CONVERSION OF LIGNIN TO HIGH VALUE, LARGE MARKET PRODUCTS

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AC	activated carbon
CLE	Catchlight Energy
DCF	Discount cash flow
DMF	N,N-dimethylformamide
DMSO	dimethyl sulfoxide
EDLC	electrochemical double layer capacitor
EMAL	enzymatic mild acidolysis lignin
FCI	fixed capital investment
FPL	Forest Products Laboratory
FRS	fermentation residual solids
HRS	hydrolysis residual solids
LAP	laboratory analytical procedure
MATS	mercury air and toxics standard
MBS	mild bisulfite
NMR	nuclear magnetic resonance
NREL	National Renewable Energy Laboratory
PV	pore volume
SA	surface area
SEM	scanning electron microscope
SPORL	Sulfite Pretreatment to Overcome Recalcitrance of Lignocellulose
SRS	saccharification residual solids
SSL	spent sulfite liquor
WOX	wet oxidation
ZC	ZeaChem

EXECUTIVE SUMMARY

One of our main tasks was to characterize the hydrolysis residual solids (HRS) and the fermentation residual solids (FRS) from the NARA Mild Bisulfite (MBS) and Wet Oxidation (WOX) pretreatment processes to determine their chemical properties. 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 had also been subjected to fermentation. The differences in the chemistry and physical properties among these different materials is significant, and the results are contained in this report.

The second task was to use the fermentation residual solids as precursors for physical and chemical activated carbon (AC) production for mercury and H_2S adsorption. This product provides an excellent opportunity from the technical, economic, and size of scale perspective. Our techno-economic analyses confirm these positive results.

INTRODUCTION

In this project, the sources of lignin were from one or more processes identified in the NARA project and from one or more steps in the process. This process is being used to supply the carbohydrates for the fermentation to isobutanol for fuel production. A key component of the proposal is to create high value products from the residual lignin. The lignin produced from the various pretreatment processes is significantly different from traditional Kraft lignins. The first part of the work (conducted in previous years) 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.

In 2011 and 2012, Weyerhaeuser put together a research team within the company's Cellulose Fibers business to participate in the Northwest Advanced Renewables Alliance (NARA) project. The objective of this particular team within Weyerhaeuser was to develop value-added "co-products" from the residues remaining after the production of isobutanol from woody biomass. These residues were comprised of the portions of the wood feedstock, primarily lignin, that were not converted isobutanol and any chemical or biological inputs from the wood to alcohol conversion process.

The residues to be used for research by the Weyerhaeuser Co-products team were received after different wood samples were subjected to pretreatment and enzymatic hydrolysis. Several different pretreatment processes have been investigated by research teams within NARA, each one resulting in residues with different characteristics. The NARA pretreatment processes from which the Weyerhaeuser team received residues between January 2012 and July 2014 and the corresponding pretreatment team principle investigator(s) are listed in Table CP-Intro.1. Some of the samples had additionally, after enzymatic hydrolysis, been subjected to fermentation and separation of the resulting alcohol. Those samples that were received that had been subjected to enzymatic hydrolysis but not fermentation are referred to in this report as saccharification residual solids (SRS). Samples that had been subjected to both a hydrolysis and a fermentation step are referred to as fermentation residual solids (FRS). In addition to a SRS or FRS sample, the pretreatment processes based on chemical treatment using bisulfite (SPORL, CLE, and MBS; see Table CP-Intro.1) also produced a water-soluble fraction referred to as spent sulfite liquor (SSL). Figure CP-Intro.1 shows a schematic of the general process pathways that produced the residues used for co-products research, with the hashed boxes representing samples received by the co-products team. The compositional analysis for the different batches of wood chips that were used as the feedstock (top box of Figure CP-Intro.1) is described in the 1st NARA Cumulative Report covering the date range of August 2011 to March 2013 (NARA, 2013). Most of the samples described in this report were produced from NARA FS-03 or FS-10 feedstock. These feedstocks consisted of wood chips generally mostly derived from Douglas-fir wood, with a minor fraction of wood coming from mixed hardwood species.

Table CP-Intro.1. NARA Pretreatment teams producing residues for co-products

Pretreatment Process	Pretreatment Team PI	Pretreatment Team Location
	Xiao Zhang	WSU Bioproducts, Sciences & Engineering Laboratory, Richland, WA
Wet Oxidation (WOX)	Birgitte Ahring	WSU Bioproducts, Sciences & Engineering Laboratory, Richland, WA
SPORL	J.Y. Zhu	USDA Forest Products Laboratory, Madison, WI
Catchlight Energy (CLE) Process	Dwight Anderson & Johnway Gao	Weyerhaeuser Technology Center, Federal Way, WA
Mild Bisulfite (MBS)	J.Y. Zhu & Johnway Gao	Dilute Acid
Milled Wood	Johnway Gao	Weyerhaeuser Technology Center, Federal Way, WA

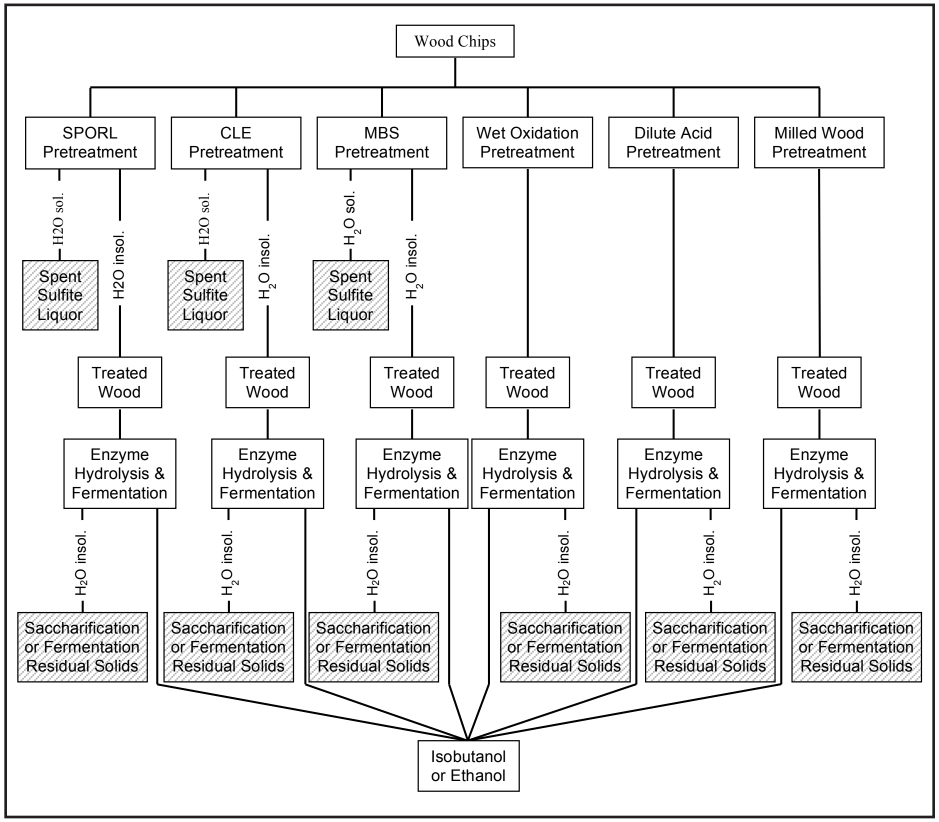

Figure CP-Intro.1. General flow diagram depicting the sources of spent sulfite liquor, saccharification residual solids, and fermentation residual solids used for NARA co-products research. The hashed boxes represent the samples received for co-products research.

The Dilute Acid pretreatment was used by NARA to determine the suitability of different woody biomass samples as feedstocks for isobutanol production. It was never intended to be a scaled-up process. The SPORL process developed at the Forest Product Laboratory was adapted from sulfite pulping, and Catchlight Energy (CLE) took the SPORL process and adapted it further. In 2013, NARA combined the SPORL and CLE processes into one pretreatment process referred to as the mild bisulfite (MBS) pretreatment process. In 2014, NARA selected the MBS as the pretreatment process that the project would move forward with to scale up in order to produce 1,000 gallons of jet fuel. The details of each NARA pretreatment process is beyond the scope of this report can be found in various technical journal articles and other NARA reports. (Gao, et al., 2013; Zhang, et al., 2012; Rana, et al. 2012; NARA, 2013).

The efforts in the last two years of the project focused on the development of activated carbons from the Saccharification or Fermentation Residual Solid. This effort started at Weyerhaeuser and was transferred to the WSU team lead by Dr. Garcia-Perez. Dr. Dallmeyer moved from Weyerhauser and continue his work at WSU. In January 2016 this task was transferred to Dr. Suliman who has been in charge of the project for the last seven months. It was found that with the new EPA requirements that coal burning facilities must reduce their mercury emissions, the market for AC designed to clean up flue gas emission has grown rapidly. Our primary goal has become to develop an AC that will be effective in mercury capture from coal combustion flue gases. The market size for this application is so large that it should consume a significant amount of the lignin produced. Furthermore the value generated should be significant. The second target is a new and emerging market, where there is a need for a sustainable, low-cost alternative to current materials. We also decide to study the production of microporous carbons for H_2S removal, this technology is very important to reduce emissions from anaerobic digestion systems. The key to designing AC materials for specific applications is to develop methodologies to prepare materials with precisely engineered pore structures and surface chemistry. We anticipate that thorough characterization of the properties of the AC materials prepared for the applications mentioned above will provide insight into other potential applications, such as the adsorption of metals, organic compounds, phosphates, and other environmental contaminants released into air and water. The research conducted on AC materials is therefore providing a platform for the development of a family of carbon products from the NARA lignin-rich biorefinery residues.

TASK 1. CO-PRODUCT SAMPLE RECEIVING AND ANALYSIS

Tables CP-1.1 and CP-1.2 list the samples that the Weyerhaeuser Co-products team received from the NARA pretreatment teams. Table CP-1.1 specifically lists the samples that were produced from the NARA FS-03 feedstock, and Table CP-1.2 specifically lists the samples produced from NARA FS-10 feedstock. One challenge faced by the co-products team was that different pretreatment teams provided samples in different formats and with different histories. For example, some of the SRS and FRS samples had been thoroughly washed with water to remove any water-soluble material, such as monosaccharide or oligomeric sugars, prior to shipment. With the intention of preparing comparable samples for compositional analysis, samples that had not been washed prior to shipment to the co-products team (or samples where it was unclear if they had been washed) were washed upon receiving. Washing consisted of suspending the SRS or FRS in deionized water, centrifuging, and decanting the supernatant a total of three times. SRS and FRS samples that were wet were then dried in a vacuum oven at 50 °C. The samples were then pulverized in a shatterbox to provide particulate samples appropriate for compositional analysis. SSL samples were analyzed as received.

