignin as Feedstock for Epoxy Application. 2013 International Wood Composite Symposium, Seattle, WA, April. 3- 4.

Qin, J., M. Wolcott, and J. Zhang. 2012. Diversifying renewable feedstocks for new biobased polymers and applications, Oral presentation at 2012 BioEnvironmental Polymer Society Meeting, Denton, Texas, Sept.18-21, 2012.

Research Presentations

Qin, J., J. Xin, M. Wolcott and J. Zhang. 2013. Use of Lignin as Feedstock for Epoxy Application. Oral presentation at 2013 International Wood Composite Symposium, Seattle, WA, April. 3- 4.

Qin, J., M. Wolcott, J. Zhang. 2012. Diversifying renewable feedstocks for new biobased polymers and applications. Oral presentation at 2012 BioEnvironmental Polymer Society Meeting, Denton, Texas, Sept.18-21, 2012.

Qin, J., M. Wolcott and J. Zhang. 2012. Use of lignin as feedstock for polymer materials: epoxies and curing agents. Poster presentation at NARA 2012 Annual Meeting, Missoula, MT, Sept 13-14, 2012.

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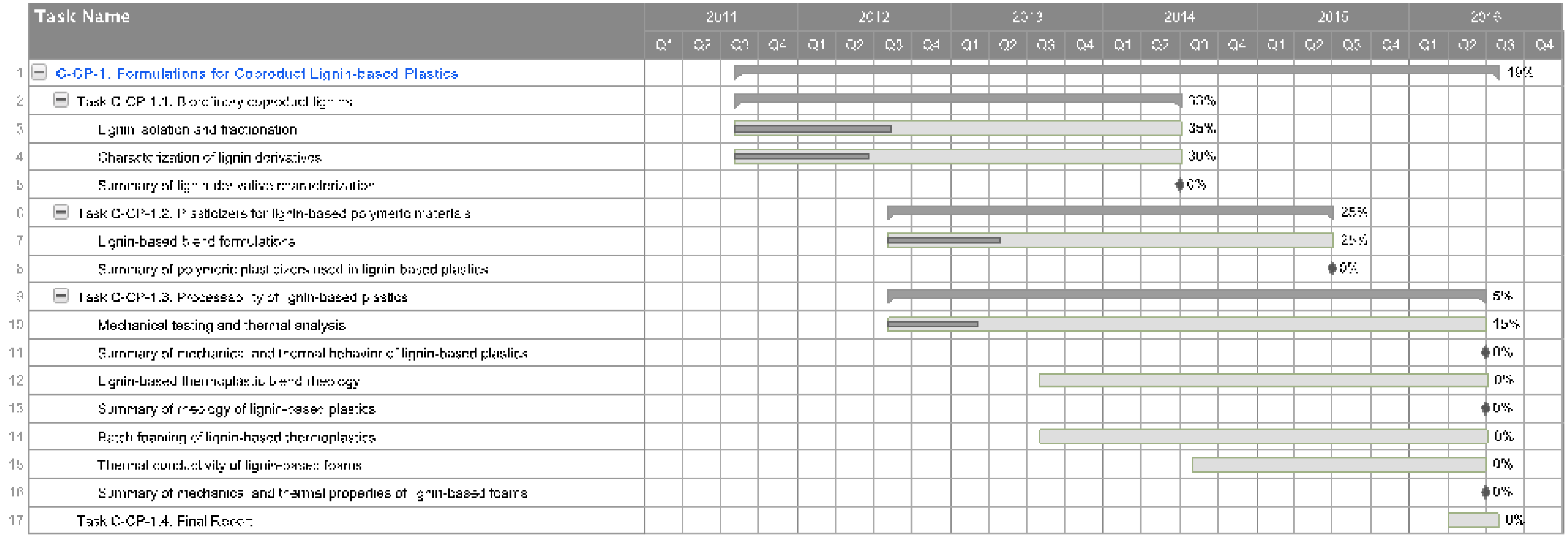
NARA



