Green Chemistry

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Journal:	*Green Chemistry*
Manuscript ID	GC-ART-02-2019-000589.R1
Article Type:	Paper
Date Submitted by the Author:	10-May-2019

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Supercritical Methanol Depolymerization and Hydrodeoxygenation of Lignin and Biomass over Reduced Copper Porous Metal Oxides

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Abstract

Supercritical methanol depolymerization and hydrodeoxygenation (SCM-DHDO) of maple wood and lignin extracted with GVL from maple wood, was studied using a copper porous metal oxide catalyst. Phenols (P or H), guaiacols (G), and syringols (S) with deoxygenated 1 to 3-carbon (C_1-C_3) alkyl tails were the early products (15 min reaction time) from both the maple wood and the GVL extracted lignin. Furthermore, at 15 min reaction time, the maple wood products showed increased levels of demethoxylation with an S/G/P ratio of 1.0/4.2/1.2 versus 1.0/1.0/0.1 from the GVL extracted lignin products. After 4 h of reacting lignin monomers, dimers and trimers were produced with both the maple wood and extracted lignin. However, the 4 h maple wood products yielded twice the amount of lignin monomers (43.1%) as compared to the 4 h GVL extracted lignin products (20.1%). The GVL extracted lignin products were in the dimer to trimer molecular weight (MW, ~180–750 Da) ranges whereas the maple wood products were in the monomer to dimer MW ranges (~94–500 Da) according to the GPC results. NMR and FT-ICR MS analyses show that both

the 4 h maple wood products and 4 h GVL extracted lignin products undergo a high degree of hydrodeoxygenation, saturation, and repolymerization by C–C bond formation. The higher yield of lignin monomers from the maple wood is likely due to the lower lignin concentration that occurs during the reaction whereas higher lignin concentration during the reaction leads to more oligomerization reactions.

Introduction

Lignocellulosic biomass, which primarily consists of three natural polymers, cellulose, hemicelluloses, and lignin, is an abundant renewable feedstock for production of fuels and chemicals.[1] Technologies for cellulose conversion, primarily to cellulosic ethanol, have been commercialized but technologies for lignin conversion still face a plethora of challenges.[2-3] These challenges arise from the low solubility of lignin in many solvents and the propensity of lignin to repolymerize during reaction. One upgrading method recently shown in literature is **S**upercritical **M**ethanol **D**epolymerization and **H**ydro**D**e**O**xygenation (SCM-DHDO) over a copper porous metal oxide (Cu-PMO or $CuMgAlO_x$).[4-9] During this process, the catalyst reforms a fraction of the methanol solvent producing CO, CO_2, and H_2.[6-7] Part of the H_2 is consumed in the process, aiding in the depolymerization by stabilizing reactive intermediates via hydrodeoxygenation and hydrogenation of the lignin. Supercritical ethanol has also been examined in literature and provides H_2 through dehydrogenative coupling and dehydrogenation reactions rather than reforming.[9-12] SCM-DHDO has also been investigated for the conversion of cellulose and has been studied as a process for converting lignocellulosic biomass in a single pot approach.[5,13-14] SCM-DHDO conversion of model lignin monomers and lignin dimeric units (with their characteristic inter-unit linkage) has also been studied. Studies with phenol and 4-propylguaiacol as model compounds revealed that methylation of the aromatic rings and hydroxyls, demethoxylation, and hydrogenation reactions were prevalent.[6-8,15] Reactions with dimeric model compounds representing various lignin linkages, (2-phenylethyl phenyl ether, benzyl phenyl ether, diphenyl ether, biphenyl, and dihydrobenzofuran) revealed that ether linkages were readily cleaved whereas C–C linkages remain intact.[7-8] Ford and associates have investigated SCM-DHDO of pine sawdust, reporting 100% conversion of pine sawdust into methanol-soluble species by 1 h at 320ºC. At 8 h, 87% mass yield to higher alcohols and ethers (HAE), and 34% mass yield to substituted cyclohexyl alcohols and ethers (CAE) was reported with >100% yields attributed to methanol incorporation.[13] Methanol incorporation has been noted for both cellulose and lignin products.[4,8,14,16]

Previous studies on lignin SCM-DHDO using $CuMgAlO_x$ have probed lignin model compounds that simulate lignin linkages or lignin monomers.[4,6-8] Although these experiments probe the reaction pathways for lignin, the heterogeneity of lignin introduces many confounding factors, such as the propensity of lignin to repolymerize under reaction conditions.[11] These studies have also used organosolv lignin and biomass feeds though, due to difficulty in product analysis, yields are typically reported by mass of the non-volatile products and use ^{1}H, ^{13}C, and HSQC NMR and GPC (gel permeation chromatography) analyses to determine bulk functionalities and molecular weights.[4-6] Monomer yields have not been reported. A reduction and passivation step for the $CuMgAlO_x$ catalyst has been shown by Galebach et al. to improve the yields from SCM-DHDO of cellulose and may influence the lignin SCM-DHDO process.[16] This work focuses on characterizing the lignin and biomass SCM-DHDO products to understand how the lignin depolymerizes as well as to understand the differences in lignin depolymerization between isolated lignin and the lignin present in solid biomass. This study uses maple wood and lignin extracted from maple wood by two methods. The first method involves γ-valerolactone (GVL) extraction of maple wood which produces the GVL extracted lignin.[17] The other method used ball milling and cellulase enzymes to produce a maple enzyme lignin (maple EL) from maple wood.[18-20] Monomer yields are determined with GC-FID comparing lignin feeds with a biomass feed. GPC is used to determine the molecular weight distributions of the non-volatile products and how they change with reaction time. Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) with atmospheric pressure photoionization (APPI) is a high-resolution mass spectrometry technique that allows for determination of elemental compositions and double bond equivalents for non-volatile species and has recently been applied to biomass products.[14,21] FT-ICR MS with APPI is used to probe the elemental compositions of the higher molecular weight oligomers. Quantitative ^{13}C and HSQC NMR have been shown to be vital for understanding lignin structures and are used to probe and quantify the non-volatile functionalities and understand the extents of hydrodeoxygenation and saturation of the products.[17,21-25]

Experimental

Catalyst preparation

The $CuMgAlO_x$ hydrotalcite catalyst was produced with a co-precipitation method as described in Galebach et al.[16] Three aqueous solutions were prepared, a solution of $Mg(NO_3)_2{\cdot}6(H_2O)$ (Sigma-Aldrich 237175), $Al(NO_3)_3{\cdot}9(H_2O)$ (Sigma-Aldrich 237973), and $Cu(NO_3)_2{\cdot}3(H_2O)$ (Sigma-Aldrich 61194), a solution of Na_2CO_3 (Sigma-Aldrich 223530), and a solution of NaOH (Sigma-Aldrich 795429). The Na_2CO_3 solution was added to a 1 L beaker and heated to 60ºC while stirring at 350 rpm with a magnetic stir bar. The MgAlCu solution was added to the Na_2CO_3 solution over the course of an hour using a syringe pump. The NaOH solution was also added using a syringe pump to maintain the pH at 10. The solution was monitored with an Ohaus ST20 temperature/pH probe and was kept at 60ºC and pH 10 while stirring. After the MgAlCu solution was completely added, the resulting product was aged in a capped bottle while stirring at 60ºC for 24 h. After aging, the precipitate underwent a washing procedure to help remove the nitrates. The precipitate was filtered with vacuum filtration to produce a filter cake. Then, the filter cake was redispersed in a solution of 150 mL H_2O and 15 g Na_2CO_3 for 1 h while stirring at 700 rpm with a magnetic stir bar. Afterwards, the precipitate went through two more stages of washing which included vacuum filtration with 500 mL of 60ºC H_2O and redispersal in 300 mL of 60ºC H_2O for about 15 minutes. After these two final stages of washing, the precipitate was vacuum filtered a final time with 500 mL of 60 ºC H_2O and the resulting filter cake was broken up, added into a crucible, and dried overnight at 110ºC. Following the drying, the catalyst was ground into a powder with a mortar and pestle and stored in a desiccator. The catalyst was stored at this stage since deactivation was noticed after a week when storing at the later stages. Prior to use, the catalyst was calcined at 460ºC for 12 h after a 5ºC/min ramp in a muffle furnace, reduced at 350ºC for 12 h after a 1ºC/min ramp under 100 mL/min H_2 flow, and passivated at room temperature for 30 min under 100 mL/min inert (Ar or He) flow and 1 h under 100 mL/min 1% O_2/inert (Ar or He) flow. After calcination, reduction, and passivation, the catalyst was stored in a desiccator and used within 1 week. After 1 week, deactivation of the catalyst was noticed through approximately 5-10% lower product carbon yields. This deactivation is thought to be primarily due to further oxidation of the Cu in the catalyst, though calcined Cu hydrotalcites have also been known to reincorporate H_2O at room temperature, thus reproducing the hydrotalcites structure.[26-28]

GVL lignin fractionation

Fractionation of maple wood was accomplished using a 2-liter stirred Parr reactor fitted with a custom high-solids mixing system (described in Klingenberg et al.[29] and Luterbacher et al.[17]) which led to effective mixing of biomass at high solid loading (20 wt% biomass). Briefly, 800 g of solvent system consisting of 80 wt% GVL, 19 wt% water and 1 wt% sulfuric acid and 200 g of biomass was mixed in the Parr reactor. In a typical run, this mixture was treated at 393 K for 30 min in the high-pressure reactor. Under the reaction conditions, the lignin and the hemicellulose fraction of the biomass were solubilized in the solvent system. The solubilized fraction was separated from the insoluble cellulose fraction by filtration. Lignin was recovered by precipitation from the filtrate with water (1 part of filtrate was mixed with 9 parts of water). The precipitate was isolated by centrifugation, the supernatant was discarded, and the precipitate was washed with hot water. The wet solid was freeze dried to obtain the dry lignin.

Reactor set-up

The batch reactors were previously described in Galebach et al.[14] The reactors are composed of a ¾″ Swagelok plug, ¾″ Swagelok to ½″ female NPT union, and ½″ NPT bleed valve as shown in Figure 1.[14] The interior volume is approximately 6 mL and the bleed valve allows for purging and gas collection.

Figure 1. One of the assembled Swagelok reactors used for all SCM-DHDO reactions. The reactors are opened via the bottom ¾″ Swagelok plug while purging and gas sampling is done through the ½″ NPT bleed valve on the top.