Table CP-1.1. List received pretreatment residues produced from NARA FS-03 feedstock

Pretreatment	Sample Type	Sample History & Format	Approx. Received Date
Dilute Acid	Saccharification residue	H_2O washed, freeze-dried particles	12/5/2012
WOX	Saccharification residue	H_2O washed, frozen particles	2/5/2013
SPORL	Saccharification residue	Particles suspended in water	1/4/2013
	Spent sulfite liquor	Liquid solution	1/4/2013
CLE	Saccharification residue	H_2O washed, refrigerated wet particles	11/5/2012
	Saccharification residue	H_2O washed, refrigerated wet particles	11/5/2012
	Spent sulfite liquor	Liquid solution	11/7/2012
	Spent sulfite liquor	Liquid solution	11/7/2012
	Spent sulfite liquor	Ultrafiltered liquid solution	1/2/2013
	Spent sulfite liquor	Ultrafiltered liquid solution	1/2/2013

Table CP-1.2. List of received pretreatment residues produced from NARA FS-10 feedstock

Pretreatment	Sample Type	Sample History & Format	Approx. Rec'd Date
WOX	Saccharification residue	Frozen particles	8/5/2013
	Fermentation residue	Frozen particles	11/26/2013
MBS	Saccharification residue	Wet particles from 4% enzyme on solids hydrolysis	7/30/2013
	Saccharification residue	Wet particles from 1% enzyme on solids hydrolysis	7/30/2013
	Fermentation residue	Wet particles (from 4% enzyme hydrolysis sample) after autoclaving at 250 °C for 60 min to remove ethanol	9/27/2013
	Spent sulfite liquor	Liquid solution	12/9/2013
	Spent sulfite liquor	Liquid solution	1/8/2014
	Fermentation residue	Dried pellets	2/5/2014
Milled Wood	Saccharification residue	Refrigerated wet particles	11/22/2013
	Fermentation residue	H_2O washed, refrigerated wet particles	1/30/2014

Compositional analysis of saccharification and fermentation residual solids

Since the NARA residues were byproducts of chemical and biological processes designed to convert wood polysaccharides to alcohol and ultimately jet fuel, it was assumed that the residues would consist primarily of the non-polysaccharide fraction of wood, mostly lignin. However, different pretreatment processes exhibit different efficiencies in polysaccharide conversion and have different chemical inputs that would carry through and ultimately end up in the residues. Therefore, it was necessary to perform compositional analysis on the residues to determine their actual lignin, polysaccharide, and inorganic ash content. The lignin content was measured by weighing the amount of insoluble residue present after acid digestion of the sample according to the method outlined in the National Renewable Energy Laboratory (NREL) laboratory analytical procedure (LAP) for determining structural carbohydrates and lignin in biomass (Sluiter et al., 2012). The carbohydrate content of the pretreatment residues were determined using the method outlined by the same NREL LAP, with the quantification of the acid digested sugars performed on a Dionex anion exchange chromatography system with pulsed amperometric detection. Ash content was measured as the mass of a sample remaining after heating to 750 °C in air. Elemental analysis was also performed on the samples. Sulfur content was determined according to ASTM D1552. Carbon, hydrogen, nitrogen, and oxygen analysis was determined according to ASTM D5373.

Table CP-1.3 shows the compositional analysis results for the SRS samples derived from NARA FS-03 feedstock, corresponding to the SRS samples listed in Table CP-1.1. The residues resulting from CLE, SPORL and dilute acid pretreatment were all comprised of approximately 2/3rds (oven dried. wt. %) acid insoluble lignin. The CLE and SPORL derived residues also contained 2.0 – 2.5% acid soluble lignin, while the dilute acid derived residue contained 1.0% acid soluble lignin. The wet oxidation derived residues contained less than 60% acid insoluble lignin and about 1.0% acid soluble lignin. This confirms that the residues are comprised primarily of lignin as expected, though a substantial fraction of the residues is not lignin. The bulk of the remaining material is comprised mainly of glucose derived residual polysaccharide, primarily unhydrolyzed cellulose. There is also a small fraction of residual hemicellulose in the form of mannans and xylans, with the mannans likely coming from the glucomannans found in Douglas-fir. The xylans likely come from hardwood hemicellulose present in the feedstock. Other hemicellulose sugars were found to be present in each of the samples, but below the quantitation limit of 0.45% for the analytical method. The CLE and SPORL pretreatment methods resulted in higher ash contents in the residues due to the added input of inorganic chemicals during pretreatment. Chemicals added during wet oxidation or dilute acid pretreatment are either volatile or water soluble, and thus those methods do not result in additional ash inside the residues. The ash present in those samples was likely present in the feedstock.

Table CP-1.3. Compositional analysis of saccharification residual solids from different NARA pretreatments using NARA FS-03 feedstock (weight % values calculated on an oven dry basis)

	KL (acid insoluble) wt. %	KL (acid soluble) wt. %	Ash wt. %	Glucan wt. %	Arabinan wt. %	Galactan wt. %	Mannan wt. %	Xylan wt. %
CLE #1	67.7	2.1	7.80	20.6	< 0.45	< 0.45	< 0.45	< 0.45
CLE #2	67.7	2.4	7.35	18.6	< 0.45	< 0.45	0.80	< 0.45
SPORL (as rec'd)	68.4	2.2	5.73	21.1	< 0.45	< 0.45	0.89	0.53
(H_2O washed)	68.2	2.0	5.89	18.3	< 0.45	< 0.45	0.83	0.45
WOX (as rec'd)	55.8	1.0	2.02	37.0	< 0.45	< 0.45	0.95	1.00
(H_2O washed)	57.5	0.8	1.93	36.2	< 0.45	< 0.45	0.92	0.95
Dilute Acid	65.2	1.0	1.99	33.4	< 0.45	< 0.45	< 0.45	< 0.45

Table CP-1.4 shows the compositional analysis results for the SRS and FRS samples derived from NARA FS-10 feedstock, corresponding to the samples SRS and FRS samples listed in Table CP-1.2. By the time the co-products team had received these samples, the focus of the project had shifted to working specifically on FRS materials rather than SRS materials. For this reason, composition data was never obtained for a washed MBS SRS sample. If it had, a higher acid insoluble lignin content and lower glucan content than the as received sample would be expected. Similar trends in the lignin, carbohydrate, and ash contents were found with these samples as were found in the samples reported in Table CP-1.3. In this case, the wet oxidation pretreatment resulted in about a 50% lignin content in the FRS product. This appears to be due to the relatively high glucan content in that sample. Table CP-1.4 also includes compositional analysis data determined by the co-products team for the untreated NARA FS-10 feedstock for comparison. In addition, it also includes data from a milled wood FRS sample that was tested. Adjustments in the sugar quantitation method reduced the quantitation limit of the analysis so that all values reported in Table CP-1.4 are valid.

Table CP-1.4. Compositional analysis of saccharification and fermentation residual solids from different NARA pretreatments using NARA FS-10 feedstock (weight % values calculated on an oven dry basis)

	KL* (acid insoluble) wt. %	KL* (acid soluble) wt. %	Ash wt. %	Glucan wt. %	Arabinan wt. %	Galactan wt. %	Mannan wt. %	Xylan wt. %
Untreated FS-10	32.2	2.7	0.2	35.0	1.0	2.6	10.3	5.4
MBS SRS (as rec'd)	43.9	6.7	4.5	36.5	0.2	0.5	3.1	1.3
MBS FRS (as rec'd)	58.4	12.0	8.9	15.7	0.1	0.2	2.2	0.7
(H2O washed)	65.3	4.1	4.1	21.0	0.1	0.1	2.2	0.5
WOX SRS (as rec'd)	53.3	3.9	1.7	37.0	0.0	0.1	1.4	1.0
(H2O washed)	56.7	2.5	0.6	37.8	0.0	0.1	1.1	1.0
WOX FRS (as rec'd)	49.6	3.4	2.0	41.9	0.1	0.2	1.1	0.6
(H2O washed)	51.2	2.2	0.5	45.4	0.1	0.1	1.0	0.7
Milled Wood FRS	61.5	2.8		15.4	0.8	3.2	5.7	3.5

*Klason Lignin

Tables CP-1.5 and CP-1.6 show the elemental analysis data for the SRS and FRS residues produced using FS-03 and FS-10 feedstocks. The point of interest in this data is that the residues resulting from the bisulfite pretreatment methods (CLE, SPORL, and MBS) contained in elevated sulfur content. The small amount of nitrogen present in the samples is likely due to the presence of small amount of enzyme left over from enzymatic hydrolysis.

Table CP-1.5. Elemental analysis of saccharification residual solids from different NARA pretreatments using NARA FS-03 feedstock (weight % values calculated on an oven dry basis)

	Sulfur wt. %	Carbon wt. %	Hydrogen wt. %	Nitrogen wt. %	Oxygen* wt.%
CLE #1	3.3	53.7	5.4	0.2	37.4
CLE #2	2.3	54.1	5.6	0.3	37.8
SPORL	1.3	55.9	5.8	0.5	36.5
WOX	0.1	55.8	5.8	0.3	37.9
Dilute Acid	0.1	56.3	5.7	0.5	37.5

* Oxygen calculated by difference

Table CP-1.6. Elemental analysis of saccharification and fermentation residual solids from different NARA pretreatments using NARA FS-10 feedstock (weight % values calculated on an oven dry basis)

	Sulfur wt. %	Carbon wt. %	Hydrogen wt. %	Nitrogen wt. %	Oxygen* wt. %
Untreated FS-10	0.0	50.0	6.2	0.0	43.8
MBS FRS (as rec'd)	2.4	51.8	5.5	0.8	39.6
(H_2O washed)	1.8	54.7	5.5	0.8	36.9
WOX SRS (as rec'd)	0.0	55.5	5.7	0.4	38.3
(H_2O washed)	0.0	56.3	5.8	0.4	37.6
WOX FRS (as rec'd)	0.1	54.2	5.8	0.4	39.5
(H_2O washed)	0.0	55.1	5.9	0.4	38.5

* Oxygen calculated by difference

Isolation of lignin from FRS and SSL for analysis

As shown in the previous segment, the residues received by the co-products team were comprised primarily of lignin, but they also contained a substantial fraction of residual carbohydrate. These non-lignin components caused the FRS to possess low solubility in solvents typically effective for dissolving higher-purity lignin. This lack of solubility for the FRS presents a substantial barrier to chemical characterization of the material. Therefore, a method was developed to isolate high purity lignin from the FRS which would then be useful for chemical analysis. The method was adapted from the Enzymatic Mild Acidolysis Lignin (EMAL) procedure developed by Professor Argyropoulos' research group at N.C. State University to extract lignin from wood chips and Kraft pulp (Guerra, et al., 2006). In our method, the FRS was washed with water, dried, and Soxhlet extracted using acetone to remove wood extractives. The extracted FRS was then ball milled in a ceramic jar for 21 days. The resulting fine powder was subjected to enzymatic hydrolysis to remove as much of the remaining carbohydrate fraction as possible, and the lignin was extracted using an azeotrope of dioxane and water (85% dioxane/15% water, v/v) containing 0.01 M hydrochloric acid. The soluble and insoluble fractions were separated, and high purity lignin was precipitated from solution. An identical procedure was performed on untreated FS-10 forest residues prepared by Wiley milling to pass a 1 mm screen. The yields from this procedure and the isolated lignin purities are shown in Table CP-1.7.

Table CP-1.7. Yields and purity of isolated lignin

Sample	Enzymatic Hydrolysis Yield*	Lignin Extraction Yield**	Extracted Lignin Purity***
FS-10 Forest Residues	42.8%	52.4%	81.0%
Mild Bisulfite FRS	64.7%	52.5%	95.4%
Wet Oxidation FRS	86.4%	44.9%	94.2%

* mass of insoluble solids after hydrolysis (OD)/original sample mass (OD) x 100%
** Klason lignin content of isolated lignin/Klason lignin content of enzyme-treated sample x 100%
*** Klason lignin content of isolated lignin x 100%

The MBS pretreatment produces a second coproducts stream in the form of spent sulfite liquor (SSL), containing primarily water soluble lignosufonates and inorganics. High purity lignosulfonic acid can be isolated from the SSL using a procedure referred to as amine extraction (Ringena, et al., 2005). In this method, the SSL is treated using a liquid/liquid extraction using a 0.2 M solution of dodecylamine in 1-octanol. The dodecylamine complexes with the lignosulfonate in the SSL and pulls it into the organic phase, and the aqueous phase is discarded. The lignosulfonate is then separated from the dodecylamine and pulled back into aqueous solution by a second liquid/liquid extraction with 0.4 M aqueous sodium hydroxide. The aqueous lignosulfonate solution is treated with an acidic cation exchange resin to remove the sodium, after which the solution is dried to complete a nearly quantitative separation of high purity lignosulfonate from the original SSL.

Table CP-1.8 displays the elemental analysis data for the isolated lignins. Unsurprisingly, the lignins isolated from MBS pretreated materials contained substantially more sulfur than lignin isolated from WOX pretreated materials or the untreated FS-10 feedstock. The sulfur content for the lignosulfonic acid isolated from the MBS SSL at 8% is higher than what is typically expected from a softwood lignosulfonate (around 6%).