	Task Name	
1	**C-CP-1. Formulations for Coproduct Lignin-based Plastics**	10%
2	Task C-CP-1.1. Biorefinery coproduct lignins	33%
3	Lignin isolation and fractionation	35%
4	Characterization of lignin derivatives	30%
5	Summary of lignin derivative characterization	0%
6	Task C-CP-1.2. Plasticizers for lignin-based polymeric materials	25%
7	Lignin-based blend formulations	25%
8	Summary of polymeric plasticizers used in lignin-based plastics	0%
9	Task C-CP-1.3. Processability of lignin-based plastics	5%
10	Mechanical testing and thermal analysis	15%
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%

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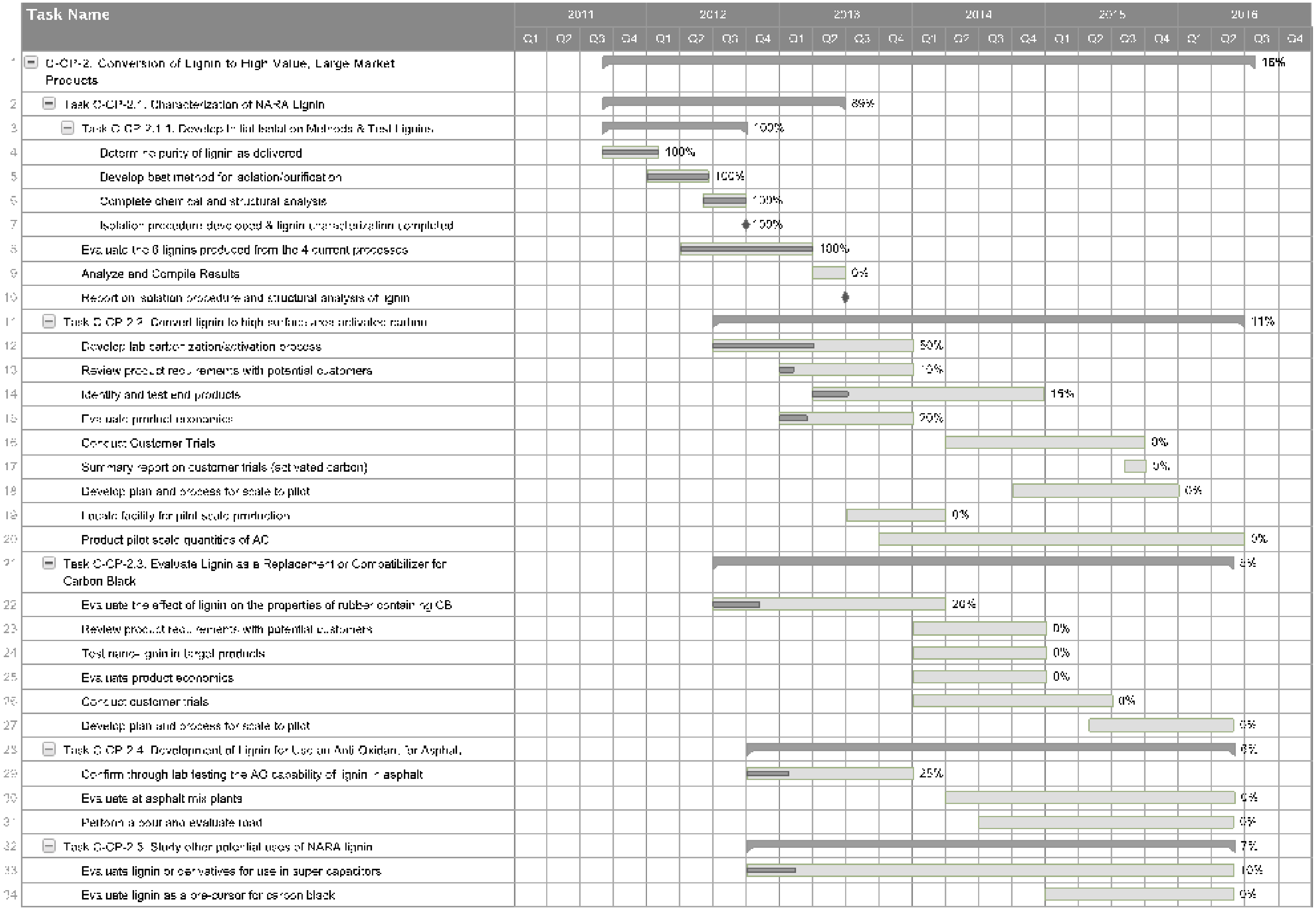
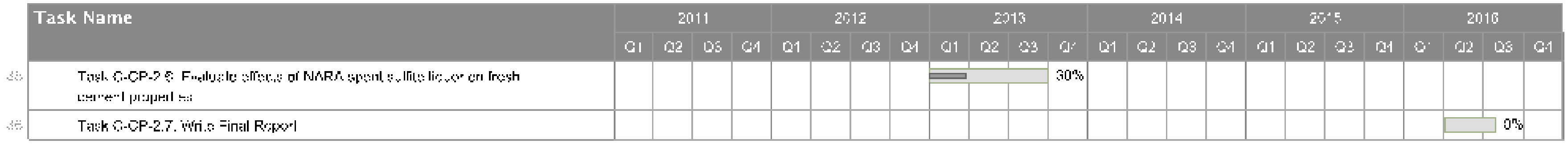