Supercritical methanol depolymerization and hydrodeoxygenation

For typical experiments, 100 mg of catalyst, 100 mg of feed, and 2.4 g of solvent (HPLC grade MeOH (Fisher Chemical A452) with 0-0.5 wt% dodecane (TCI D0968)) were added to the batch reactors. Dodecane was added as a tracer to determine the methanol loss during the reactions. After determining the methanol loses for various time-points (15 min: 7%, 30 min: 9%, 1 h: 10%, 2 h: 14%, and 4 h: 18%), dodecane was no longer used as it interfered with GPC, NMR, and MS analyses. After adding the catalyst, feed, and solvent to the reactors, the reactors were sealed and purged through the gas valve 5 times with 50 psig He and filled to 5 psig He for the reaction. The reactors were shaken, vortexed, and then suspended in a sand bath at 300ºC. The sand bath temperature dropped to 290ºC and heated back up to 300ºC within 5 minutes. Once the sand bath reached 300ºC, the reactors were assumed to reach 300ºC as well and the reaction time was started. The reaction times varied from 15 min to 4 h. The operating pressure is approximately 3300 psi based on comparisons with supercritical methanol isotherms by Bazaev et al. at operating conditions (2.4 g methanol in 6 mL batch reactor (ρ = 0.4 g/mL) at 300ºC).[30] After the reaction, the reactors were gently shaken off to remove excess sand and quenched in ice water. Following the quenching, gas samples were collected from the reactors through the gas valve into a graduated inverted water cylinder to determine the gas volume and collected in a gas bag for GC analysis. After collecting the gas samples and ensuring complete depressurization of the reactors, the reactors were opened for liquid sample collection. The liquid was collected through a needle and syringe to minimize evaporation and prevent collection of the solids. The liquid samples were filtered with 0.22 µm PTFE syringe filters and stored in the refrigerator while 0.5 mL of each sample was immediately sent for GC-FID analysis for quantification of the products. The reactors along with the solids were left to dry overnight after which, the solids were collected and further dried in a vacuum oven at 60ºC and -7.5 psig. The total catalyst turnovers are estimated to be 4.2 mol lignin monomers/mol Cu sites for the 4 h GVL extracted lignin reaction and 2.2 mol lignin monomers/mol Cu sites for the 4 h maple wood reaction. The lower turnovers for the 4 h maple wood reaction could be due to lower lignin concentrations, competition for catalytic sites with other components, or poisoning of the catalyst sites by other components.

GC-FID and GC-MS

The liquid products were analyzed with GC-FID, GC-MS, and high-temperature GC-FID. The monomer products were identified and quantified with the GC-FID and GC-MS. The GC-FID was a Shimadzu GC-2010 instrument with an RTX-VMS column and was operated with the following temperature profile: 5 min hold at 40ºC, 7.5ºC/min ramp to 240ºC with a 15 min hold. The GC-MS was a Shimadzu GCMS-QP2010 mass spectrometer with an RTX-VMS column and was operated with the following temperature profile: 5 min hold at 35ºC followed by a 5ºC/min ramp to 140ºC, and a 50ºC/min ramp to 230ºC with a 20 min hold. Standards were unavailable for many of these products, so GC-FID response factors were estimated using cyclohexanol, 4-propylphenol, 4-propylguaiacol, and 4-propylsyringol calibrations coupled with effective carbon number estimations.[31] The MS fragmentation patterns of peaks that were not in the GC-MS library were inspected to categorize the peaks as either cyclohexanols (fragment m/z = 82 and 57) or phenols (fragment m/z = 94). The concentrations were then estimated in the GC-FID with cyclohexanol, 4-propylphenol, 4-propylguaiacol, and 4-propylsyringol response factors. Some of the cellulose products overlap with lignin products in the GC-FID. The cellulose products' contributions to the GC-FID areas were estimated with 4 h Avicell cellulose SCM-DHDO experiments, weighted for the cellulose and hemicellulose content in the maple wood, and subtracted out from the lignin product GC-FID peaks to determine the lignin monomer carbon yields for reactions with the maple wood feed.

The high-temperature GC-FID was used to estimate the amount of dimer and trimer species and included a Restek MXT-1HT Sim Dist non-polar column and operated under the following conditions: a 5 min hold at 40ºC followed by a 15ºC/min ramp to 415ºC with a 5 min hold. The GC-FID spectra were split into four distinct regions by retention times. The first two regions were confirmed with standards to be the light oxygenate and lignin monomer regions whereas the third and fourth regions were assumed to be the dimer and trimer regions. This GC-FID method has previously been calibrated for use with linear C_6-C_{40} alkanes and although the oxygenated and unsaturated lignin products did not fall at the same retention times, the lignin products were assumed to follow similar trends. Dimer and trimer yields were estimated by determining the ratios of the dimer and trimer areas to the monomer areas in the high-temperature GC-FID and comparing those ratios to the lignin monomer yields from the lower temperature GC-FID. This assumes that to the first approximation, the carbon response factors of the dimers and trimers are similar to those of the monomers.

GPC

Analytical GPC was performed on a Shimadzu LC20 with a photodiode array detector (SPD-M20A). Separation was performed using two PSS PolarSil linear S columns (7.8 mm x 30 cm, 5μm) in series. For each analysis, a 1 μl sample containing 1 mg/mL lignin or reaction product was injected. The mobile phase was 0.1 M lithium bromide (LiBr) in *N,N*-dimethylformamide (DMF) at 40°C and a flow rate of 0.3 mL/min. The molecular weight distribution was calibrated at λ=280 nm using Polystyrene ReadyCal Standard Set M(p) 250–70 000 Da (P/N 76552; Fluka, Sigma/Aldrich, St. Louis, MO, USA). While the polystyrene calibration standards may not perfectly represent how the lignin and lignin fragments elute, they allow for accurate comparisons between samples and are the most common calibration standard for GPC used in literature to generate an approximate lignin MW.

NMR

The GVL lignin and SCM-DHDO products were characterized by quantitative 1D ^{13}C, 2D HSQC, and 2D HMBC NMR. The methanol reaction solvent was evaporated in a vacuum oven at 50ºC and the samples were dissolved in DMSO-d_6 and pyridine-d_5 to produce a solution of 10 wt% sample, 72 wt% DMSO-d_6, and 18 wt% pyridine-d_5. The quantitative ^{13}C NMR experiments were acquired on a Bruker Biospin (Billerica, MA) AVANCE III 500 MHz spectrometer fitted with a DCH (^{13}C-optimized) cryoprobe using the standard Bruker pulse sequence "zgig30" with an inter-scan relaxation delay of 15 s, a sweep width of 240 ppm, O1P at 110 ppm, TD of 59520 with an acquisition time of 1 s, and 512 scans. The quantitative ^{13}C NMR experiments were analyzed with MestraNova software with the DMSO solvent peak as the internal reference at 39.50 ppm. The 2D HSQC and HMBC NMR experiments were carried out on a Bruker Biospin (Billerica, MA) AVANCE 600 MHz spectrometer fitted with a cryogenically cooled 5 mm TXI gradient probe. The standard Bruker pulse sequences "hsqcedetgpsisp2p3" and "hmbcetgpl3nd" were used with an inter-scan relaxation delay of 2 s, 8 scans, sweep widths of 220 ppm in F1 and 12 ppm in F2, O1P of 110 ppm in F1 and 5.5 ppm in F2, and TD of 3366 in F1 and 1000 in F2 for a total of 5 h per experiment. Bruker's Topspin 3.5 software was used to process spectra. The DMSO solvent peak was used as internal reference (δH/δC: 2.49/39.50).

FT-ICR MS

Mass spectrometric data were acquired by Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometry. Two instruments were used for data collection. One is a Bruker solariX

XR with a 15 T actively shielded superconducting magnet, whereas the other is a Bruker APEX with a 12 T actively shielded superconducting magnet. Instrument control, data acquisition and preliminary processing were performed on Bruker Daltonics ftmsControl and Bruker Compass DataAnalysis software provided by the vendor. The ionization method was selectively chosen for each experiment to most efficiently ionize each sample. Electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), and atmospheric pressure photoionization (APPI) were used. Samples were diluted as needed in LCMS grade methanol and/or toluene prior to analysis. Typical final concentrations were 20-100 ppm. The diluted samples were directly injected using the instrument-controlled syringe pump, and flow rate was modified as needed for stable ionization and signal. Typical flow rates were 100-300 μL/h. Ionization settings were modified as needed to optimize each experiment. All values selected were within normal ranges recommended by the vendor for analysis. On both instruments, nitrogen was used for all drying and sheath gases. The data were processed by using a sine-squared apodization method. On the APEX instrument, data was maintained in magnitude mode whereas the solariX data was generally additionally processed in absorption mode. Each mass spectrum was an average of many scans, with 100 scans being typical. After acquisition, elemental formulas for each peak were assigned using PetroOrg software.[32]

Determination of Bulk, Envelope, and Skeletal Densities

Bulk densities were measured with a 10 mL graduated cylinder and fine scale. The GVL extracted lignin or maple wood was added to the 1 mL mark of the graduated cylinder and weighed. The bulk density (g/mL) of the sample was the mass of the sample in grams to occupy the 1 mL volume. The envelope and skeletal densities of the GVL extracted lignin and maple wood were measured respectively with mercury porosimetry (Micromeritics' AutoPore IV 9500 Series) and

He gas pycnometry (Micromeritics' Accupyc II 1340 Pycnometer) by the Particle Testing Authority in Norcross, GA.

Results and Discussion

Lignin and biomass comparisons

Previous studies of lignin SCM-DHDO have used a calcined (unreduced) CuMgAlOx catalyst[4-8,10-13] whereas Galebach et al. have shown increased product yields from SCM-DHDO of cellulose with a reduced and passivated CuMgAlOx catalyst.[16] As shown later in Figure 5 and SI Table S2 for 4 h reaction time, a reduction and passivation step for the CuMgAlOx catalyst had little effect on the total monomer carbons yields which were 20.7% with the non-reduced $CuMgAlO_x$ catalyst and 20.1% with the reduced and passivated $CuMgAlO_x$ catalyst, although the latter had increased amounts of saturated species resulting in an aromatic/cyclohexyl (A/C) ratio of 0.71 compared to 1.43 for the non-reduced catalyst. The main identified products with both catalysts were 4-ethylcyclohexanol, 4-propylcyclohexanol, and 4-propylphenol, with carbon yields for the non-reduced $CuMgAlO_x$ catalyst of 0.9%, 1.5%, and 1.1%, respectively, and 1.5%, 2.4%, and 0.7% with the reduced and passivated $CuMgAlO_x$ catalyst. Peaks corresponding to unknown compounds that could be categorized by GC-MS as aromatics or cyclohexanols, were quantified by GC-FID using the response factors from known analogs. The unidentified aromatics and cyclohexanol yields were 10.9% and 6.3% with the non-reduced $CuMgAlO_x$ catalyst and 7.7% and 7.8% with the reduced and passivated $CuMgAlO_x$ catalyst. A reduced and passivated CuMgAlOx catalyst was used for the rest of the study since this catalyst has shown superior activity in other studies.

Figure 2 shows the major aromatic and cyclohexanol products identified by GC-MS during SCM-DHDO. Figure 3shows the time-course experiments for SCM-DHDO of the GVL extracted lignin. At the 15 min time-point, the products were primarily aromatics, including guaiacols and syringols, totaling a 4.1% carbon monomer yield. The initial monomer products help us understand how the depolymerization occurs. The GC-FID and GC-MS identified products mainly included guaiacols and syringols without alkyl tails (C_0) or with alkyl tails of lengths of 1 to 3 carbons (C_1-C_3), with carbon yields of 0.1/0.4/1.0/1.9% (C_0/C_1/C_2/C_3). The monolignols have propenol tails that, after radical coupling during lignification, have hydroxyl (or ether) units on the α and γ positions and either an ether linkage at the β-position (as in the case of the most abundant β-ether unit in lignin characterized by its β–O–4 linkage) or a C–C bond between the β-position and another monolignol.[3] The identified lignin monomers' alkyl tails contained no hydroxyl units and only 55% of the monomers contained 3-carbon alkyl tails, indicating that both hydrodeoxygenation and C–C bond cleavage occurs during the lignin depolymerization.