Table CP-1.8. Elemental analysis of isolated lignins (wt%)

Sample	Sulfur	Carbon	Hydrogen	Nitrogen	Oxygen
FS-10 Lignin	0.032%	61.0%	6.0%	0.07%	32.9%
Wet Oxidation FRS lignin	0.096%	64.9%	5.3%	0.96%	28.7%
Mild Bisulfite FRS lignin	1.13%	63.3%	5.7%	1.01%	28.9%
Mild Bisulfite lignosulfonic acid	8.10%	52.1%	4.8%	0.36%	34.7%

The hydroxyl group content of the isolated lignins was determined using quantitative ^{31}P NMR. The lignin samples were prepared by derivatizing them with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, which reacts readily with the hydroxyl groups in lignin. The chemical environment of hydroxyl groups can then be determined by NMR chemical shift of the attached phosphorous nucleus. Table CP-1.9 displays the data from this analysis. There is a marked decrease in the number of aliphatic hydroxyl groups and an increase in the number of aromatic hydroxyl groups between the untreated FS-10 lignin and the lignin isolated from the pretreated samples. This is consistent with trends previously reported in the literature on biomass samples that have undergone various pretreatments for biofuel production. The C-5 substituted OH column is a subset of the aromatic OH. This column gives an indication of the degree to which lignin sub-units react and re-condense during pretreatment, and higher degrees of condensation are generally related to lower solubility of the lignin. The data in Table CP-1.9 indicates only a slight increase in the degree of condensation for the lignin isolated from the MBS FRS compared to the untreated FS-10 lignin.

Table CP-1.9. Hydroxyl group contents of isolated lignins (mmol/g)

Sample	Aliphatic OH	Aromatic OH	C-5 Substituted OH	COOH
FS-10 Lignin	4.31	2.56	1.45	0.03
Wet Oxidation FRS lignin	1.93	4.18	1.32	0.21
Mild Bisulfite FRS lignin	1.38	4.37	1.66	0.22
Mild Bisulfite lignosulfonic acid	2.42	5.69	1.73	0.10

Conclusions/discussion

Further efforts have been made to characterize the MBS and Wet Ox FRS and corresponding isolated lignins by 2-dimensional 1H-13C HSQC NMR spectroscopy. This analytical technique is powerful for examining the different chemical linkages between monolignol units, and it is becoming a common method in lignin and biomass analysis. This would be possible for the lignins isolated from the FRS since it was found that they are soluble in dimethyl sulfoxide (DMSO), which is a suitable NMR solvent. The FRS themselves were not soluble, though it was found that ball-milled FRS could be made soluble by acetylating them with acetic anhydride in DMSO/N-methylimidazole (DMSO/NMI, 2:1). Unfortunately, the analysis was hindered by difficulty in scheduling suitable instrument time. We recommend that this analysis be pursued further after the Weyerhaeuser NARA co-products research team exits from NARA, as this analysis could provide a wealth of information about the lignin chemistry. One potential avenue would be to use instruments available at the WSU NMR laboratory, which according to a previous inquiry has instrumentation suitable for this analysis.

Attempts have also been made to characterize the molecular weight distributions of the isolated lignins using size exclusion chromatography/multi angle light scattering (SEC-MALS). Originally the lignins isolated from the FRS and the untreated FS-10 were reacted with acetyl bromide in acetic acid to prepare a derivative soluble in tetrahydrofuran (THF). However, the acetylbromination reaction with the untreated FS-10 lignin was the only one of the three that was successful. Next, the FS-10 lignin, MBS FRS lignin, and the Wet Ox FRS lignin was subjected to acetylation with acetic anhydride in pyridine. The reaction with the MBS and Wet Ox FRS lignins was successful, but the reaction with the FS-10 lignin never went to completion (i.e. never became homogeneous in the reaction solution). Of the acetylated MBS and Wet Ox FRS lignins, only the acetylated Wet Ox FRS lignin was soluble in THF, while the acetylated MBS FRS lignin was not soluble in THF. To facilitate a direct comparison between the isolated lignins (excluding the lignosulfonate), attention was then turned to using N,N-dimethylformamide (DMF) with 10mM LiBr as the mobile phase for the SEC-MALS analysis. All three lignins dissolve in the DMF/LiBr solvent system. The refractive index increment (dn/dc) at 785 nm in this solvent system was determined to be 0.209 mL/g and 0.179 mL/g for the Wet Ox FRS lignin and MBS FRS lignin, respectively. The experiment to determine the dn/dc for the FS-10 lignin was inconclusive and needs to be re-run. The results of the SEC-MALS analysis show a very narrow polydispersity index and low mass recovery of the sample, indicating that more method development is needed for reliable results.

TASK 2. CONVERT LIGNIN TO HIGH SURFACE AREA ACTIVATED CARBON

Introduction

The development of valuable co-products from lignin-rich residues (SRS, FRS, and lignosulfonate) of the jet fuel production process was a key objective of the Weyerhaeuser Co-Products team. Of particular importance in selecting the proper applications for these residues was identifying applications with large existing and growing markets, and with production processes that could realistically be deployed at a large scale. Lignosulfonates have some established markets, so it was assumed that the lignosulfonates could most effectively be used for traditional applications such as concrete additives. The insoluble lignins (FRS and SRS) presented a more complex problem due to their physical characteristics. After consideration of a few alternatives, the NARA Co-Products team decided to pursue the production of activated carbon (AC) materials from FRS/SRS. This decision was based on a few important criteria:

1) The world market for AC materials is relatively large, roughly 1 million metric tons annually. The largest market is water treatment, followed by air and gas purification. There are also a multitude of other niche markets that use AC, mostly as an adsorbent for the separation of trace impurities from mixtures.
2) Increasing environmental awareness among the public and regulatory actions aimed at reducing harmful emissions are creating new markets for AC materials in emissions control. For example, a significant market opportunity for AC is emerging in control of mercury emissions from coal-fired power plants. This increased demand is driven by the EPA Mercury Air and Toxics Standard (MATS). MATS will require control of mercury emissions by coal-fired power plants starting in April 2015 (or April 2016, if an extension is used). AC injection is one of the most developed technologies for mercury capture from coal combustion flue gas.
3) Emerging markets for AC such as porous electrode materials for electrochemical capacitors are being researched extensively and could grow considerably in the coming years.
4) The AC production process is proven at commercial scale. The process consists basically of pyrolysis/carbonization at temperatures in the 600-1000°C range followed by activation to increase the porosity and surface area. Specific details of the process are largely dependent on the characteristics of the precursor and the desired characteristics of the end product.
5) Lignocellulosic materials such as wood and nutshells are known precursors for AC. In addition, lignin-rich feedstocks are known to have a higher char yield compared to those higher in cellulose and hemicellulose, resulting in a favorable increase in yield of AC per unit of precursor input.

Two activation strategies were studied to convert the SPORL fermentation residual solid into Activated Carbons. The physical activation was used to produce mesoporous ACs for mercury removal. The chemical activation strategy with KOH and H_3PO_4 was used to produce microporous AC for H_2S removal. Characterizing the properties such as surface area, pore volume, and pore size distribution of the AC material produced under different activation conditions was essential in order to generate an understanding of the relationship between the AC properties and the performance in specific applications.

Physical activation

In the period from June 2015 – June 2016, the first priority was moving toward completion and submission of a manuscript on the preparation of mesoporous AC by physical activation and its application in the capture of elemental mercury (Hg^0) from simulated coal combustion flue gases. A manuscript with the results of these studies was submitted to Energy & Fuel in May 2016. Also during this period, a non-provisional patent application was submitted on the process for making mesoporous AC from FRS using physical activation.

In September of 2015, a final round of mercury adsorption testing was conducted in the Process Chemistry lab at AECOM (formerly URS Corp.) in Austin TX. AC materials used in this final round of testing were prepared from calcium-SPORL fermentation residual solids (FRS) using conditions determined experimentally in a previous work. The char was first prepared by heating 2.5 g of FRS powder at a heating rate of 10 °C/min to 700oC under a flow of nitrogen gas (0.5 $L.min^{-1}$) in a 3-zone tube furnace (Lindberg Blue M). The FRS was held isothermally for 1 hour under N2 flow at 700oC for charring. After cooling the system to room temperature, the char was removed from the furnace and ground with mortar and pestle to break up larger particles, sieved through an 80 mesh screen, and then returned to the furnace for activation. The char was heated under N^2 flow at 10°C/min up to 700°C and the gas flow was switched to CO_2 at a flow rate of 0.1 L.min-1 and allowed to activate for 90 minutes at 700oC. After activation, the AC powders were further ground with mortar and pestle to pass a 325 mesh (45 mm) screen. This process was repeated three times and the average overall yield of AC based on initial FRS weight was 22.3%.

Three samples were prepared using the conditions above and submitted to AECOM along with two samples of a commercially available coal-based AC used for mercury capture (Darco Hg). The breakthrough curves for the individual samples and a summary of the results are shown in Figure CP-2.1 and Table CP-2.1, respectively.

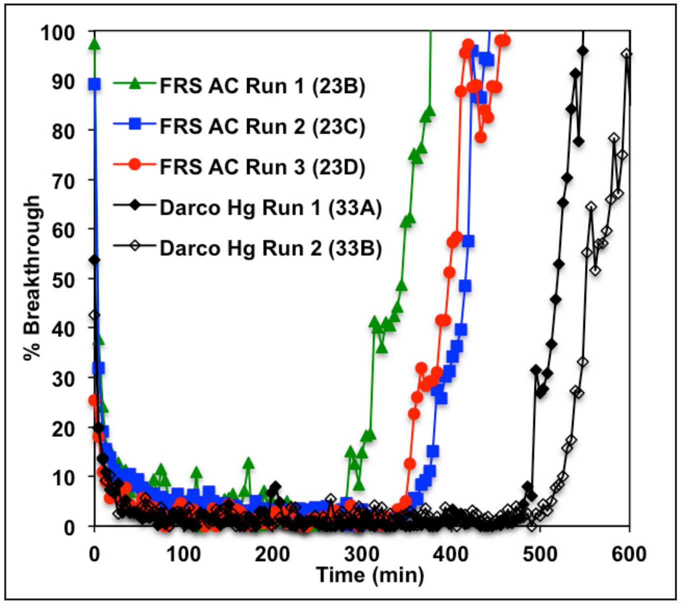

Figure CP-2.1. Breakthrough curves showing the percentage of inlet Hg^0 concentration detected at the outlet of the AC bed during fixed bed adsorption testing.

Another task during this period was to evaluate new lignin samples for conversion to AC by physical activation. This task was necessary because the supply of FRS used in previous work was nearly used up. Only a few tens of grams of this material is available and is being stored as a reference material. Previously, all experiments were performed with FRS obtained in February 2014 from a pretreatment/ fermentation process that used calcium bisulfite-based SPORL pretreatment with a pretreatment residence time of 240 minutes and temperature of 145°C (herein referred to as Ca-FRS). However, these conditions were not the same as the conditions the conversion team was planning to use for the 1000-gallon pilot trial being planned to demonstrate scale-up of biojet fuel production. There was concern in the NARA Co-Products group that the changes in the pretreatment conditions such as cation (Mg instead of Ca), time and temperature would change the qualities of the lignin produced for conversion to AC, so a sample of the SRS (saccharification residual solids) produced in small scale runs conducted at ZeaChem was requested. The exact conditions for production of this material were not known to the NARA Co-Products group, but it has been communicated to us that the cation was Mg^{2+}, the temperature used was higher, around 180-185°C, and the residence time was considerably shorter, somewhere around 45 minutes. This material was assumed to be representative of the SRS that would be produced in the 1000-gallon pilot trial run. This SRS was delivered with a label reading "NARA FS-20 NR03 ZeaChem Resid. Solids 150903," but herein we will refer to this material as "ZC Mg-SRS".

Table CP-2.1. Comparison of porosity and mercury capture performance for FRS AC and Darco Hg. (SBET = Apparent BET surface area, V_{total} = total pore volume measured by N_2 adsorption, V_{meso} = Mesopore volume calculated by NLDFT, V_{micro} = Micropore volume measured with NLDFT). Average percent Hg^0 removed calculated as average of data points from breakthrough curves between first drop below 10% breakthrough and final point before 10% breakthrough was reached as saturation was approached.