	Task Name	
1	C-CP-2. Conversion of Lignin to High Value, Large Market Products	15%
2	Task C-CP-2.1. Characterization of NARA Lignin	89%
3	Task C-CP-2.1.1. Develop Initial Isolation Methods & Test Lignins	100%
4	Determine purity of lignin as delivered	100%
5	Develop best method for isolation/purification	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	0%
10	Report on isolation procedure and structural analysis of lignin	
11	Task C-CP-2.2. Convert lignin to high surface area activated carbon	11%
12	Develop lab carbonization/activation process	50%
13	Review product requirements with potential customers	10%
14	Identify and test end products	15%
15	Evaluate product economics	20%
16	Conduct Customer Trials	0%
17	Summary report on customer trials (activated carbon)	0%
18	Develop plan and process for scale to pilot	0%
19	Locate facility for pilot scale production	0%
20	Product pilot scale quantities of AC	0%
21	Task C-CP-2.3. Evaluate Lignin as a Replacement or Compatibilizer for Carbon Black	8%
22	Evaluate the effect of lignin on the properties of rubber containing CB	20%
23	Review product requirements with potential customers	0%
24	Test nano-lignin in target products	0%
25	Evaluate product economics	0%
26	Conduct customer trials	0%
27	Develop plan and process for scale to pilot	0%
28	Task C-CP-2.4. Development of Lignin for Use an Anti Oxidant for Asphalt	6%
29	Confirm through lab testing the AO capability of lignin in asphalt	25%
30	Evaluate at asphalt mix plants	0%
31	Perform a pour and evaluate road	0%
32	Task C-CP-2.5. Study other potential uses of NARA lignin	7%
33	Evaluate lignin or derivatives for use in super capacitors	10%
34	Evaluate lignin as a pre-cursor for carbon black	0%


Task Name
2011
2012
2013
2014
2015
2016
Q1
Q2
Q3
Q4
45
Task C-CP-2.6. Evaluate effects of NARA spent sulfite liquor on fresh cement properties
30%
46
Task C-CP-2.7. Write Final Report
0%