The GVL extracted lignin feed has a syringyl (S) to guaiacyl (G) to phenyl (P as will be denoted in this paper but often referred to as H-units in the lignin literature) ratio of ~3/1/0. The S/G/P ratio of the products at 15 min was 1.0/1.0/0.1 indicating that either demethoxylation of S units are occurring or that G units are being removed at a higher rate than S units from the lignin polymer. The low amount of P shows that there was little demethoxylation of G units at this point in the reaction. At the 30 min time-point the S and G carbon yields increased bringing the S/G/P ratio to 1.0/1.6/0.2. The overall monomer carbon yields increased from 4.1% at 15 min to 8.1% at 30 min. By the 1 h time-point, the G and S aromatic units disappear through methylation, demethoxylation, and hydrogenation reactions forming 4-propylphenol and 4-propylcyclohexanol in carbon yields of 1.1% and 1.2% and unidentified aromatics and cyclohexanols in carbon yields of 9.2% and 5.1%.[4,6] The overall carbon yield further increased to 16.9% at 1 h.

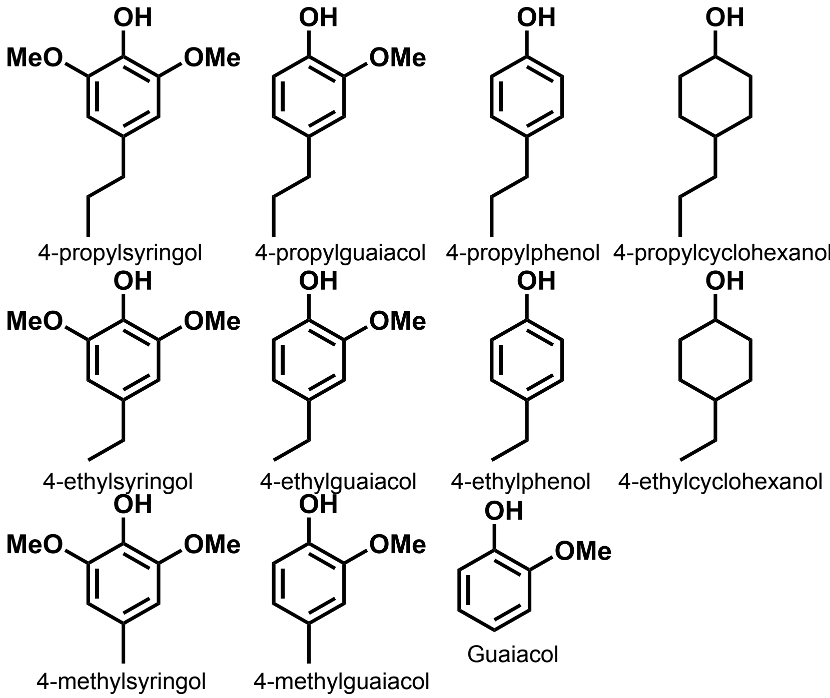

Figure 2. Aromatic and cyclohexanol products from lignin SCM-DHDO identified by GC-MS.

At 2 h, 4-ethylcyclohexanols formed with a 1.4% carbon yield and 4-propylcyclohexanols had risen to 2.4% carbon yield. There was no evidence of C–C bond cleavage during SCM-DHDO of 4-propylguaiacol under similar reaction conditions.[4,6] This indicates that the 4-ethylcyclohexanols likely arise from the demethoxylation and hydrogenation of 4-ethylguaiacol and 4-ethylsyringol. Additionally, at 2 h reaction time 4-propylphenol decreased to 1.0% carbon yield while the unidentified aromatics and unidentified cyclohexanols increased to 11.1% and 8.1% carbon yield respectively. The total monomer carbon yield reaches its highest yield of 24.1% at 2 h.

After 4 h, the cyclohexanols only slightly changed, with the 4-propylcyclohexanols remaining at 2.4%, the 4-ethylcyclohexanols increasing slightly to 1.5% and the unidentified cyclohexanols dropping to 7.7%. The unidentified aromatics sharply declined to 7.8% and the 4-propylphenols decreased to 0.8% at this same reaction time. The total monomer carbon yield decreased to 20.1% at 4 h which may be due to repolymerization to higher molecular weight species. Overall, in this reaction methyl, ethyl, and propyl guaiacols and syringols were formed early in the reaction and then were converted into 4-propyphenols, 4-ethylcyclohexanols, 4-propylcyclohexanols, and unidentified cyclohexanols and aromatics.

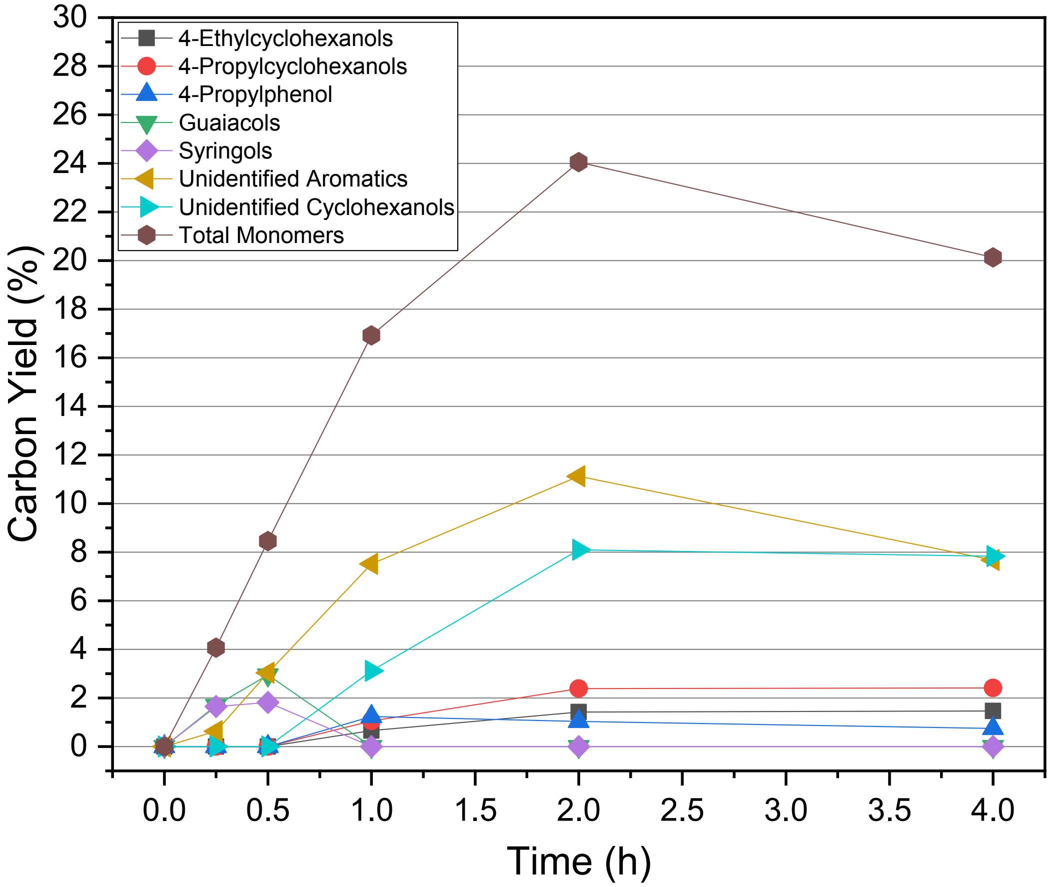

Figure 3. SCM-DHDO of GVL extracted lignin time-course experiments highlighting the yields of specific groups of aromatics and cyclohexanols. Standard reaction conditions: 100 mg CuMgAlOx catalyst, 100 mg GVL extracted lignin, 2.4 g MeOH, 5 psig He, and 300ºC with a 3 min heat-up period.

Figure 4 reports the 15 and 30 min lignin yields for SCM-DHDO of GVL-extracted maple lignin and SCM-DHDO of maple wood with more detailed information including S/G/P ratios, alkyl tail lengths ratios, and dimer/trimer yields in SI Table S1. No cellulose and hemicellulose products overlapped with lignin products in the GC-FID chromatograms. [14,16] The maple wood is 25 wt% lignin which is used to calculate the lignin fraction carbon yield for the maple wood.[17] However, the total lignin monomer carbon yield from conversion of the maple wood at 15 min was 15.4% which is 3.8 times higher than the total monomer carbon yield from conversion of the extracted GVL extracted lignin at this same time. Additionally, the maple wood products have a S/G/P ratio of 1.0/4.2/1.2 compared to 1.0/1.0/0.1 for the GVL extracted lignin. This indicates that more demethoxylation occurs during maple wood conversion than GVL extracted lignin conversion. At the 30 min time-point, the carbon yield from the maple wood was roughly the same as the 15 min time-point. The 15 min GVL extracted lignin products had an estimated 2.3% carbon yield to dimers and no detected trimers. The 15 min maple wood products had no dimers and trimers.