Carbon	**S_{BET} (m^2/g)**	**V_{total} (cm^3/g)**	**V_{meso} (cm^3/g)**	**V_{micro} (cm^3/g)**	**Inlet [Hg^0] in flue gas (mg Hg^0/Nm^3)**	**Equilibrium Hg^0 Adsorption Capacity (mg Hg^0/g AC) @ 50 mg Hg/Nm^3**	**Average Percent Hg^0 Removed (%)**
Darco Hg	660	0.718	0.474	0.209	21.8	1133	98.5
Darco Hg	660	0.718	0.474	0.209	26.5	1226	97.8
FRS AC 1	659	0.621	0.402	0.188	27.0	674	95.1
FRS AC 2	686	0.670	0.442	0.191	25.9	863	96.0
FRS AC 3	682	0.665	0.440	0.189	21.8	857	97.6
Average (FRS AC)	**676**	**0.652**	**0.428**	**0.189**	**24.9**	**798**	**96.2**

AC was first prepared with the same conditions described above (700°C, 90 minutes under CO_2, herein referred to as the "standard activation conditions") and compared with the results obtained using calcium-based FRS produced in earlier work. The char yield for the ZC Mg-SRS was similar to previous results (40.5%), but the reactivity toward physical activation was significantly lower than Ca-FRS. Using the standard activation conditions, a burn-off of only 12.5% was observed for ZC Mg SRS char compared to ~45-50% for Ca-FRS char. Additional experiments were also conducted to understand differences in the porosity development at higher degrees of burn-off. Activations were also carried out for 300 minutes and 390 minutes, and burn-offs of 32.5% and 41.7% were reached, respectively. These AC samples were then characterized by N_2 and CO_2 adsorption to characterize their porosity as described in previous reports. Nitrogen adsorption isotherms for these materials are shown in Figure CP-2.2. Compared with previous materials prepared from Ca-FRS, it is clear from the isotherms shown in Figure CP-2.2 that ZC Mg-SRS produces AC materials with very different porosity compared to AC produced from Ca-FRS. This difference can be discerned by the absence of adsorption-desorption hysteresis loops and the higher N_2 uptake at low pressure, indicating a predominantly microporous carbon.

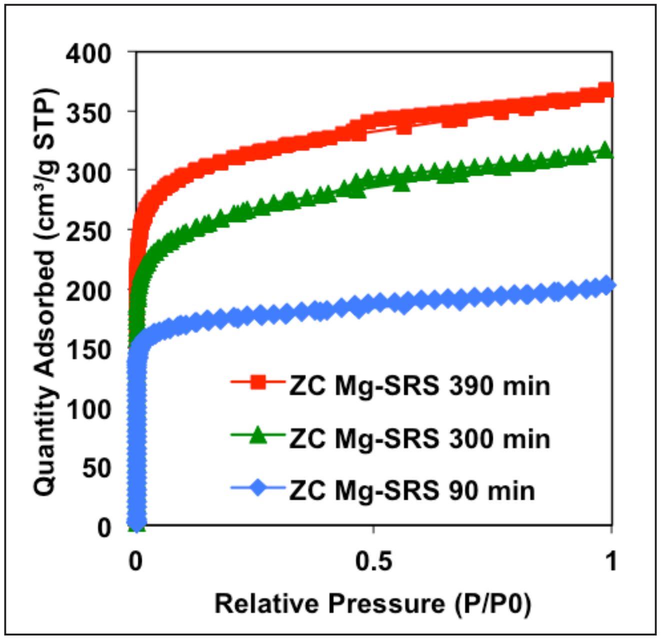

Figure CP-2.2. Nitrogen adsorption isotherms of AC materials prepared from ZC Mg-SRS at 700°C using activation times of 90, 300, and 390 minutes.

Because the results of experiments with ZC Mg-SRS were so different than previous experiments and because the supply of lignin feedstock for mesoporous AC was very low, a new sample of SRS was requested from FPL. It was requested that the same conditions from previous work be used for pretreatment be used in order to allow us to produce more mesoporous AC for adsorption experiments. This sample was herein referred as FPL Ca-SRS. Again the standard activation conditions were used to prepare AC, and it was confirmed that mesoporous AC can be produced from SRS produced under these conditions. We also prepared AC from another Mg-based SRS material delivered to WSU from FPL in March 2015 (pretreatment conditions: Mg2+, 140°C, 120 minutes residence time), again using the standard activation conditions. This material (herein referred to as "FPL Mg-SRS") also produced a mesoporous AC. Figures CP-2.3 and Cp-2.4 are shown to facilitate comparison of the pore size distributions of the AC materials prepared from the four samples discussed previously (Ca-FRS, FPL Ca-SRS, ZC Mg-SRS, and FPL Mg-SRS). While slight differences can be seen among the AC materials, it was clear that the ZC Mg-SRS material behaved much differently than the other SPORL-based FRS and SRS samples. This was true even considering the slightly different degrees of burn-off for the various samples. A summary of the sample preparation conditions, char yield and burn-off, and porosity of these four samples are shown in Table CP-2.2.

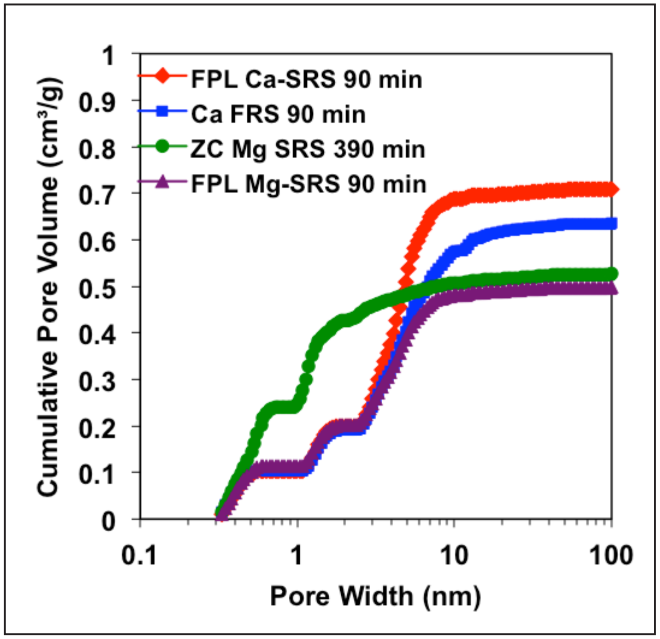

Figure CP-2.3. Cumulative pore volume vs. pore size in the pore size range 0.3 – 100 nm (logarithmic scale) for AC materials prepared from 4 different samples of SPORL residual lignin (Ca-FRS, FPL Ca-SRS, FPL Mg-SRS, and ZC Mg-SRS)

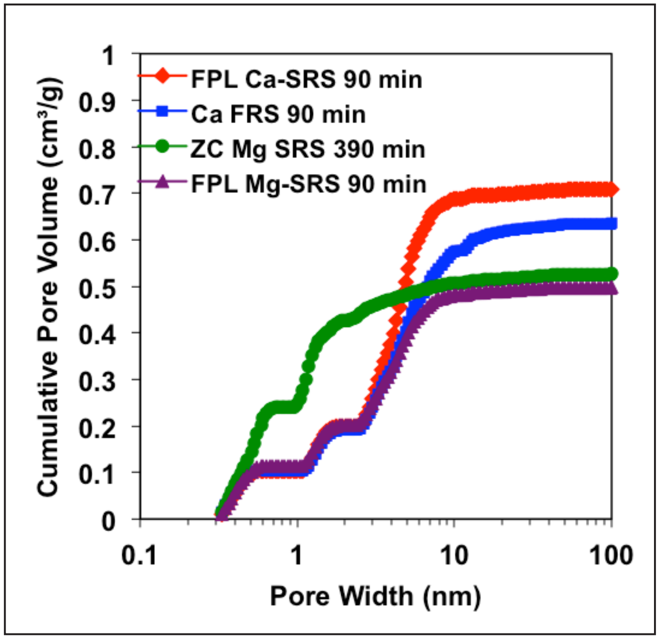

Figure CP-2.4. Differential pore volume vs. pore size in the pore size range 0-10 nm (linear scale) for AC materials prepared from 4 different samples of SPORL residual lignin (Ca-FRS, FPL Ca-SRS, FPL Mg-SRS, and ZC Mg-SRS)

Table CP-2.2. Comparison of porosity for Ca-FRS, FPL Ca-SRS, FPL Mg-SRS, ZC Mg-SRS (S_{BET} = Apparent BET surface area, V_{total} = total pore volume measured by N_2 adsorption, V_{meso} = Mesopore volume calculated by NLDFT, V_{micro} = Micropore volume measured with NLDFT).

Sample	Char yield (%)	Activation Time (min)	Burn-off (%)	S_{BET} (m^2/g)	Total Pore Volume (cm^3/g)	Mesopore Volume (V_{meso}, cm^3/g)	Micropore Volume (V_{micro}, cm^3/g)	V_{meso}/V_{micro}
Ca-FRS	42	90	46.5	676	0.652	0.428	0.189	2.26
FPL Ca-SRS	40.8	90	44.2	769	0.742	0.501	0.202	2.48
FPL Mg-SRS	35.7	90	37.7	662	0.519	0.296	0.201	1.47
ZC Mg-SRS	40.5	390	41.7	1172	0.569	0.098	0.427	0.23

Chemical Activation

In the summer 2015, the NARA co-products team started to study the use of chemical activation as a way to produce activated carbons rich in micro-pores. Two activation chemical agents were tested: KOH and H_3PO_4. The application targeted with these new activated carbons is the production of supercapacitors and the removal of H_2S from flue gases. In this section we describe the progress made in the production and characterization of chemically activated carbons.

Activation with KOH

The first chemical activation method studied was with potassium hydroxide (KOH). KOH activation is typically used for the preparation of highly microporous carbons. Chemically activated carbons with very high surface area and pore volume were made from a slightly different type of lignin compared to the FRS mentioned above due to unavailability of enough Ca^{2+} FRS. This material was SPORL pretreated with Mg^{2+} at unknown conditions and saccharified, but not fermented, so this material will be referred to as Mg^{2+} saccharification residual solids (Mg^{2+} SRS).

AC was prepared in a tube furnace from oven-dried SRS under 9 different activation conditions using activation temperatures (herein denoted T_{act}) of 700, 750, and 800°C and KOH:SRS weight ratios of 2, 3, and 4. Prior to being heated in N_2 atmosphere, mixtures of SRS and KOH were made by physical mixing of dry SRS powder and an appropriate volume of 50% aqueous solution of KOH to reach the desired KOH:SRS ratio. The mixtures were oven-dried overnight at 105°C to remove water. The oven-dried mixture was then transferred to the tube furnace and heated at 10 °C/min to 150°C and held for 1 hour to drive off moisture, then the sample was heated further at 10 °C/min to the final temperature (700, 750, or 800°C) and held for another hour. After cooling to room temperature under N_2 atmosphere, the samples were washed with water and HCl (10% w/w) to remove the KOH. The AC materials were characterized as in previous work with gas physisorption analysis in terms of their surface area, pore volume, and pore size distribution. An AC was also prepared by physical activation of the same starting material (Mg^{2+} SRS) to compare the effect of physical vs. chemical activation on the porosity. The data obtained from gas physisorption analysis is shown in Table CP-2.3.