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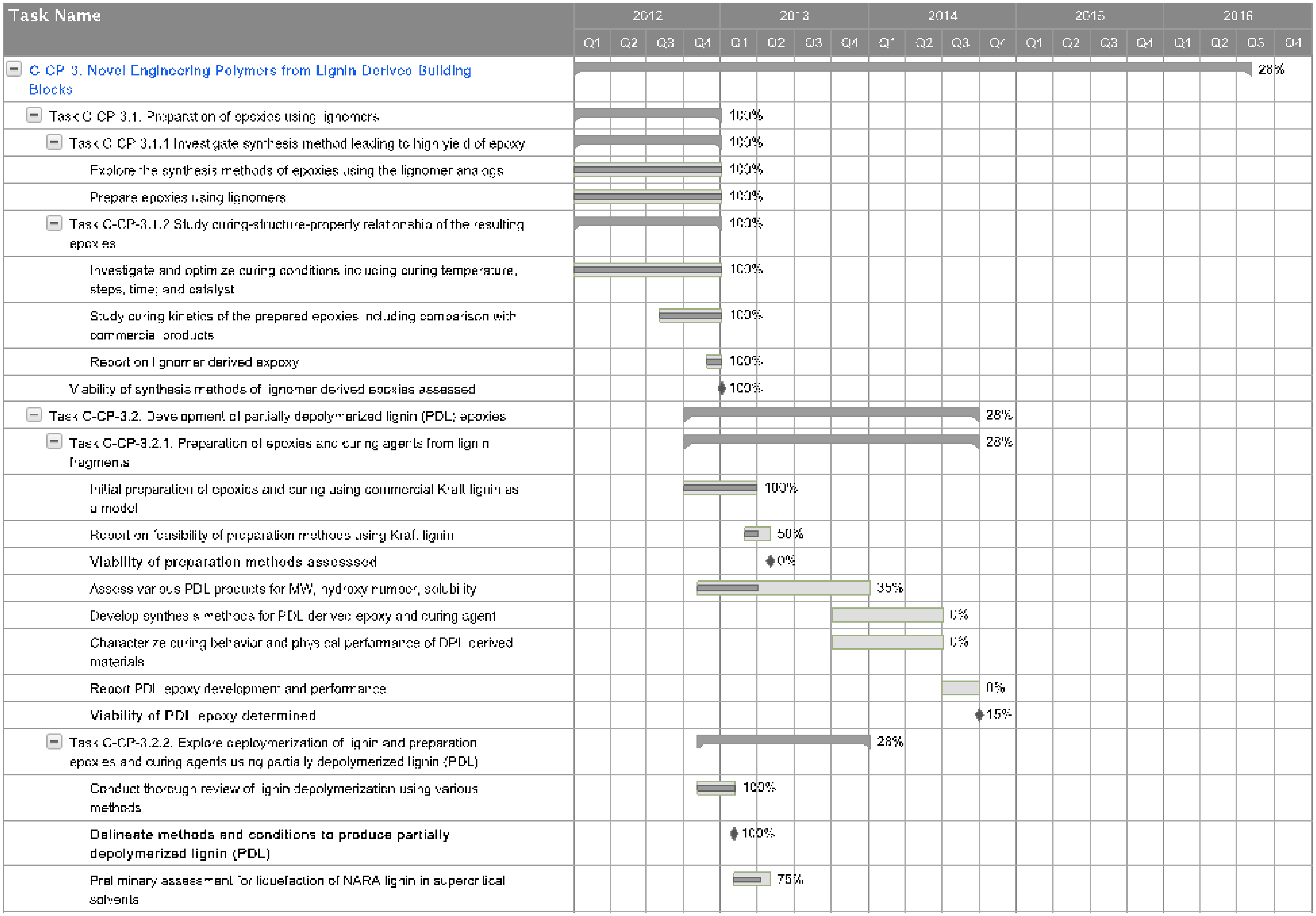
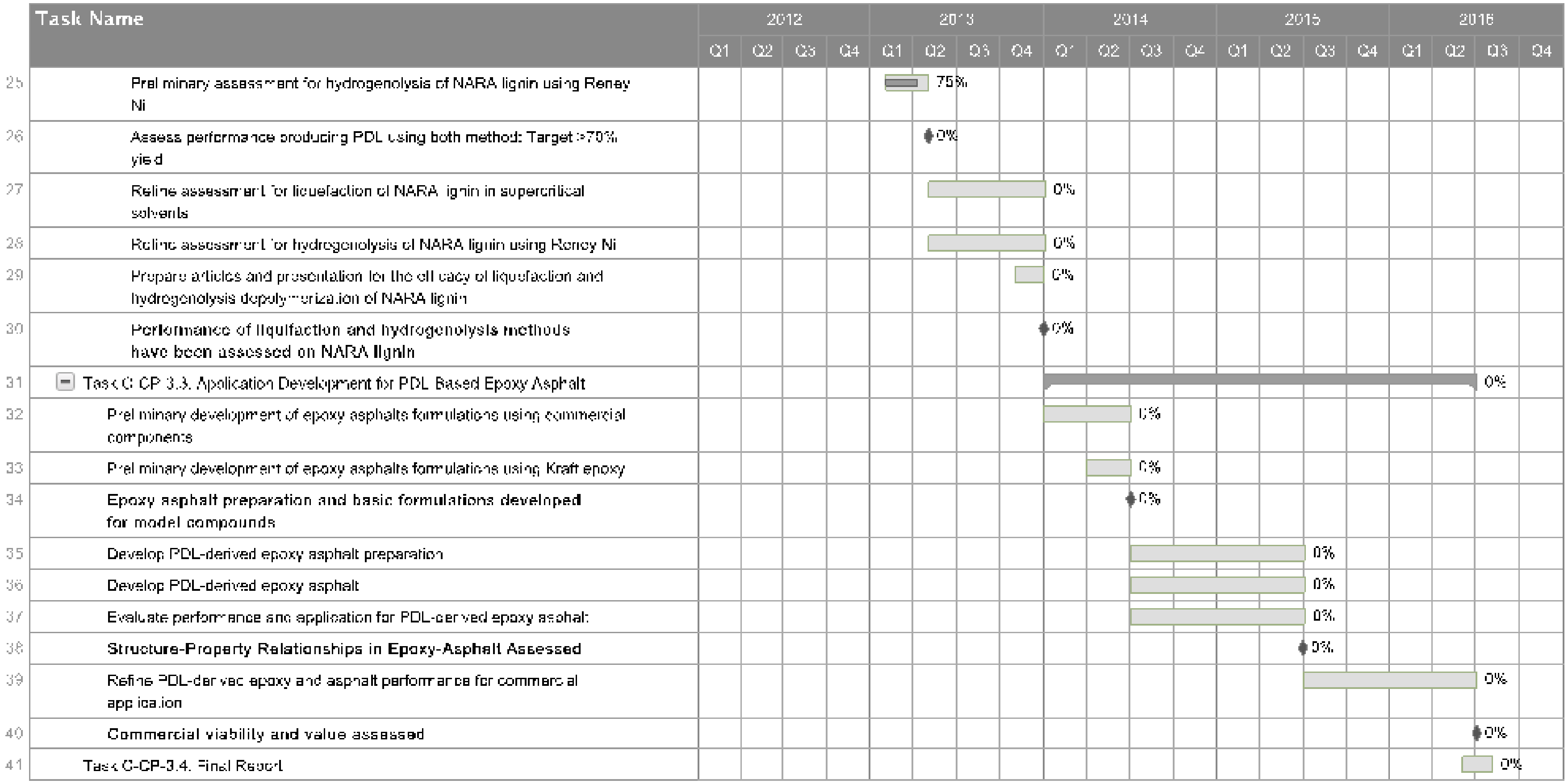
NARA