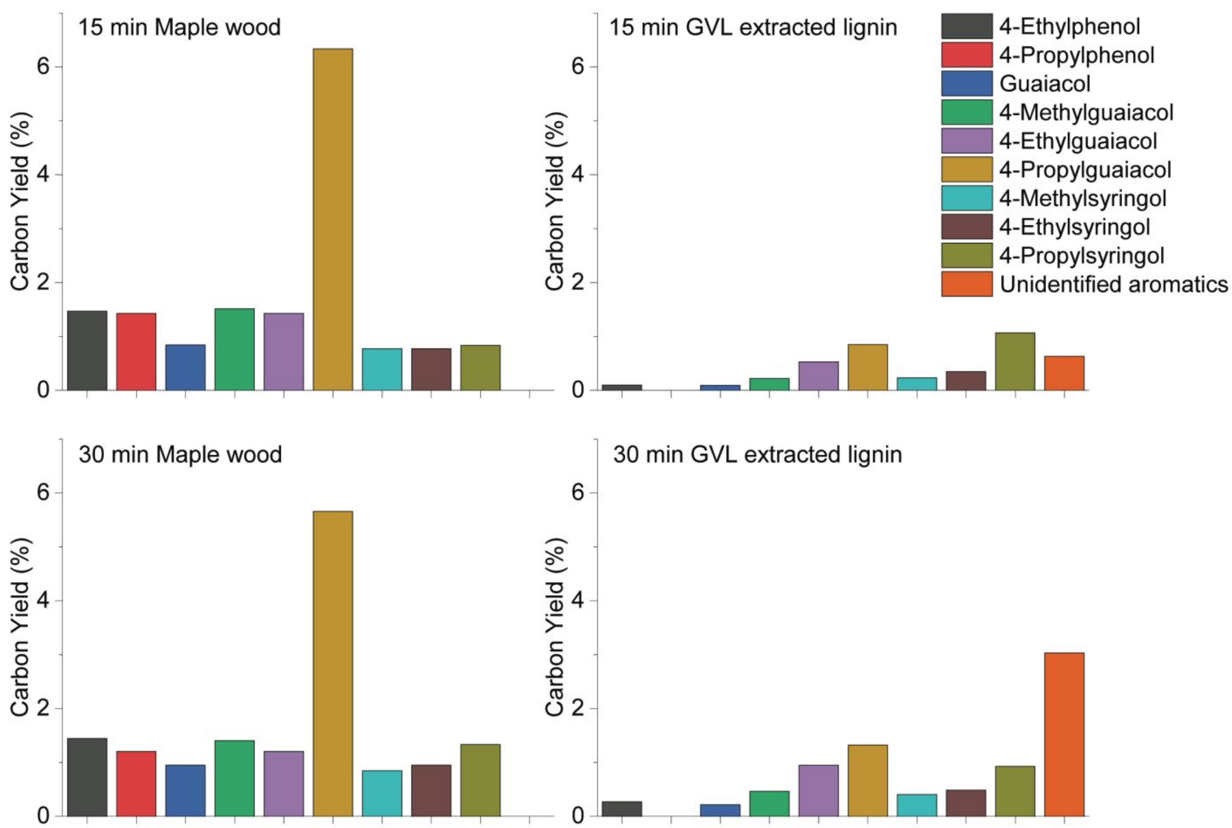

Figure 4. Lignin fraction carbon yields of 15 and 30 min from SCM-DHDO experiments with maple wood and GVL extracted lignin. Reaction conditions: 100 mg feed, 100 mg CuMgAlOx catalyst, 2.4 g MeOH, 5 psig intial He pressure, and 300ºC reaction temperture.

The 4 h SCM-DHDO experiments are shown in Figure 5with both maple wood and the GVL extracted lignin. At 4 h, the maple wood lignin monomer carbon yield reached 43.2%, over double that of the GVL extracted lignin (20.1%). The maple wood products had an aromatic to cyclohexanol ratio of 0.42 compared to 0.70 for the GVL extracted lignin products. The dimer and trimer yields for the 4 h maple wood products were 54% and 6% respectively and were 57% and 7% respectively for the 4 h GVL extracted lignin products. The total yields were 103% for the 4 h maple wood products and 84% for the GVL extracted lignin products. The above 100% yield is potentially due to inaccuracies with estimating the dimer and trimer yields.

We conducted two experiments with a higher ratio of catalyst to GVL extracted lignin (25 mg GVL extracted lignin with 100 mg catalyst and 100 mg GVL extracted lignin with 150 mg catalyst) to determine if the higher lignin monomer yields were due to a difference in the lignin to catalyst ratio. There were minimal differences with the lignin monomer carbon yield when the catalyst to GVL lignin ratio was increased although the aromatic to cyclohexanol ratio decreased. Since adjusting catalyst ratio had no effect on the total monomer yield, other factors needed to be considered.

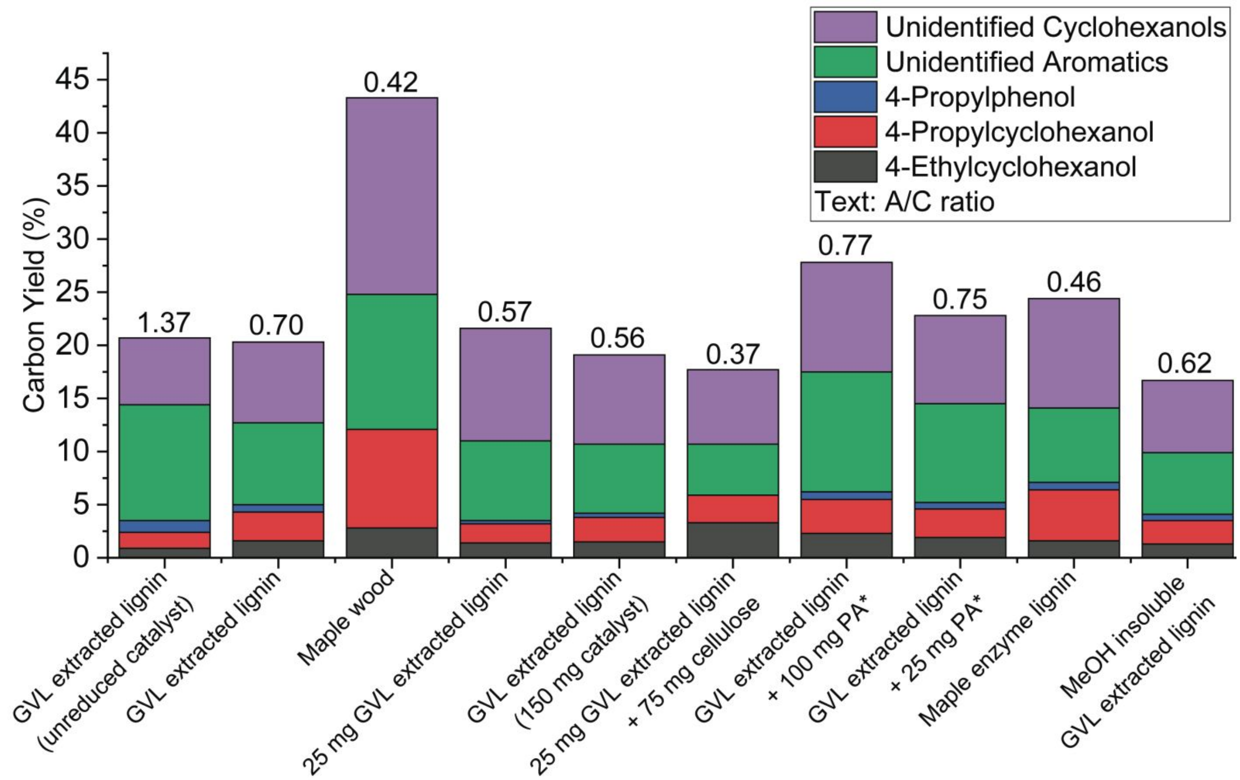

Figure 5. Carbon yields from 4 h SCM-DHDO experiments with various feedstocks. Base reaction conditions: 100 mg feed, 100 mg CuMgAlOx catalyst, 2.4 g MeOH, 5 psig initial He pressure, 300ºC reaction temperature, and 4 h reaction time. PA products are not deconvoluted from the lignin products.

Evaluating possible contributing factors to higher lignin monomer yields from maple wood

Figure 5 and SI Table S2 additionally show the SCM-DHDO of maple wood, GVL extracted lignin and GVL extracted lignin with various additives. SCM-DHDO of a physical mixture of 25 mg GVL extracted lignin and 75 mg cellulose resulted in a lignin monomer yield of 17.7%, which is slightly lower than the GVL extracted lignin base case. This indicates that products from cellulose are not protecting the lignin from repolymerizing, nor are they aiding in depolymerization. Luterbacher and coworkers have shown that the addition of aldehydes during lignin extraction stabilizes the lignin by forming acetal protection groups across the α- and γ-hydroxyl groups of the alkyl tails to prevent lignin condensation.[33] They have shown that propionaldehyde (PA) had the highest enhancement of monomer products from lignin. In their method, the aldehydes were added during a dioxane extraction process to mitigate lignin condensation but similar protections may be occurring during SCM-DHDO. The known protecting group PA was added in 25 mg and 100 mg amounts to the SCM-DHDO reactions to observe if protection could be active under SCM-DHDO reaction conditions. These experiments saw small increases of the lignin monomer yields from 20.1% to 22.8% and 27.8% respectively.. These small increases are likely due to aldol condensation production from PA which overlap with the lignin monomer products in the GC-FID and not to an increase in the lignin monomer products.

Another hypothesis is that the GVL extracted lignin may have condensed during the GVL extraction process.[34] This would result in the formation of new C-C linkages between potential lignin monomers which would not be broken by the SCM-DHDO process and not have been observed by NMR studies. A maple enzyme lignin (EL) was prepared and tested for SCM-DHDO with a 4 h reaction. Previously, it has been shown that the EL has little condensation and is a good representative for native lignin.[19] The products from SCM-DHDO of maple EL had a slightly increased lignin monomer carbon yield of 24.4% compared to the SCM-DHDO product from GVL extracted lignin (20.1%). This indicates that any condensation that is occurring for the lignin during the GVL extraction has minimal impact on the lignin monomer yield.

A final hypothesis is that the lignin in the maple wood is solubilizing more slowly than the GVL extracted lignin and that this slower solubilization lowers the lignin concentrations in the solution during the SCM-DHDO process. The rate of repolymerization of lignin fragments is likely 2nd order with respect to lignin concentration and thus lower lignin concentration will result in decreased lignin oligomer formation. Approximately 50% of the GVL extracted lignin is soluble in MeOH at room temperature whereas the maple wood components are minimally soluble at room temperature. To test our hypothesis, the relative amount of lignin solubilization from the GVL extracted lignin was measure by fractionating with MeOH. The MeOH-insoluble GVL extracted lignin was tested for SCM-DHDO in a 4 h reaction. The MeOH-insoluble GVL extracted lignin had a lignin monomer yield of 16.8%, lower than the GVL extracted lignin at 20.1%. It is likely that the MeOH-insoluble fraction still solubilizes at reaction conditions more rapidly than the lignin in the maple wood. Additionally, the MeOH insoluble GVL extracted lignin are likely the higher MW fraction of the GVL extracted lignin and this may affect the monomer yields in other ways.

The densities of the maple wood and GVL lignin may offer some insight into how the lignin is solubilizing and how the solubilization may affect concentrations. The densities were analyzed and the results are displayed in Table 1. The bulk densities were measured with a graduated cylinder and scale whereas the envelope and skeletal densities were measured with mercury porosimetry and He gas pycnometry respectively by the Particle Testing Authority in Norcross, GA. The GVL extracted lignin has bulk and envelope densities of 0.48 and 0.52 g/mL, higher than the maple wood at 0.25 and 0.31 g/mL, respectively. The skeletal densities are similar at 1.39 g/mL for the GVL extracted lignin and 1.45 g/mL for the maple wood. However, the maple wood is only 25 wt% lignin and when this is accounted for, the lignin densities in maple wood drop to 0.06, 0.08, and 0.36 g_{lignin}/mL for the bulk, envelope, and skeletal densities, less than 25% of the GVL extracted lignin which could lead to lower concentrations during dissolution under reaction conditions.

Table 1. Lignin densities in GVL extracted lignin and maple wood.