Table CP-2.3. Porosity data for AC made from KOH activation of Mg^{2+} SRS

Type of Activation	Maximum Temperature (°C)	KOH: Lignin ratio (w/w)	Total Pore Volume (cm^3/g)	Mesopore Volume (cm^3/g)	Micropore Volume (cm^3/g)	Mesopore/ Micropore Ratio (v/v)	Apparent BET surface area (m^2/g)
Physical (CO_2)	700	n/a	0.37	0.05	0.29	0.17	791
Chemical (KOH)	700	2	0.78	0.07	0.63	0.11	1719
Chemical (KOH)	700	3	0.92	0.08	0.73	0.11	1989
Chemical (KOH)	700	4	0.74	0.04	0.62	0.06	1705
Chemical (KOH)	750	2	1.13	0.19	0.83	0.23	2236
Chemical (KOH)	750	3	1.22	0.20	0.91	0.22	2405
Chemical (KOH)	750	4	1.41	0.43	0.84	0.51	2487
Chemical (KOH)	800	3	1.20	0.51	0.55	0.93	1691

The data in Table CP-2.3 show that very high values of surface area and pore volume as high as 2487 m^2/g and 1.4 cm3/g, respectively, can be obtained with KOH activation of Mg^{2+} SRS. Setting T_{act} = 700°C produced materials with relatively narrow micropore size distribution whereas increasing T_{act} to 750°C resulted in a wider pore size distribution and higher surface area. Increasing T_{act} to 800°C appeared to negatively affect the pore volume and surface area. The effect of the KOH:SRS ratio was not as pronounced as the effect of temperature although increasing the amount of KOH did slightly increase the total pore volume at T_{act} = 750°C. At 700°C the highest total pore volume was obtained at a KOH:SRS ratio of 3 and the value decreased at a KOH:SRS ratio of 4. Taken together these results show that chemical activation with KOH is an effective method to generate very highly activated microporous AC from SRS.

In addition, an interesting result of the chemical activation experiments was observed by SEM, as shown in Figure CP-2.5. Figure CP-2.5 shows that in addition to the microporosity, KOH-activated materials also have macroporosity with pore dimensions in the micrometer size range. This finding is significant because macropores are known to play an important role in the rapid transport of adsorptive species to the adsorption sites. Chemical activation is therefore one interesting route to obtain macroporosity in AC materials.

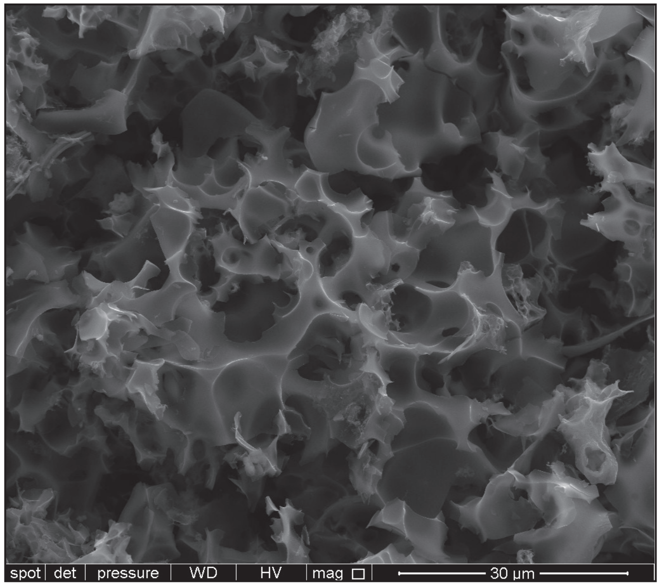

Figure CP-2.5. SEM image of AC made from Mg^{2+} SRS by chemical activation with KOH. Scale bar = 30 mm.

It is also of interest to highlight the results of physical activation of the SRS material used in KOH activation experiments (Table Cp-2.3, first entry). Physical activation of the Mg^{2+} SRS with CO_2 at 700ºC to 50% burn-off produced a microporous material with less than half the pore volume and surface area compared to the chemically activated materials. This physically activated material had considerably lower mesoporosity than previous materials prepared from either Ca^{2+} or Mg^{2+} FRS. This finding highlights the importance of understanding the effect of the SPORL pretreatment conditions and subsequent processing on the characteristics of the AC precursor.

Activation with H_3PO_4

The chemical activation studies with phosphoric acid started in January 2016 after the transfer of the research activities of this task from Dr. Dallmeyer to Dr. Suliman. The main goal was to produce high surface area activated carbon from the Ca^{2+} BS SRS by chemical activation and to optimize the production/activation conditions. Six different experiments were designed to prepare AC materials using H_3PO_4 as activation agent. The NARA lignin received (Ca^{2+} BS SRS), was washed, dried, grounded and sieved to a particle size of approximately 200 micron. The lignin was mixed with H_3PO_4 and kneaded for one hour, the mixture was then dried at 105 °C to prepare the impregnated samples that were subjected to activation at temperatures between 500 and 1000 °C. The AC materials were washed sequentially with hot water to remove residual chemicals, and then dried at 110ºC. Both N_2 and CO_2 adsorption isotherms were measured on each AC sample to quantify its porosity, mainly surface area, pore volume, and pore size distribution. Prior measuring the isotherms, the AC samples were degassed at 300ºC for 12 hours to clean its surface from any adsorbed component.

Figure CP-2.6 shows the yield of activated carbon obtained as a function of pyrolysis temperature for (H_3PO_4/NARA lignin ratio: 3). The yield of activated carbon is a very important parameter defining the economic viability of AC production.

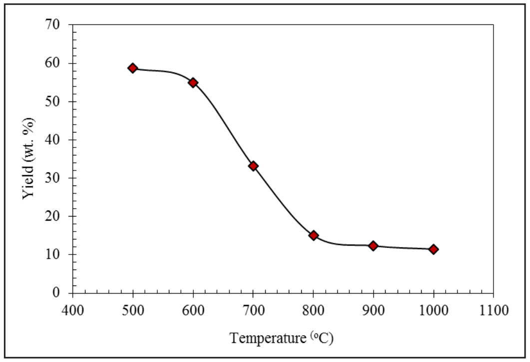

Figure CP-2.6. Yield of activated carbon as a function of pyrolysis temperature (H_3PO_4/NARA lignin ratio: 3)

Figure CP-2.7 shows the effect of final temperature and time at the final temperature (herein reported as activation time) on the surface area and pore volume of AC produced with H_3PO_4/NARA lignin ratio of 3. Clearly an increase in activation temperature did not result in higher surface areas and pore volumes. Higher temperatures also resulted in lower yields.

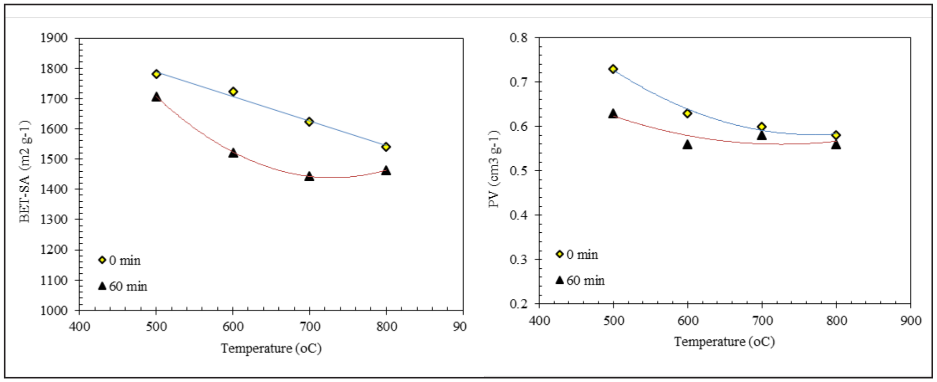

Figure CP-2.7. Effect of activation temperature on the surface area of resulting AC

The NARA Co-products Team also studied the effect of H_3PO_4 concentrations on the surface area and pore volume of resulting ACs. Series of activated carbons were prepared at 700°C for one hour residence time under N_2 flow at the rate of 0.5 l/min. Four concentrations of H_3PO_4 (25, 45, 65, and 85%) were used to compare the effect of increased H3PO4 concentration on the surface area and pore size, since both characteristics are critical in the performance of AC. The effect of sulfuric acid concentration on the yield of resulting AC is shown in Figure CP-2.8.

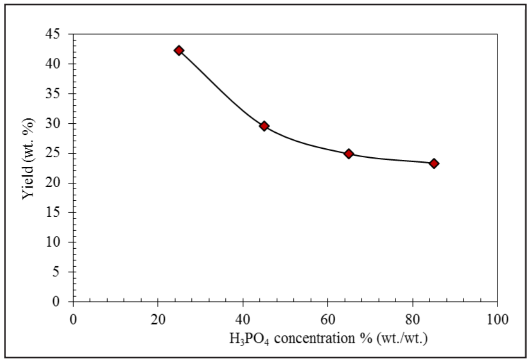

Figure CP-2.8. Effect of H_3PO_4 concentration on the yield of AC (H_3PO_4/NARA lignin ratio: 3, temperature: 700 °C)

Figure CP-2.9 shows how that the degree of activation (surface area and pore volume) increases as the H_3PO_4 concentration augment. Therefore, the AC obtained by activating lignin at 85% H_3PO_4 present well-developed porosity, with 1246 m^2/g of surface area and 0.45 cm^3/g of pore volume. Although higher concentrations of H_3PO_4 resulted in AC lower yields they have an effect of increasing the surface area of the AC produced.

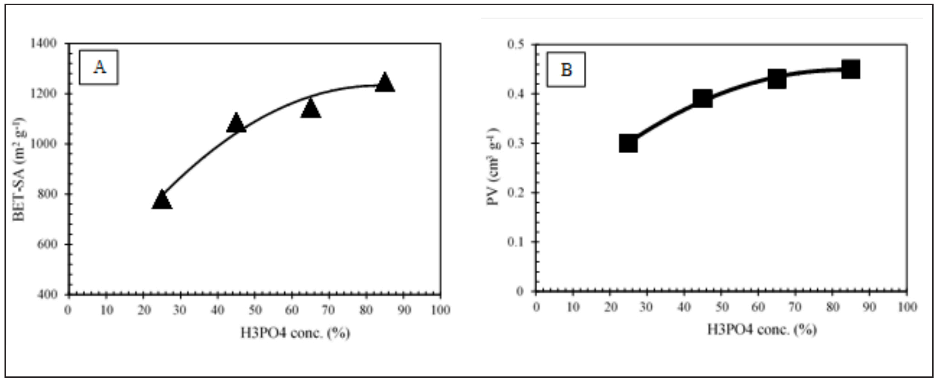

Figure CP-2.9. Effects of phosphoric acid concentration (P conc.) on: (A) the apparent BET-surface area (BET-SA), and (B) pore volume (PV) of the activated carbons produced from NARA lignin (700 °C)

Alone the same lines, the co-products team studied the effect of impregnation ratio and activation time (time at the final temperature) on the yield, surface area and pore volume (PV) of ACS. In this study the H_3PO_4/Lignin (P/L) ratio was changed: 1, 2, and 3 (The results are shown in Figure CP-2.10). The impregnated samples were heated up to 700°C at the rate of 10°C/min and held at the final temperature for one hour. Each lignin sample was mixed thoroughly with the H_3PO_4 and headed for one hour before oven drying.

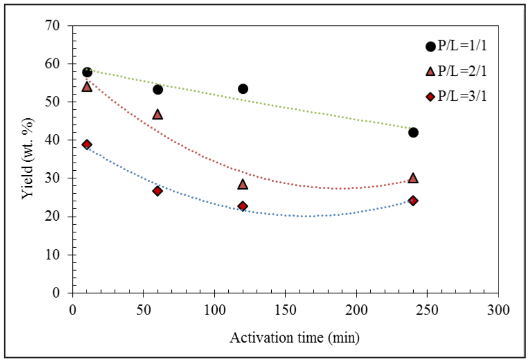

Figure CP-2.10. Effect of Activation Time and H_3PO_4/Lignin (P/L) ratio on AC yield.

The effect of activation time (residence time at final temperature) on the surface area (SA) and pore volume is shown in Figure CP-2.11. The surface area and pore volumes decreased as the activation time increases. Giving that both the residence time and the surface area decrease when increasing the residence time it is clear that holding the samples at the final temperature does not provide any positive effect and on the contrary will result in higher operational costs.