	Task Name	
1	C-CP 3. Novel Engineering Polymers from Lignin Derived Building Blocks	28%
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	28%
12	Task C-CP-3.2.1. Preparation of epoxies and curing agents from lignin fragments	28%
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	50%
15	Viability of preparation methods assessed	0%
16	Assess various PDL products for MW, hydroxy number, solubility	35%
17	Develop synthesis methods for PDL derived epoxy and curing agent	0%
18	Characterize curing behavior and physical performance of DPL derived materials	0%
19	Report PDL epoxy development and performance	0%
20	Viability of PDL epoxy determined	15%
21	Task C-CP-3.2.2. Explore depolymerization of lignin and preparation epoxies and curing agents using partially depolymerized lignin (PDL)	28%
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	75%



	Task Name
25	Preliminary assessment for hydrogenolysis of NARA lignin using Reney Ni
26	Assess performance producing PDL using both method: Target >70% yield
27	Refine assessment for liquefaction of NARA lignin in supercritical solvents
28	Refine assessment for hydrogenolysis of NARA lignin using Reney Ni
29	Prepare articles and presentation for the efficacy of liquefaction and hydrogenolysis depolymerization of NARA lignin
30	**Performance of liquifaction and hydrogenolysis methods have been assessed on NARA lignin**
31	⊟ Task C CP 3.3. Application Development for PDL Based Epoxy Asphalt
32	Preliminary development of epoxy asphalts formulations using commercial components
33	Preliminary development of epoxy asphalts formulations using Kraft epoxy
34	**Epoxy asphalt preparation and basic formulations developed for model compounds**
35	Develop PDL-derived epoxy asphalt preparation
36	Develop PDL-derived epoxy asphalt
37	Evaluate performance and application for PDL-derived epoxy asphalt
38	**Structure-Property Relationships in Epoxy-Asphalt Assessed**
39	Refine PDL-derived epoxy and asphalt performance for commercial application
40	**Commercial viability and value assessed**
41	Task C-CP-3.4. Final Report