	Density (g/mL)			Volume (mL/g)		
Sample	Bulk	Envelope	Skeletal	Void	Pore	Solid
GVL extracted lignin	0.48	0.52	1.39	0.15	1.21	0.72
Maple wood 45-80 mesh	0.25	0.31	1.45	0.75	2.55	0.69

Lignin fraction of maple wood (25 wt%)	0.06	0.08	0.36

GPC of non-volatile SCM-DHDO products from GVL extracted lignin and maple wood time-course

GPC is an effective tool for probing the molecular weight distributions of polymers and has been used in understanding the degree of polymerization of lignins and lignin products.[4,6,8,21] In Figures 6 and 7, the molecular weight distributions of the GVL extracted lignin, 15 min to 4 h GVL extracted lignin products, and 15 min to 4 h maple wood products are shown. The GVL extracted lignin shown in both Figures 6 and 7 has a large molecular weight distribution with the molecular weight of the peak maximum (M_p) at 3,500 Da. This corresponds to a degree of polymerization of approximately 16 units, assuming an S/G ratio of 3/1. The molecular weight for the GVL extracted lignin products decreases to an M_p at 250 Da after 15 min of SCM-DHDO reaction. The M_p decreases further to 200 Da after 30 min reaction before increasing to 270 Da after 4 h of reaction. This corresponds to the dimer (200-400 Da) to trimer (300-600 Da) ranges where the oligomer ranges are broad due to variations in the alkyl tail lengths and the degree of methylation and demethoxylation reactions during SCM-DHDO. The maple wood products are noticeably lower in molecular weight and start with an M_p at 130 Da at 15 min reaction. It shifts to 120 Da at 30 min reaction and splits into an M_p at 110 Da with a 200 Da shoulder peak at 1 h reaction. This peak splitting is further accentuated at the 2 h reaction time-point, with an M_p at 130 Da with a 220 Da shoulder peak and at the 4 h reaction time-point with an M_p 240 Da with a 150 Da shoulder peak. The maple wood products are in the monomer range (100-200 Da) initially, while a second peak in the dimer range (200-400 Da) forms after 1 h reaction. The shifts in the molecular weight distributions for both the GVL extracted lignin and maple wood products are consistent with primarily depolymerization for 15 min to 1 h, then a transition from 1 h to 4 h to repolymerization as the dominant reaction.

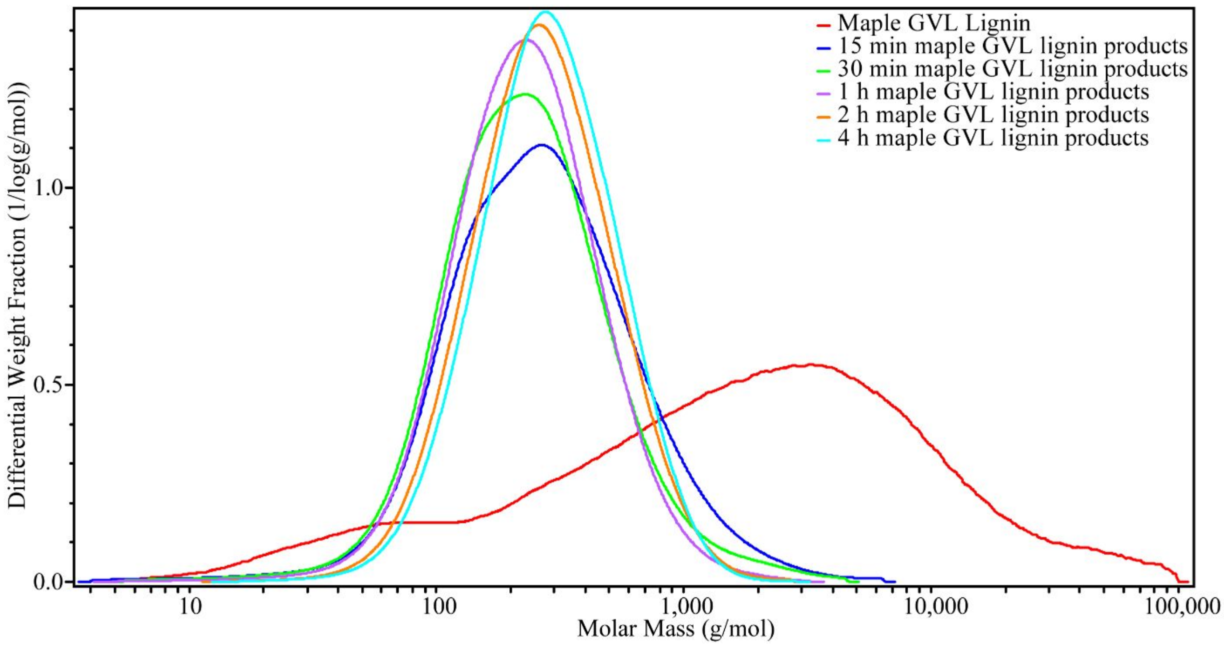

Figure 6. GPC molecular weight distributions of GVL extracted lignin and SCM-DHDO products of GVL extracted lignin at 15 min to 4 h maple

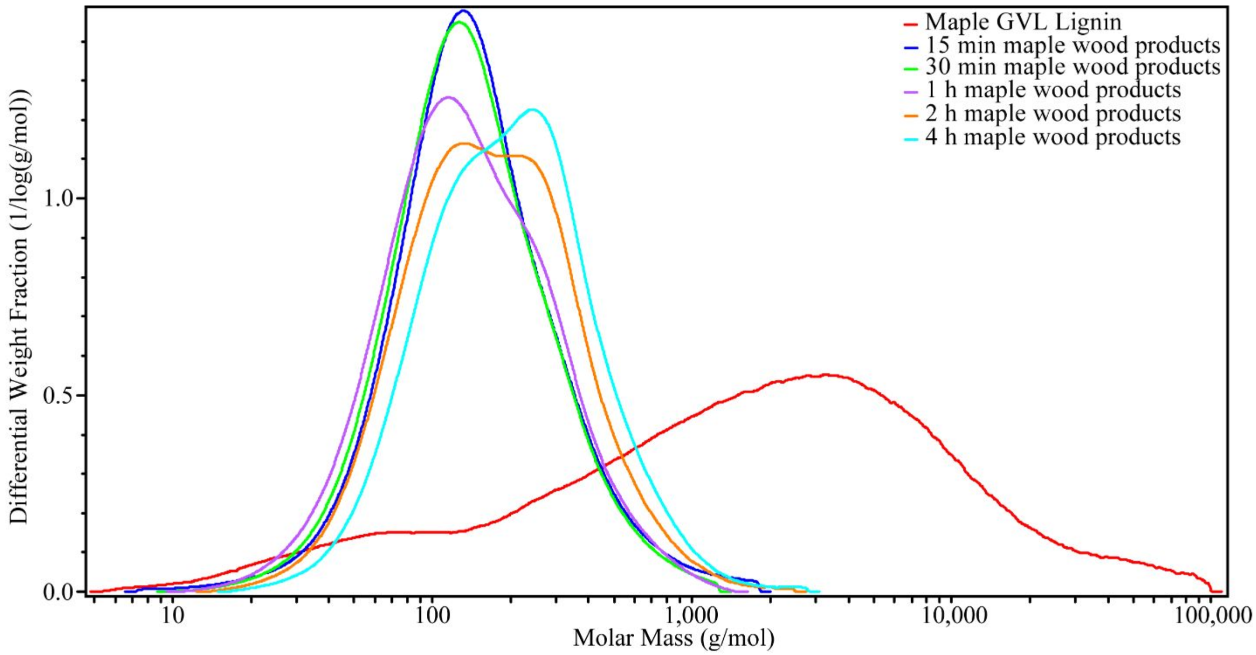

Figure 7. GPC molecular weight distributions of GVL extracted lignin and SCM-DHDO products of maple wood from 15 min to 4 h.

Quantitative ^{13}C and HSQC NMR of non-volatiles from GVL extracted lignin SCM-DHDO

NMR has proven to be a valuable tool for understanding carbon functionalities when analyzing lignin and lignin products.[21-22,24] NMR experiments were conducted to uncover the functionality distributions of the GVL extracted lignin and the SCM-DHDO 1 and 4 h products. Samples from SCM-DHDO maple wood were not analyzed with NMR due to difficulty in sample preparation and potential signal overlaps from non-lignin products. The quantitative ^{13}C NMR allows for quantification of the functionalities grouped into carbonyl, aromatic, C–O aliphatic, and C–C aliphatic regions, along with the methoxyl subregion as shown in Table 2. The GVL extracted lignin has 69% of the carbon in the aromatic region, 24% in the C–O aliphatic region, and 7% in the C–C aliphatic region. Approximately half (13 of 24%) of the C–O aliphatic region is contained in the methoxyl subregion. The carbon peaks in the C–O aliphatic region in lignin are from two main sources, the methoxyl units and the hydroxylated alkyl tails of the lignin units. The C–O aliphatic region decreases from 24% in the GVL extracted lignin to 9% at 1 h and 8% at 4 h while the methoxyl subregion decreases from 13% to 3% at 1 h and 1% at 4 h indicating that demethoxylation predominately occurs at earlier reaction times. During the SCM-DHDO reaction new C–O aliphatics, cyclohexanols, form from the saturation of the phenolic structures in lignin. The depolymerization process has been shown to fully remove the hydroxyl groups from the alkyl tails of the monomers; thus, the remaining C–O aliphatic carbons are likely the C–O carbon of cyclohexanols which appear to be relatively stable under SCM-DHDO reaction conditions. The aromatic region decreases from 69% to 50% and 20% at 1 and 4 h, respectively highlighting a consistent saturation of the phenolic structures during SCM-DHDO. The C–C aliphatic region increases from 7% to 41% by 1 h and 72% by 4 h as expected with the saturation of the aromatic carbons and the hydrodeoxygenation of the C–O aliphatic carbons. These trends agree with the literature though saturation and hydrodeoxygenation of the lignin appears to be occurring to a larger extent than reported by Barrett et al. They performed SCM-DHDO at similar 6 h reactions with organosolv poplar lignin and an unreduced CuMgAlOx catalyst which resulted in approximately 22% of carbons in the aromatic region, 16% in the C–O aliphatic region, and 63% in the C-C aliphatic region.[4]

Table 2. Quantitative ^{13}C NMR of GVL extracted lignin and the 1h and 4 h SCM-DHDO products showing the carbonyl, aromatic, C-O aliphatic, and C-C aliphatic regions along with the methoxyl subregion.