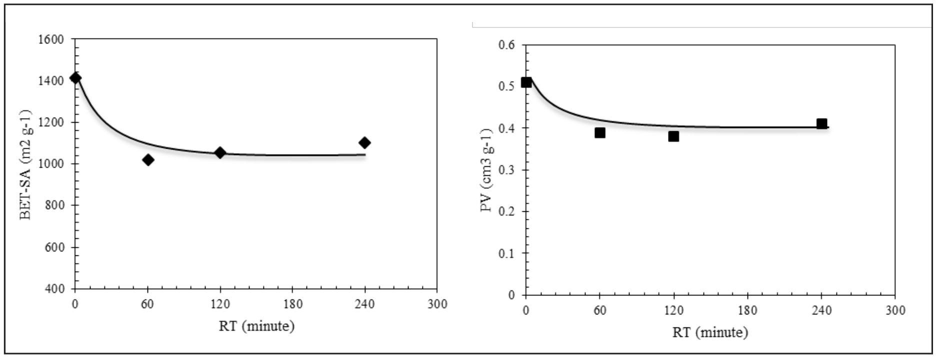

Figure CP-2.11. Effects of residence time (activation time) on: (A) the apparent BET-surface area (BET-SA), and (B) pore volume (PV) of the activated carbons produced from NARA lignin. Lignin samples were firstly impregnated with 85% phosphoric acid for 1 hour with a P/L ratio of 3. The carbonization process was carried out at 700°C under N_2 flow with 10°C/min of heating rate. Periods of 0, 60, 120, and 240 minutes were used to evaluate the effect of residence time on the ACs characteristics.

The surface area and pore volume of ACs prepared at different P/L ratios are shown in Figure CP-2.12. The results revealed that both SA and PV increase as the P/L ratio increase.

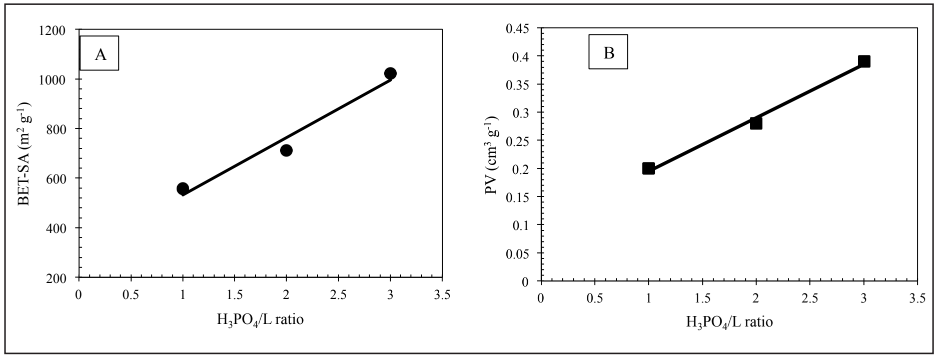

Figure CP-2.12. Effects of phosphoric acid/ lignin (P/L) ratios on: (A) the apparent BET-surface area (BET-SA), and (B) pore volume (PV) of the activated carbons produced from NARA lignin.

The potential effect of intermediate heat treatment, intermediate residence time, and CO_2 on the surface area (SA) and pore volume (PV) of ACs was also studied. These experiments were conducted in parallel to evaluate the influence of the intermediate heat treatment of activation and its intermediate residence time in presence of CO_2 flow on AC porosity development. Briefly, 500 and 700°C were selected to be intermediate and final temperatures, respectively. The H_3PO_4 impregnated material was first heated up to 500°C for certain intermediate time and then heated up to 700°C for final residence time. In case of using CO_2 (used as a combination between physical and chemical activations), the sample was brought into contact with CO_2 at the cooling stage from 700 to 100°C. The results of these experiments are shown in Table CP-2.4. The results showed that activated carbon produced at 700°C, with 500°C as an intermediate heat treatment, has the maximum surface area (≈ 1250 m^2/g), including the external or non-micropores surface area of 140 m^2/g. The resultant activated carbons were found to be essentially microporous carbons, regardless the activation conditions used. The findings showed that the surface area, microporosity, and mesoporosity of lignin-based activated carbons could be tuned by controlling the activation parameters; mainly, acid to lignin ratio, temperature, and duration of exposure to heat.

Table CP-2.4. Effects of intermediate heat treatment, intermediate residence time, and CO_2 on the surface area (SA) and pore volume (PV) of ACs.

		Heat treatment		Residence Time (RT)		SA and PV (N_2)	
P/L ratio	CO_2	Intermediate Temp. T1 (°C)	Final Temp. T2 (°C)	RT for T1 (min)	RT for T2 (min)	BET-SA (m2/g)	PV (cm3/g)
1	0.1 l/min	500	700	60	5	410	0.16
2	0.1 l/min	500	700	60	5	778	0.31
3	0.1 l/min	500	700	60	5	875	0.34
1	Non	500	700	60	5	558	0.20
2	Non	500	700	60	5	712	0.28
3	Non	500	700	60	5	1021	0.39
1	0.1 l/min	500	700	60	60	526	0.21
2	0.1 l/min	500	700	60	60	923	0.35
3	0.1 l/min	500	700	60	60	1246	0.45
1	Non	500	700	60	60	540	0.23
2	Non	500	700	60	60	983	0.36
3	Non	500	700	60	60	1054	0.38
1	0.1 l/min	500	700	5	60	555	0.21
2	0.1 l/min	500	700	5	60	1054	0.40
3	0.1 l/min	500	700	5	60	1244	0.45
1	Non	500	700	5	60	405	0.12
2	Non	500	700	5	60	1009	0.38
3	Non	500	700	5	60	1026	0.38
1	0.1 l/min	500	700	180	60	712	0.27
2	0.1 l/min	500	700	180	60	1204	0.44
3	0.1 l/min	500	700	180	60	1356	0.49
1	Non	500	700	180	60	701	0.28
2	Non	500	700	180	60	986	0.38
3	Non	500	700	180	60	1104	0.41

Based on our experimental results the conditions recommended for the production of AC are: *Activation Temperature: 500 °C, Retention time at final temperature: 1 min,* H_3PO_4*/lignin ratio: 3,* H_3PO_4 *concentration: 85 wt. %. These conditions will be used in our techno-economic analyses.*

We did some preliminary studies comparing the capacity of the AC produced with a commercial product to remove H_2S from biogas and methylene blue from water. A flow-through system was used to evaluate the H_2S adsorption capacities of NARA-500/0 (our developed NARA-lignin-based activated carbon) and Norit M-2058-H_2S (a commercial activated carbon made specifically for H_2S removal). In brief, a glass tube (5.0 mm O.D. × 120 mm length, 4.0 mm I.D.) was packed with 1000-1100 mg of each activated carbons (NARA-500/0 and Norit M-2058-H_2S) between glass wool plugs, followed by conditioning for 1 h under helium flow (100 mL/min). The adsorbent tube was connected to the GC injection port in which the H_2S was periodically detected in the effluent from the adsorbent tube. We determined the H_2S breakthrough time, breakthrough volume and specific breakthrough volume of both activated carbons used. The specific breakthrough volume is defined as the breakthrough volume (L) divided by the quantity of the activated carbon (g). From these results we found that the breakthough time for NARA-500/0 (11 days) is longer than that of Norit M-2058-H_2S (8 days), which related to the adsorption affinity between the adsorbent used and the H_2S. These are very promising results.

TASK 3. STUDY OTHER POTENTIAL USES OF NARA LIGNIN

The NARA Co-products Team also worked to develop a wider variety of activated carbon products from lignin in addition to the powdered AC products described above. More specifically, we worked on the development of granular, activated carbon products from lignin. The motivation was twofold: 1) whereas powdered AC typically sell for $1/lb or less, granular carbon selling prices are in the range $1.00 – $4.00/lb, and 2) insoluble lignin after saccharification typically takes the form of a "mud" with 50-70% moisture content that can very easily be formed into granules or blocks by simply molding them into the desired size and shape without the need for any additional binder. Initial carbonization experiments indicate that the granules can also retain their form after carbonization (not necessarily true of other types of lignin). The photographs in Figure CP-3.1 and CP-3.2 show SRS granules before and after carbonization, respectively. The photographs in Figures CP-3.1 and CP-3.2 show that SRS can be converted to char granules without any binder, which may allow an inexpensive route to the production of low cost granular AC based on lignin.

Figure CP-3.1. SRS granules before carbonization.

Figure CP-3.2. SRS char granules after carbonization at 700°C.

TASK 4. TECHNO-ECONOMIC ANALYSIS

We conducted the techno-economic analyses of all the three technologies studied for activated carbon production (chemical activation: H_3PO_4, KOH and physical activation).

Physical activation

The fermentation residue solids (FRS) is collected after Douglas-fir forest residuals were pretreated in calcium bisulfite pretreatment method with a solid content of 8.2%. The excess water is removed in two steps – centrifugation and drying. The dried solids are available at 40 tons per hour. These solids are then transferred to a physical activation process area. Following are a brief description of physical activation process: **(1)** In a flow rate of 40 tons/hr, the dried solids are carried to a rotary kiln where pyrolysis occurs at 700°C for 1 hour. The char yield was 42.7%. The rest was off gas which vented to the furnace for combustion purposes. The dimension of the rotary kiln was 2.9 m X 8.7 m. **(2)** The char was conveyed to another rotary kiln for activation. The activation process carried out in 700°C for 90 minutes. The yield was reported to be 53% of the incoming char which is 23% of the FRS feedstock. This kiln has the same dimension as the previous one **(3)** The physically activated carbon was conveyed to a rotary cooler for 2 hours. The dimension of the rotary cooler is 1.8 m X 5.3 m **(4)** A sieve tray is assigned to screen all the specified fines. 5% of the solid fines are lost in this stage. A summary of the operational parameters of the physical activation process studied is shown in Table CP-4.1.

Table CP-4.1. Input and output summary for the physical activation study

Feedstock	Fermentation residual stillage (FRS)
FRS flow rate (t/h)	40
Production (days)	350
Pyrolysis temperature (°C)	700
Pyrolysis time (h)	1
Activation temperature (°C)	700
Activation time (h)	2
Product yield (wt.% of FRS) (%)	23
Activated carbon production (kg/year)	65,140,740

Capital expenditure (CAPEX)

The purchasing costs of the main equipment for the physical activation process is shown in Table CP-4.2.

Table CP-4.2. Purchased cost estimation of major equipment for the physical activation process

Major equipment	Capacity	Unit	Purchased cost, $
Rotary kiln (Pyrolysis)	36280	kg/h	1,012,819
Rotary kiln (Activation)	36280	kg/h	1,012,819
Rotary cooler	8163	kg/h	961,454
Screen	8163	L	49,517
Total purchased equipment cost			3,036,609

Delivery cost: 10 % of total purchased cost. So the total delivery equipment cost: $ 3,340,270.

The fixed capital investment (FCI) for physical activation is estimated using percent delivered equipment cost method (see Table CP-4.3). The total capital expenditure: $ 22,190,808.

Table CP-4.3. Percent delivered equipment cost method for physical activation

Direct cost	Fraction (%)
Total purchased delivery cost	100
Purchased equipment installation	39
Instrumentation and controls (installed)	26
Piping installation	31
Electrical systems (installed)	10
Buildings (including services)	29
Yard improvements	12
Service facilities (installed)	55
Total installed cost (TIC)	302
Indirect costs	
Engineering and supervision	32
Construction expenses	34
Legal expenses	4
Contractor's fee	19
Contingency	37
Total indirect cost	126
Fixed capital investment (FCI)	428
Working capital (15% of corrected FCI)	75
Capital expenditure	503

Operational expenditure (OPEX) (see Table CP-4.4)

Table CP-4.4. OPEX for materials required

Materials	Flow rate	Unit	Price, 2015	Unit	Annual cost, $
Beer stillage [a]	36280	Kg/hr	0.039	$/kg	11 852 554
Electricity [b]	0.112	MWhr	77.5	$/MW	72 912
Natural gas [c]	58	MMBTU/hr	8.29	$/MMBTU	4 066 742
N_2 [d]	21768	kg/hr	0.06	$/kg	10 886 400
CO_2 [e]	5442	Kg/hr			8 064 000
Bags for AC [f]	n/a	n/a	n/a	n/a	4 090 000
Total Materials					39 032 609

[a] The cost of lignin is compared with the current cost of coal based on higher heating value.

[b–e] These utilities are consumed at the same rate as described in the NARA physical activation report (NARA co-product dept.)

[f] Taken from NARA physical activation report

The labor costs are shown in Table CP-4.5. Total number of labor force: 21, total number of operating days: 350 days, benefits: 20 % of total salary. The other operating costs were calculated as percentages of the fixed capital investment (see Table CP-4.6)

Table CP-4.5. Labor costs[a]

Function	Number of workers	Yearly salary, $
Plant manager	1	157,646
Plant engineer	1	75,069
Maintenance supervisor	1	61,131
Maintenance technicians	2	85,823
Lab manager	1	60,056
Administrative assistant	1	38,651
Shift supervisor	2	103,068
Plant operators	11	450,569
Delivery coordinators and quality control	1	58,432
Total salaries without benefits		1,090,445
Total salaries with benefits		1,308,534

[a]: All the fractions are taken from Peters & Timmerhaus (Peters M, Timmerhaus K, West R, Peters M: Plant Design and Economics for Chemical Engineers, 5th Edition, 2003)

Table CP-4.6. Other fixed operating costg

Property insurance	0.4% of fixed capital investment	$ 77,185
Local taxes	1% of fixed capital investment	$ 192,964
Maintenance and Repair	2% of fixed capital investment	$ 385,927
Plant overhead cost	50% of operating labor and maintenance	$ 1,124,204

Discount cash flow (DCF) analysis

A DCF analysis is carried out to determine the minimum selling price of activated carbon. The following assumptions were adopted for the economic analysis (see Table CP-4.7). Minimum selling price of physically activated carbon: **0.93 $/kg**. Current market price for AC is between 1.5 and 2 $/kg. The production of chemically activated carbon from the FRS seems to be economically viable.

Table CP-4.7. Financial assumptions for the DCF analysis

Parameters	Assumptions
Year Of Cost Analysis	2015
Project life (years)	22
Construction time (years)	3
% spent in year 1	8
% spent in year 2	60
% spent in year 3	32
Startup period (year)	0.5
Startup variable expenses (%)	75
Startup fixed expenses (%)	100
Working capital (% of FCI)	15
Federal tax rate (%)	16.5
Loan term (year)	10 (8% APR)
Depreciation	200% declining balance; MACRS; 7 year recovery period
Finance (Debt/equity) (%/%)	50/50

Chemical activation (H_3PO_4)

Figure CP-4.1 shows a schematic of the technology studied for the chemical activation with H_3PO_4. The activation with KOH is similar but the material is impregnated with KOH. In the physical activation process a second rotary kiln is used for post-pyrolysis activation. The fermentation solid residue is collected from Gevo Inc. with a solid content of 8.2%. The excess water is removed in two steps – centrifugation and drying. The dried solids are available at 40 tons per hour. These solids are then transferred to activated carbon production area. Following are a brief description of H_3PO_4 chemical activation process: **(1)** In a flow rate of 40 tons/hr, the dried solids are carried to a hammer mill with an energy requirement of 30 kW/ton. **(2)** The ground solid particles are mixed with 85% (v/v) H_3PO_4 in a soaking vessel for 2 hours. Solids to acid mixing ratio was 3:1. **(3)** After the acid impregnation step, the soaked solids are taken to a rotary dryer which has a dimension of 2.4 m X 15 m. **(4)** The dried solids are taken to a rotary kiln where pyrolysis and activation occurs at a temperature of 500°C. The dimension of the rotary kiln will be: 3.6 m x 10 m. **(5)** The high temperature solid output of the kiln is cooled down in a rotary cooler with a dimension of 3.3 m x 9.9 m. **(6)** The cooled activated carbon (AC) is taken to a water wash tank to remove all the acids. It is assumed that 90% of initial acid recovered and recycled back to acid impregnation process. It is also assumed that for every kg of AC product, 1 L of water was required. **(7)** 13% of the AC product is assumed to be lost in the waste water. (7) Another dryer (2.6 m x 5.5 m) was used to dry up all the wet porous solids. **(8)** A sieve tray is assign to screen all the specified fines. 5% of the solid fines are lost in this stage. In our analyses we will consider an activated carbon yield of 52 % of activated carbon. The operational parameters used in our techno-economic analysis are shown in Table CP-4.8.

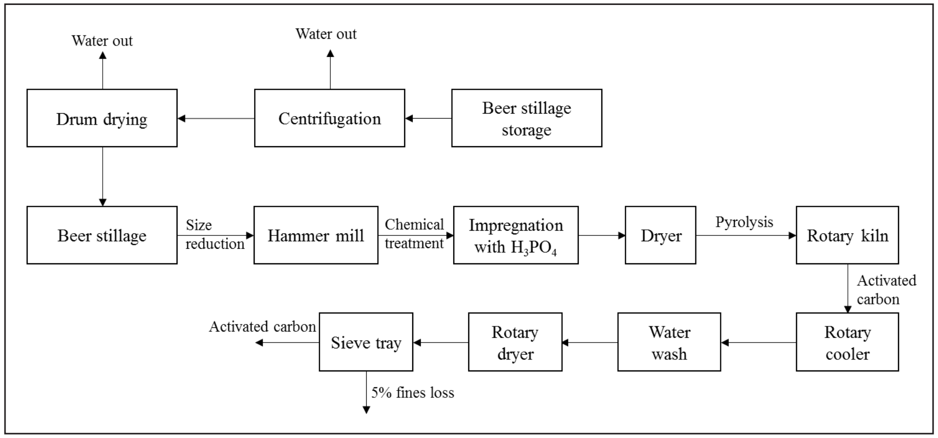

Figure CP-4.1. Flow diagram of the chemical activation process for the production of AC from fermentation stillage residues.

Table CP-4.8. Input and output summary for the chemical activation study with H_3PO_4

Feedstock	Fermentation residual solid (FRS)
FRS Flow rate (short tons/h)	40
Operating times (day/year)	350
H_3PO_4 conc. (% v/v)	85
Activation temperature (°C)	600
Activation time (hr)	2
Product yield (wt.%)	53.6
Feedstock : acid ratio	1:1
Activated carbon production (kg/year)	133 897 953

Capital expenditure

In calculating CAPEX, the process is divided into two processes – the beer stillage processing and chemical activation. Beer stillage processing involves centrifugation to reduce the initial water content. This is followed by a drying system to dry out the beer stillage. The beer stillage processing is similar to that of physical activation process. Therefore, CAPEX for the beer stillage drying is directly taken from the NARA co-product dept. On the other hand, chemical activation required a separate analysis (see Purchase cost estimation of main equipment in Table CP-4.9).

Table CP-4.9. Purchased cost estimation of major equipment in the chemical activation process

Major equipment	Capacity	Unit	Purchased cost, $
Hammer mill	15	horsepower	674,719
Pretreatment vessel	4 000	Liter	1,398,870
Dryer	5.92	m^2	478,415
Rotary kiln	3 396	ft^2	1,432,866
Rotary cooler	5.2	m^2	323,245
Water wash tank	8 000	Liter	651,331
Acid storage tank	8 000	Liter	61,868
Dryer	1.8	m^2	540,798
Screen	3 120	ton/day	76,297
Total purchased equipment cost			5,638,409
Total cost of delivered equipment (10 % transportation)			6,202,250

Capital investment

A percent delivered method is adopted to estimate rest of the CAPEX. The main chemical expenditures are shown in Table CP-4.10.

Table CP-4.10. Capital Investment

Item	Fraction	Cost $
Direct Cost		
Total purchased delivery cost	100	6,202,250
Equipment installation	39	2,418,877
Instrumentation and controls	26	1,612,585
Piping Installation	31	1,922,697
Electrical systems	10	620,225
Buildings	29	1,798,652
Yard improvements	12	744,270
Service facilities	55	3,411,237
Total Installed Cost (TIC)	302	18,730,795
Indirect Costs		
Engineering and supervision	32	1,984,720
Construction expenses	34	2,108,765
Legal expenses	4	248,090
Contractor's fee	19	1,178,427
Contingency	37	2,294,832
Total indirect cost	126	7,814,835
Fixed Capital Investment (FCI) + other costs*	428	31,545,630
Working capital (15 % FCI)	75	4,731,844
Capital expenditure	503	36,277,474

*Other Costs: Land (4 % TDCE): $ 248,090, Beer stillage storage tank: $ 1,000,000, Solid bowl centrifuges and system: $ 2,500,000, Solid drum dryer and system: 1,500,000

Operational costs (see Tables CP-4.11 and CP-4.12)

Table CP-4.11. Main expenditures in chemicals

Material	Capacity	Unit	Annual cost, $/year
Lignin	35,982	Kg/h	11,755,245
H_3PO_4	3,412	Kg/h	17,198,652
Water	19,286	Kg/h	143,702
Electricity	9	MWh	5,831,181
Natural Gas	58	MMBTU/hr	4,066,742
N2	35,982	Kg/year	17,995,038
Bags for AC	n/a	n/a	4,090,000
Total Materials			61,080,559

Table CP-4.12. Other operational costs associated with the production of AC

Other Operational Cost Items	Annual Cost, $/year
Labor (salary + benefits)	1,617,495
Property Insurance (0.4 % of fixed capital investment)	126,183
Local Taxes (1 % of fixed capital investment)	315,456
Maintenance and Repair (2 % of fixed capital investment)	630,913
Overhead Cost (2 % of fixed capital investment)	1,124,204
Other Operational cost	3,814,251

Discount cash flow (DCF) analysis

A DCF analysis is carried out to determine the minimum selling price of activated carbon (see Table CP-4.13). The following assumptions were adopted for the economic analysis: minimum selling price of physically activated carbon: **0.63 $/kg**. Current market price for AC is between 1.5 and 2 $/kg. The production of chemically activated carbon from the FRS seems to be economically viable.

Table CP-4.13. Financial assumptions for the DCF analysis

Parameters	Assumptions
Year Of Cost Analysis	2015
Project life (years)	22
Construction time (years)	3
% spent in year 1	8
% spent in year 2	60
% spent in year 3	32
Startup period (year)	0.5
Startup variable expenses (%)	75
Startup fixed expenses (%)	100
Working capital (% of FCI)	15
Federal tax rate (%)	16.5
Loan term (year)	10 (8% APR)
Depreciation	200% declining balance; MACRS; 7 year recovery period
Finance (Debt/equity) (%/%)	50/50

Chemical Activation (KOH)

The activation conditions with KOH were very similar to those used for the activation with acids but in this case the feedstock to KOH ratio was 1:1 and the yield of products was 32.5 wt. %.

Capital expenditure

The capital expenditure for the KOH activation was very similar to the capital expenditure for the H_3PO_4 activation (Purchased equipment cost: $ 5,405,801, capital investment: $ 32,357,354).

Operational costs

The main expenditures in chemicals and materials and shown in Table CP-4.14 and the other operational costs in Table CP-4.15.

Table CP-4.14. Main expenditures in Chemicals.

Material	Capacity	Unit	Annual cost, $
Lignin	35 982	kg/h	11,755,245
KOH	2 021	kg/h	18,671,443
Water	11 709	kg/h	87,240
Electricity	35.9	MWh	23,403,939
Natural Gas	58.4	MMBTU/hr	4,066,742
N2	35 982	kg/year	17,995,038
Bags for AC	n/a	n/a	4,090,000
Total materials			80,069,646

Table CP-4.15. Other operational costs associated with the production of AC

Other Operational Cost Items	Annual Cost, $/year
Labor (salary + benefits)	1,617,495
Property Insurance (0.4 % of fixed capital investment)	112,547
Local Taxes (1 % of fixed capital investment)	281,368
Maintenance and Repair (2 % of fixed capital investment)	562,737
Overhead Cost (2 % of fixed capital investment)	1,090,116
Other operational cost	3,664 264

Discount cash flow (DCF) analysis

A DCF analysis is carried out to determine the minimum selling price of activated carbon. We used the same financial assumptions that in the other two cases. The minimum selling price obtained was: **1.26 $/kg**.