Sample	Carbonyl Region (165-215 ppm)	Aromatic Region (95-165 ppm)	C–O Aliphatic Region (55-95 ppm)	C–C Aliphatic Region (0-55 ppm)	Methoxyl Subregion (subset of C-O Aliphatic Region) (55-57 ppm)
GVL extracted lignin	0%	69%	24%	7%	13%
1 h GVL extracted lignin products	0%	50%	9%	41%	3%
4 h GVL extracted lignin products	0%	20%	8%	72%	1%

2D HSQC was also performed, as shown in Figure 8, for the C–C aliphatic (a_1-c_1), C–O aliphatic (a_2-c_2), and aromatic and aldehyde (a_3-c_3) regions of (a) the GVL extracted lignin, (b) 1 h SCM-DHDO GVL extracted lignin products, and (c) the 4 h SCM-DHDO GVL extracted lignin products. Figure 8 (a_1) shows the C–C aliphatic region for the GVL extracted lignin which has few signals in this region. These signals correlate to residual GVL in the sample. After 1 h, the region undergoes drastic changes as seen in Figure 8 (b_1). The most prominent changes are the formation of alkyl chain CH/CH_3 (red circled) and CH_2 (orange circled). The increases in signals in the alkyl CH_2 region (orange circled) can be attributed to the saturation of the aromatics, forming cyclohexyl CH_2 groups. Additionally, any CH_2 in α or β positions of the alkyl tails off of the cyclohexyl species or any CH_2 in β position of the alkyl tails off of the phenolic species will show up in this region. The new peaks in the red-circled region can be attributed to two main sources: 1) terminal CH_3 from either methyl, ethyl, and propyl cyclohexyl groups or ethyl and propyl phenyl groups and 2) cyclohexyl CH groups. The purple- and green-circled regions, correlate to aromatic bound CH/CH_3 and CH_2. The increase in signals in the green-circled region can be attributed to CH_2 in the α-positions of the ethyl or propyl tails off of the phenolics. For the purple-circled region, the signals around δ_H/δ_C 2.1/12.0 and δ_H/δ_C 2.1/16.0 likely correlate to aromatic bonded methyl groups (Ar–**CH₃**) while the signals at δ_H/δ_C 2.1/20.7 have been hypothesized in pyrolytic lignins to be diaryl methine linkages (Ar– (**CH**–R) –Ar) where a carbon is bonded to two aromatics (Ar), a hydrogen (H), and an alkyl chain (R).[21] The diaryl methine linkages have been proposed to form during lignin condensation between the α on the alkyl tail of one lignin unit and the aromatic ring of a second lignin unit.[34] By 4 h, Figure 8 (c_1), the signals in three regions continue to increase with the sole exception being the Ar–CH_2 region (green circled region). The signals in this region both increase and decrease which can be explained with changes in functionalities of the aromatics through demethoxylation and methylation reactions which may shift these peaks and saturations of the aromatic rings which decrease the peak intensities.

The C–O aliphatic region displayed in Figure 8 (a_2-c_2) highlights changes in the lignin ether linkages and methoxyl groups. In Figure 8 (a_2), the GVL extracted lignin is shown to have signals for the three prominent interunit linkages (β-O-4 ether (A), phenylcoumaran (B), and resinol (C) units) and a large aromatic methoxyl group peak. After a 1 h reaction shown in Figure 8 (b_2), the ether linkages have disappeared and the methoxyl group signal has decreased. New unidentified CH/CH_3 (blue) and CH_2 (green) peaks have formed. The CH peaks in this region may be from the **CH**–O–R/H in cyclohexanols formed from the saturation of phenolics or potentially $\mathbf{CH_3}$–O–R from methoxylated alkanes or esters. The CH_2 are terminal alcohol or ether groups (R–$\mathbf{CH_2}$–O–R/H) potentially formed from coupling of the methanol solvent.[14,16]

The aromatic and aldehyde regions are shown in Figure 8 (a_3-c_3). The GVL extracted lignin in Figure 8 (a_3) contains $S_{2/6}$ units, G_2 units, and $G_{5/6}$ units. After 1 h of reaction in Figure 8 (b_3), the $S_{2/6}$, G_2, and $G_{5/6}$ shift to $S''_{2/6}$, G''_2, and $G''_{5/6}$ as has previously been seen with pyrolytic lignin which has been attributed to the deoxygenation of the alkyl tails of the lignin units.[21] Additionally, these signals have decreased in intensity which matches with hydrogenation and methylation of the aromatic rings. A region of new signals has formed around δ_H/δ_C 6.7/128 ppm. These new signals are likely from methylated and demethoxylated S and G units and are close to reported $H_{2/6}$ units (δ_H/δ_C 7.1/126.0).[21,24] After 4 h reaction time in Figure 8 (c_3), the $S''_{2/6}$, G''_2, and $G''_{5/6}$ signals have decreased while additional signals have arisen in the orange-circled region. In the aldehyde region (δ_H/δ_C 9.0-10.0/185-200), cinnamaldehyde is identified in the GVL extracted lignin (Figure 8 (a_3)) and disappears after 1 h (Figure 8 (b_3)) and 4 h (Figure 8 (c_3)) reaction times.

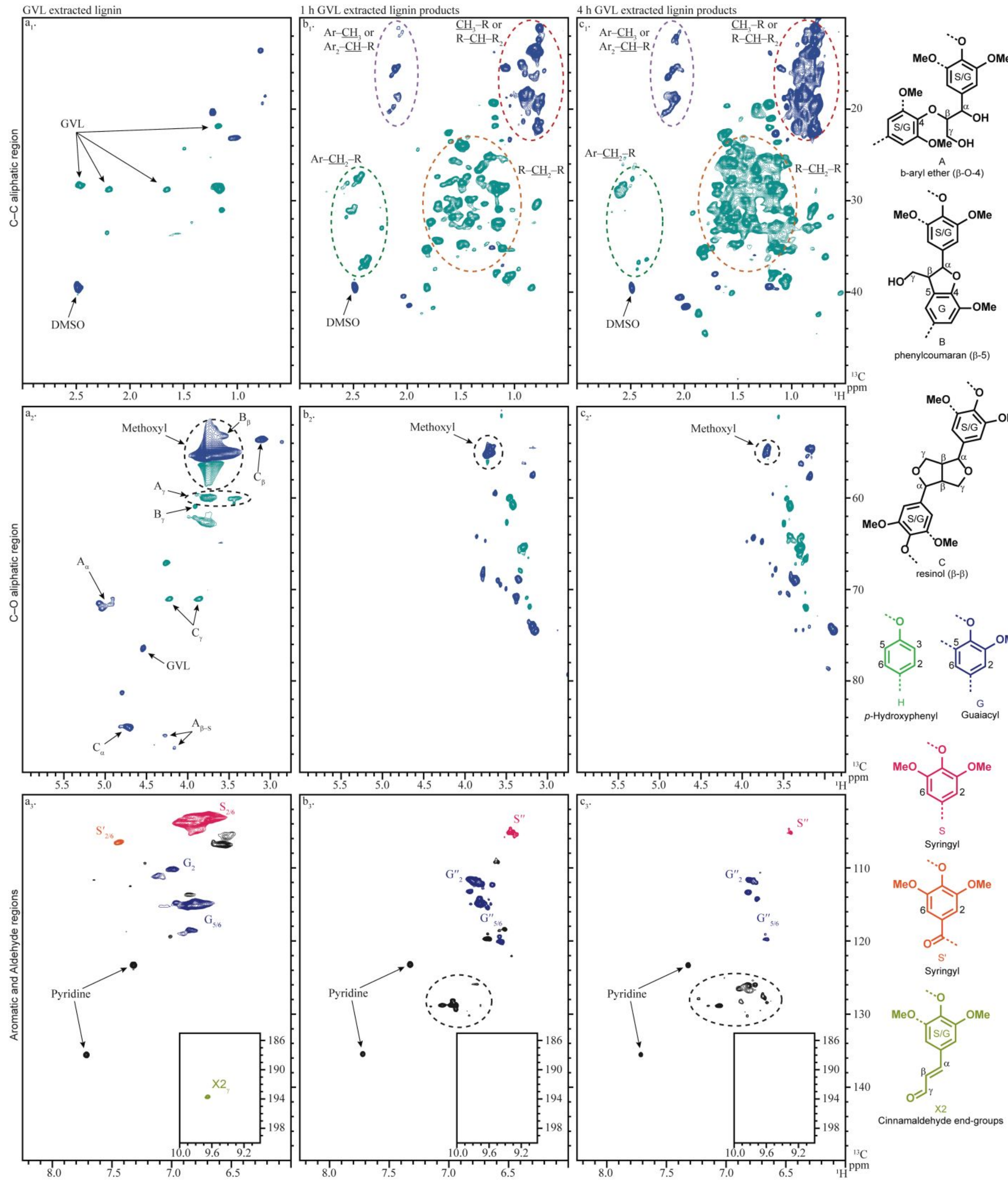

Figure 8. Edited HSQC NMR of GVL extracted lignin (a), 1 h GVL extracted lignin products (b), and 4 h GVL extracted lignin products (c) split into C–C aliphatic (a_1-c_1), C–O aliphatic (a_2-c_2), and aromatic and aldehyde (a_3-c_3) regions. C–C aliphatic and C–O aliphatic regions are edited with CH/CH_3 in blue and CH_2 in green. No aldehyde peaks are present in the 1 and 4 h products (b_3 and c_3).

FT-ICR MS of non-volatiles from lignin and biomass SCM-DHDO at 4 h reaction time

The high-resolution mass spectrometry technique FT-ICR MS with APPI was used to understand the elemental compositions of higher molecular weight species of the 4 h maple wood and GVL extracted lignin SCM-DHDO products. Our group has previously applied this technique to cellulose SCM-DHDO and pyrolytic lignin to study higher molecular weight species.[14,21] The average molecular compositions and elemental ratios of the GVL extracted lignin and the 4 h maple wood products and 4 h GVL extracted lignin products are shown in Table 3. Estimates for the molecular compositions and elemental ratios were determined by the molecular compositions of the distinct molecular weights. The distinct molecular weight analyzed include only C, H, and O, while the ^{13}C and N containing compounds were omitted. The ionization method, atmospheric pressure photoionization (APPI) is boiling point limited, and only species with molecular weights between 150-1000 Da were observed. The GPC results have shown the 4 h maple wood products and 4 h GVL extracted lignin products to be within this range. The GVL extracted lignin extends to higher molecular weights with the primary peak at 3500 Da. Despite this, the trends in the O/C, H/C, and H/C_{eff} ratios should be representative for the whole GVL extracted lignin since the higher molecular weights only vary in the number of units. The O/C, H/C, and H/C_{eff} ratios in the native lignin of the maple wood were assumed to be similar to the GVL extracted lignin for the FT-ICR MS analysis of the 4 h maple wood products.

The GVL extracted lignin has a higher detected average molecular weight (625 Da) than the GVL extracted lignin products (489 Da) and maple wood products (476 Da). The differences in elemental composition becomes evident when comparing the elemental ratios. The O/C ratio decreased from 0.32 in the GVL extracted lignin to 0.06 and 0.04 in the GVL extracted lignin and maple wood products respectively. The H/C ratios increased from 0.99 in the GVL extracted lignin to 1.44 and 1.51 in the GVL extracted lignin and maple wood products respectively. These changes in the O/C and H/C ratios support the quantitative ^{13}C NMR findings in the effectiveness of hydrogenation and hydrodeoxygenation of the SCM-DHDO process. The H/C_{eff} ratio, a descriptor of the value of a carbon source as a fuel, increased from 0.35 in the GVL extracted lignin to 1.31 and 1.44 in the GVL extracted lignin and maple wood products respectively. Overall, SCM-DHDO highly deoxygenated the GVL extracted lignin and the native lignin in the maple wood, while the maple wood products were slightly more deoxygenated than the GVL extracted lignin products.

Table 3. Number Average (stdev) double bond equivalents (DBE), C, H, and O contents by FT-ICR MS with O/C, H/C, and H/C_{eff} ratios.