Based on the results of our techno-economic analysis we can confirm that all the technologies studied for the production of activated carbons from the NARA lignin have minimum selling prices (**0.63, 0.93, and 1.26 $/kg**) lower than current activated carbon market prices (**between 1.5 and 2 $/kg**). The chemical activation process with H_3PO_4 seems to be the most economically viable process. It results in the production of a microporous carbon with great potential for air cleaning.

TASK 5. EVALUATION OF AC MATERIALS IN ELECTRODES FOR SUPERCAPACITORS

Two electrode electrochemical double layer capacitor (EDLC) cells were fabricated by Stephanie Candelaria at the University of Washington in the laboratory of Professor Guozhong Cao. AC materials were prepared from WOX FRS and CLE FRS by carbonizing at 800ºC for one hour under N_2 and activating with CO_2 at 800ºC for 15 minutes at 0.5 L/min flow rate, resulting in materials with ~32 and 42% burn-off for WOX and CLE FRS, respectively. Electrode preparation was carried out in an argon-filled glove box. AC powders were mixed with poly(tetrafluoroethylene) as a binder in a w/w ratio of 9/1. No conductive additive was used in electrode preparation. The electrolyte was tetraethylammonium tetrafluoroborate (TEATFB) dissolved in a 1/1 (v/v) mixture of ethylene carbonate and dimethyl carbonate (EC/DMC). The two electrode cells were characterized with cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy.

Only a small amount of work was done on preparing electrode materials for electrochemical capacitors (also called EDLCs, supercapacitors, or ultracapacitors). As mentioned in the experimental section, two samples were prepared (one from CLE FRS and one based on WOX FRS) at 800ºC and characterized at the University of Washington for their electrochemical performance.

Figures CP-5.1 and CP-5.2 shows the cyclic voltammograms and galvanostatic charge-discharge curves, respectively, of cells prepared with CLE and WOX FRS AC.

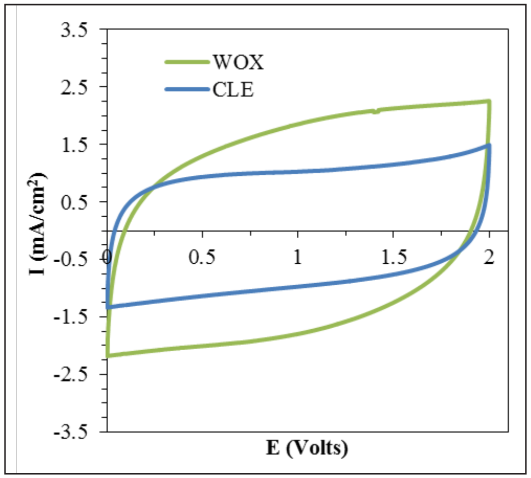

Figure CP-5.1. Cyclic voltammorgrams of two electrode cells prepared with FRS-based AC taken at 10 mV/s. The electrolyte was TEATFB in 1/1 EC/DMC (v/v)

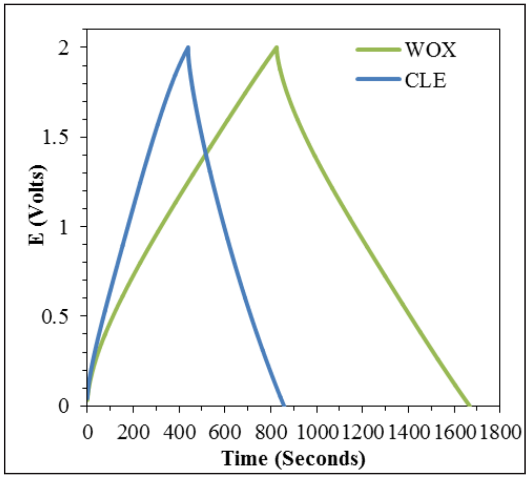

Figure CP-5.2. Galvanostatic charge-discharge (Current = 0.5 mA) test of two electrode cells made with FRS-bases AC.

The data indicated that the FRS-based AC do function as EDLC electrodes, but the capacitances, energy, density, and power density of the cells were moderate to low in performance. The data is summarized in Table CP-5.1.

Table CP-5.1. Electrochemical performance of two electrode cells prepared with FRS-based AC.

Sample	S_{BET} (m^2/g)	Total Pore Volume (cm^3/g)	Specific Capacitance (F/g) @ 0.5 mA	% capacitance retained after 500 cycles	Equivalent Series Resistance (Ω)	Charge Transfer Resistance (Ω)	Energy density @ 0.5 mA (Wh/kg)	Power density @ 0.5 mA (kW/kg)
CLE	432	0.274	26	93	1.76	33.1	14.5	35.4
WOX	871	0.413	53	98.9	1.83	10.8	29.5	34.4

Referring to Table CP-5.1, WOX-based AC had a higher capacitance and energy density and comparable power density to the CLE-based AC. The higher capacitance and energy density might be expected from the higher apparent surface area and pore volume. WOX-based AC also had better capacitance retention compared to CLE. This may be due to the higher purity (lower ash content) of the WOX AC, but this point is currently only speculative. Washing the carbons prior to electrode fabrication is probably an important step to consider for future work, given that EDLC electrode carbons typically have high purity. Electrode carbons also often have very high surface areas accessible for ion electrosorption, so considering different activation procedures to increase porosity is warranted in future work. It is important to generate an understanding of how the PSD affects the electrochemical performance. To illustrate this point, Figures CP-5.3 and CP-5.4 show the effect of the current on capacitance, energy density and power density.

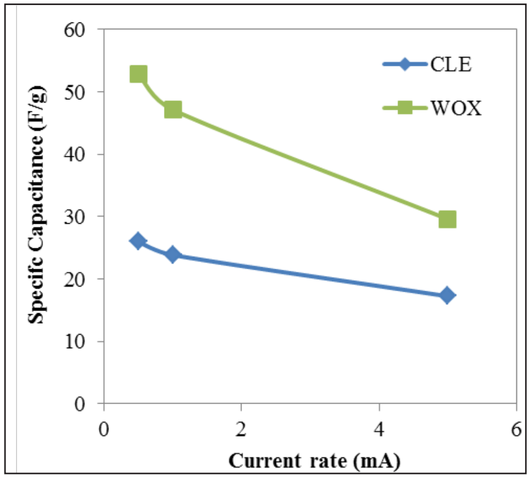

Figure CP-5.3. Capacitance vs. current for two electrode EDLCs made with FRS-based AC.

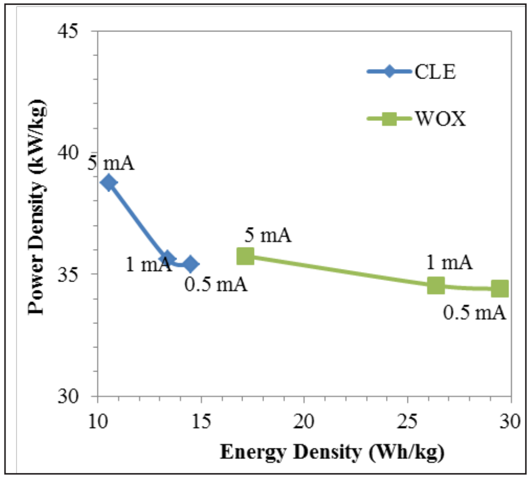

Figure CP-5.4. Ragone plot power density vs. energy at different currents for two electrode cells made with FRS-based AC.

It is of interest to note that the specific capacitance of the CLE AC decreases less with increasing current compared to WOX AC (Figure CP-5.3). Power density of the CLE AC is also noticeably higher at the higher current tested while it is comparable with WOX AC at lower currents. This suggests that mesoporosity contributes to increased power at higher currents since CLE carbons are more mesoporous than WOX carbons. This behavior would suggest that mesopores facilitate rapid ion transport in the AC materials. An appropriate balance of mesopores and micropores is likely necessary for the desired electrochemical performance depending on device application. The energy density is clearly lower for CLE compared to WOX, likely due to the lower surface area and pore volume. While the electrochemical performance of the FRS-based carbons is relatively low, it is promising that moderate values could be obtained with AC materials prepared with a very simple process. Future work should continue to develop low-cost pathways to AC materials engineered for improved performance in EDLCs.

TASK 6. SEARCH AND OBTAIN AN INDUSTRIAL PARTNER TO HELP WITH COMMERCIAL DEVELOPMENT

The team signed a research tool agreement with Calgon (a leading activated carbon company: http://www.calgoncarbon.com/) to study the performance of the physically activated carbons obtained in this project as supercapacitors. Calgon required large quantities of samples, so we worked for one month to produce a specific activated carbon for the supercapacitor study. In brief, the AC sent to Calgon was produced by physical activation (700°C for 90 minutes and activated with CO_2 for 60 minutes). Prior shipment to Calgon, the sample was characterized for elementals, ash content, and porosity (N_2 and CO_2 adsorption isotherms). The ash content and more specifically the presence of transition metals are the main challenges to use the ACs produced in supercapacitors and batteries. The surface area of the physical activated carbon was also slightly lower than the Calgon carbons. In the next weeks we plan to evaluate the performance of several acid washing methods for the removal of these metals from our activated carbons.

RECOMMENDATIONS/CONCLUSIONS

Regarding the observed differences in different types of NARA lignin with respect to AC production, we conclude that it is very important to document the origin of all types of FRS and SRS to the same extent as the Ca-FRS material (which is very well-characterized and has a published manuscript describing its preparation). Physical and chemical activation studies (with KOH and H_3PO_4) were conducted.

The results showed in general that the FRS-based AC obtained by physical adsorption (with important volume of mesoporous) was able to efficiently remove greater than 95% of the Hg^0 from the simulated coal combustion flue gas, only slightly less than the commercially available carbon, Darco Hg. The average saturation adsorption capacity of the FRS AC was about 70% of that measured for Darco Hg. Overall, we found that mesoporous FRS-based AC was a fairly good sorbent for vapor-phase mercury capture, and it can be noted that FRS AC has much better performance than some low cost sorbents that have been reported in the literature and are based on biochar materials, which have a microporous structure. A manuscript with the results of the work performed was submitted to Energy and Fuels. The studies conducted by Calgon suggest that the main challenge to use our physically activated AC as capacitors for energy storage applications is the high content of metals, chlorides and others. So we will study the potential of several acid washing schemes to remove the content of these metals.

While chemical activation is more expensive than physical activation, it has the potential to increase both the yield of AC and result in a material with high surface area mainly as microporous. The microporous AC obtained by H_3PO_4 chemical activation has H_2S adsorption capacity comparable with commercial activated carbons. This activated carbon can be produced at 0.63 $/kg which is lower than the current selling price of these products (between 1.5 and 2 $/kg).

Granular AC materials might be readily obtained from FRS/SRS if proper processing conditions are chosen to give granules with attractive physical properties (combination of strong granules and suitable porosity). The production of low cost granular AC is a potential way to further diversify the portfolio of carbon products that can be produced from a common precursor (SRS/FRS). Granular materials are preferable for fixed bed adsorption applications where the pressure drop across the sorbent bed must be controlled and minimized. Examples of applications for granular materials include drinking water purification, stormwater filtration, and hydrogen sulfide adsorption from biogas.

NARA OUTPUTS

Conference proceedings and abstracts from professional meetings

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.

Research presentations

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.

Refereed publications (submitted, accepted or published)

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Intellectual property

A non-provisional patent application on mesoporous AC by physical activation of biorefinery lignin has been submitted in July 2015.

NARA OUTCOMES

- The unique physico-chemical properties of the NARA lignin was thoroughly characterized.
- The optimal condition for the production of a mesoporous activated carbon for mercury removal using the NARA lignin was identified and the product thoroughly characterized.
- The optimal conditions for the production of a microporous activated carbon for H_2S removal were identified and the product thoroughly characterized.

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