Average (Stdev)	DBE	C	H	O	O/C	H/C	H/C_{eff} ((H-2O)/C)	# of Distinct Molecular Weights	Molecular Weight [Da]
Maple GVL lignin	18.5 (5.1)	34.6 (9.8)	34.1 (10.8)	10.9 (3.2)	0.32	0.99	0.35	1657	625 (174)
4 h GVL extracted lignin products	10.5 (4.0)	33.8 (10.8)	48.5 (16.9)	2.1 (1.6)	0.06	1.44	1.31	3479	489 (148)
4 h maple wood products	9.2 (3.8)	33.6 (11.0)	50.9 (17.7)	1.3 (1.2)	0.04	1.51	1.44	2473	476 (147)

Another way to view the data is by plotting the number of oxygens on each molecule as shown Figure 9. The GVL extracted lignin molecules have between 5 to 19 O. The GVL extracted lignin SCM-DHDO products have low oxygen contents with 19% with zero oxygen (HC), 29% with one oxygen (1O), and 25% with two oxygen (2O). Likewise, the maple wood SCM-DHDO products have 41% with zero oxygen (HC), 32% with one oxygen (1O), and 19% with two oxygen (2O).

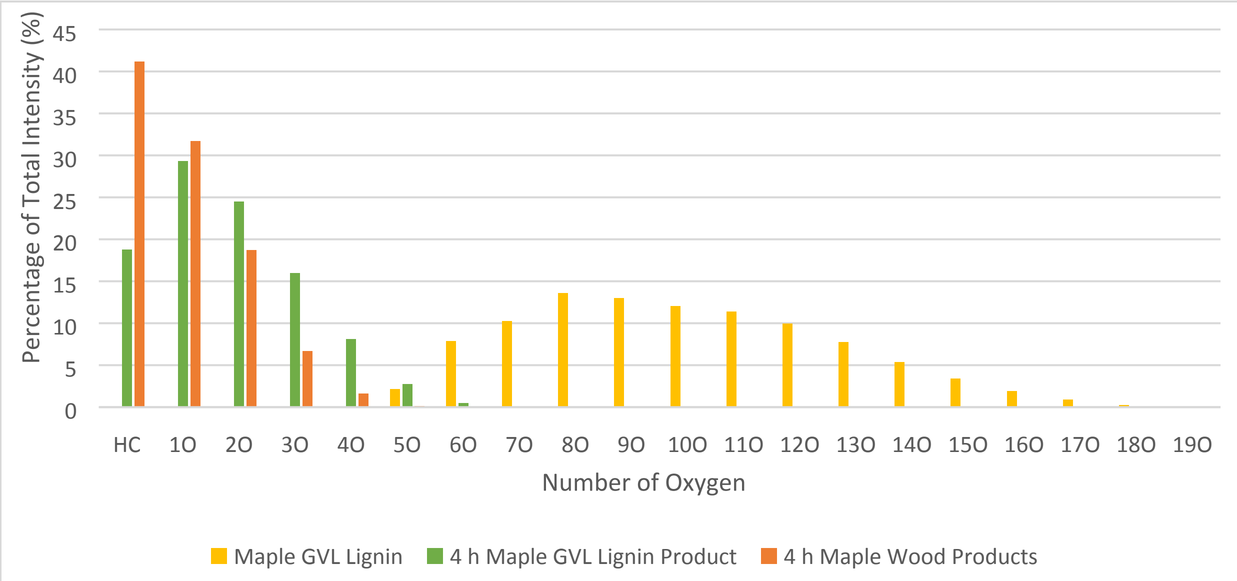

Figure 9. Heteroatom class distribution of GVL extracted lignin, 4 h GVL extracted lignin products, and 4 h maple wood products as determined by FT-ICR MS with APPI (HC = zero oxygen on species).

Further analyses of the FT-ICR MS data can be done by plotting the C number vs DBE of the species. The spectra for GVL extracted lignin, 4 h GVL extracted lignin products, and 4 h maple wood products are plotted in Figure 10 (a_1, b_1, and c_1). Also shown is the C number vs DBE for different oxygen (O) contents in Figure 10 (a_2-a_4, b_2, and c_2). The GVL extracted lignin (Figure 10 (a_1)) has four main clusters corresponding to dimers (20 C, 10 DBE), trimers (30 C, 15 DBE), tetramers (39 C, 21 DBE), and pentamers (49 C, 25 DBE). This corresponds to an increase of ~9.7 C and 5 DBE per added monomer, matching the addition of one propylphenyl monomer (9-11 C and 4-6 DBE depending on monomer and linkage type) Likewise the 4 h GVL extracted lignin products and 4 h maple wood products in Figure 10 (b_1 and c_1) each have two main clusters corresponding to dimers and trimers with another smaller cluster corresponding to monomers. The FT-ICR MS has difficulty detecting the monomers under the conditions used so the monomer intensity may be understated. For the GVL extracted lignin products these monomers, dimers, and trimers have carbon numbers and DBE of 1) 11 C, 4 DBE; 2) 19 C, 6 DBE; and 3) 27 C, 8 DBE; respectively or 8 C and 2 DBE per additional unit. Interestingly, this correlates to dimers and trimers having only 1 unsaturated unit with the additional units being mostly saturated (1 saturated ring has 6-11 C and 1 DBE; 1 unsaturated ring has 6-11 C and 4 DBE depending on alkyl tail length and number of methoxyl units). The 4 h maple wood products have slightly higher amounts of saturation. The monomers, dimers, and trimers were (12 C, 4 DBE), (21 C, 5 DBE), and (30 C, 6 DBE) respectively or 9 C and 1 DBE per additional unit which correlates to one saturated unit. Both the GVL extracted lignin and maple wood oligomers primarily have only 1 unsaturated phenolic unit with the others being saturated cyclohexyl units.

The O content increases with the C content for the GVL extracted lignin (Figure 10 (a_2-a_4)). Contrarily, the O content of the GVL extracted lignin products (Figure 10 (b_2)) and the 4 h maple wood products (Figure 10 (c_2)) does not correlate with the C content. The C content ranges up to 60 while a bulk of the species have lower than 3 O. Since 1 linkage is present per 6-11 additional C, this implies that units in the GVL extracted lignin and maple wood products are bound through C–C bond linkages as opposed to ether linkages.

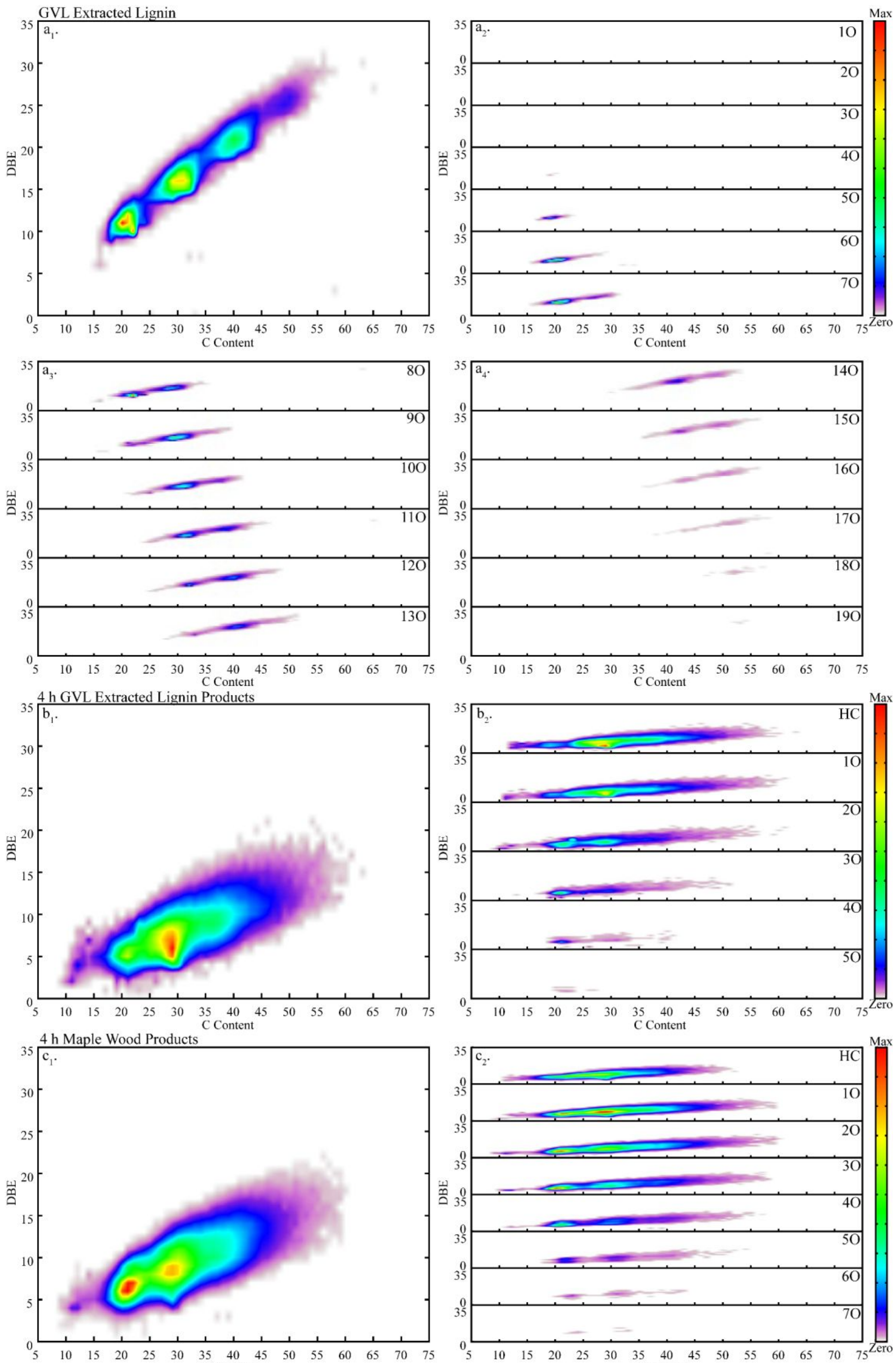

Figure 10. FT-ICR MS of GVL extracted lignin (a_1-a_4), 4 h GVL extracted lignin products (b_1-b_2), 4 h maple wood products (c_1-c_2) showing intensity with C number vs DBE. Overall spectra are displayed in a_1, b_1, and c_1 while spectra are further split by O number (0O (HC) to 19O) and displayed in a_2-a_4, b_2, and c_2.

The conversion of lignin in the SCM-DHDO process is summarized in Figure 11. The lignin is first extracted from the biomass and solubilized with the supercritical methanol. The solubilized lignin depolymerizes through ether, C–O, and C–C cleavage on the alkyl tails along with initial demethoxylation of aromatic rings forming lignin monomers. From there, a portion of the lignin monomers further convert into cyclohexanols through demethoxylation, hydrogenation of the aromatics, and methylation of the aromatic and cyclohexyl rings. Alternatively, the lignin monomers or larger lignin fragments polymerize through C–C bond formation accompanied with hydrodeoxygenation to form high molecular weight species with low DBE and O contents. While the GVL extracted lignin, enzymatic lignin, and the lignin in maple wood all appear to follow this path, the GVL extracted and enzyme lignin have lower monomer yields compared to the non-extracted lignin potentially due to the higher lignin concentrations during solubilization which occur with the extracted lignins. This repolymerization process is likely higher order with respect to lignin concentration as compared to hydrogenation or other reactions. Thus, one key consideration in any lignin conversion technology should be to keep the lignin concentration low and catalyst concentration high in the reactor to mitigate repolymerization reactions and promote hydrogenation and other reactions to stabilize the lignin monomers and oligomers.

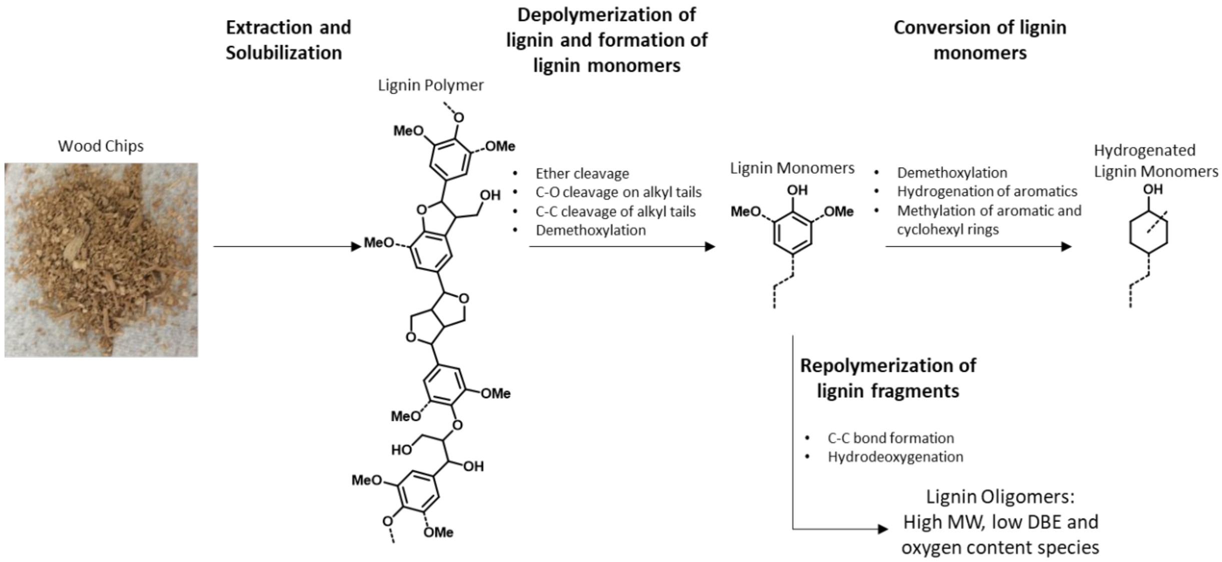

Figure 11. Progression of lignin through the SCM-DHDO process

Comparison to other lignin conversion technologies

The SCM-DHDO process is one of multiple notable technologies for converting lignin into monomers that have recently been reported in the literature.[3,27-28,33-41] All of these involve conversion of biomass in a condensed phase in a hydrogen or oxygen atmosphere with various types of catalysts and are summarized in Table 4. The Luterbacher group described a two-step process that involves, first the protection and extraction of lignin from biomass and second, a hydrolysis to depolymerize the lignin to produce aromatic monomers.[33-34] The first step includes an extraction of the lignin at 80ºC for 1.5-5 h with a 1,4-dioxane solvent, HCl, and an aldehyde such as propionaldehyde (PA). The PA forms a cyclic acetal with the α- and γ-hydroxyl groups on the alkyl tail of the lignin to prevent condensation between the α-position of the alkyl tail and aromatic ring of other lignin units. After finishing with the lignin separation, a 5-20 h hydrolysis step at 200-250ºC with 40 bar H_2, and a Ru/C, Pd/C or Ni/C catalyst produced 48% monomer yields with hardwoods birch and 78% monomer yield with a F5H transgenic poplar (a modified wood with high S lignin) and 20% with the softwood spruce. The 48% lignin monomer yields from birch extracted lignin are over double that of SCM-DHDO of GVL extracted lignin but similar to the lignin monomer yields from maple wood at 43%. The SCM-DHDO process has the advantage of having the solubilization and hydrogenation processes occur in a single step, having a shorter residence time (4 h vs 15 h), not requiring added hydrogen, and not requiring 1,4-dioxane and propionaldehyde which are difficult to recover. In addition the SCM-DHDO process makes fuel range alcohols in high yields from the cellulose and hemicellulose.[14,16] The catalyst has shown recyclability over 5 reactions with eucalyptus chips and cellulose as well as over 100 h time on stream in a continuous reactor with glycerol.[13,42] A key disadvantage to the SCM-DHDO process is the higher temperatures (300ºC), pressures (2000-3000 psig), and the high utilization of methanol.

The Stahl group has demonstrated another lignin depolymerization approach consisting of aerobic oxidation of extracted lignins followed by formic-acid-induced hydrolytic depolymerization.[36,43] The aerobic oxidation converts the C_α alcohols in lignin into ketones at over 90% yields using HCl, HNO_3, and AcNH-TEMPO (homogeneous oxidation catalyst) (28 h, 65ºC) whereas the formic-acid-induced hydrolytic depolymerization cleaves the β-O-4 linkages with up to 42 wt% monomer yields at low temperatures (24 h, 110ºC). This process obtains lignin monomer yields comparable to maple wood SCM-DHDO of maple wood. Its advantages include milder reaction temperatures and high monomer yields but requires long reaction times (28 h pretreatment oxidation and 24 h reaction) and a potentially costly pretreatment oxidation step with homogenous catalysts which may be difficult to recover.

The Sels, Beckham, and Román-Leshkov groups have demonstrated a process called reductive catalytic fractionation (RCF or CRF) of lignocellulosic biomass.[27-28,37-39] Sels's process involves a 3 h solubilization of biomass (birch) in supercritical methanol at 250ºC and 435 psig initial H_2

pressure during which the solubilized lignin passes into a catalyst basket containing a commercial Ni/Al_2O_3 catalyst. The resulting product is subjected to a liquid-liquid extraction with dichloromethane and water to separate out the lignin oil with a final lignin monomer carbon yield up to 43%. The process was tuned to produce 4-propylsyringol in up to 34 wt% yields.[37-38] Furthermore, the Sels group has developed a method for processing the 4-propylsyringols into bis-syringols, a potentially benign bisphenol A replacement to make aromatic polyesters.[37] The Román-Leshkov and Beckham groups have focused on exploring the RCF process in a semi-continuous flow system.[28,39] Their system involves two parallel biomass solubilization beds and a catalyst bed to first solubilize the biomass (primarily the lignin fraction) before reacting and stabilizing the lignin products in the catalyst bed over Ni/C 50/50 SiO_2 with H_2 flow. They have demonstrated up to 16.9 wt% lignin monomer yields with up to 45 wt% total oil yields. Furthermore, catalyst deactivation by sintering, leaching, and poisoning was observed. The RCF process similarly uses supercritical methanol to solubilize and depolymerize the lignin in biomass reaching the same lignin monomer yields of 43%. RCF requires the addition of H_2 since the Ni catalysts do not reform the methanol and produces a carbohydrate pulp from the hemicellulose and cellulose fractions of biomass.[37] Although RCF is not able to process the hemicellulose and cellulose fractions, the carbohydrate pulp can be converted to bio-ethanol through saccharification and fermentation.[38]

The Rinaldi group has described the Catalytic Upstream Biorefining (CUB) process for lignin conversion to monomers which utilizes a Raney nickel catalyst with a 2-propanol(IPA)/water solvent system at 160-220ºC to produce a non-pyrolytic lignin bio-oil with up to 25 wt% yields and holocellulose pulp.[41,44] A tunable secondary hydrodeoxygenation reaction produces aliphatic rich or aromatic rich products from the lignin oil with 40-45% mass yields to hydrocarbons for a cumulative weight yield of around 10% of the lignocellulosic weight.[41] The aliphatic hydrocarbon products were obtained with a phosphidated Ni/SiO_2 catalyst with 725 psig initial hydrogen pressure and 300ºC reaction temperature while aromatic hydrocarbon products were obtained by reducing the initial hydrogen pressure to 0.5-1 MPa and increasing the reaction temperature to 350ºC. The aliphatic hydrocarbon products were 100% aliphatics while the aromatic hydrocarbon products were 22% aliphatics and 78% aromatics. Ni/SiO_2 catalyst recycling experiments noted slight deactivation through the increased content of oxygenated species in the aliphatic hydrocarbon products of the second and third runs (<0.2%). An advantage of CUB is that it can convert lignin in biomass into lignin bio-oil in a subcritical solvent process which imparts lower pressure requirement on reactor systems. When coupled with hydrodeoxygenation, it can produce tunable products of either aromatics or aliphatics. Downsides to the process are the lower products yields and its inability to process the cellulose and hemicellulose.

In summary, the Luterbacher and Stahl group technologies require costly reagents, more steps and difficult separations but can obtain higher lignin yields with lower temperatures and pressures. Contrarily, the SCM-DHDO and RCF technologies utilize higher temperatures and pressures (supercritical in most cases) though are able to produce high lignin monomer yields without prior lignin extraction. Additionally, RCF has been demonstrated in a semi-continuous flow process though at lower monomer yields. The CUB process is a subcritical process for producing a lignin oil has resulted in lower yields and requires a second hydrodeoxygenation upgrading to produce a tunable aliphatic or aromatic stream. While the SCM-DHDO, RCF, and CUB+hydrodeoxygenation processes all can process lignin from whole biomass, RCF and CUB+hydrodeoxygenation leave the carbohydrates as a pulp while SCM-DHDO produces C_2-C_6 alcohols from the cellulose/hemicellulose portion of the biomass.

Table 4. Comparison of lignin conversion technologies

Technology	Catalyst/ Reagents	Solvent/ Feeds	Reaction Conditions	Lignin Carbon Yields	Other Notes on Process
SCM-DHDO	$CuMgAlO_x$	Solvent: MeOH Feeds: Maple wood and extracted maple lignins	Batch reactor 300 ºC up to 3000 psig	43% monomers, 54% dimers, and 6% trimers from maple	Processes cellulose and hemicellulose into C_2-C_6 alcohols
Luterbacher Group[33-34] **1. Extraction/ aldehyde protection +** **2. hydrolysis**	1. HCl, and PA 2. Ru/C, Pd/C, or Ni/C	Solvent: 1. Dioxane 2. Dioxane Feeds: Birch wood, spruce wood, or F5H transgenic poplar wood	Batch reactor 1. 80 ºC 1.5-5 h 2. 200-250ºC 580 psig H_2 5-20 h	48% monomers from birch, 78% monomers from F5H transgenic poplar	
Stahl Group[36,43] **1. Aerobic oxidation of extracted lignins +** **2. formic-acid-induced hydrolytic depolymerization**	1. HCl, HNO_3, AcNH-TEMPO 2. HCO_2H, HCO_2Na	Solvent: 1. AcN + H_2O 2. HCO_2H Feeds: Various extracted lignins	Batch reactor 1. 65ºC 29 psig O_2 28 h 2. 110ºC 24 h	Up to 42% monomers from extracted lignins	Requires extraction of lignin prior to upgrading
Sels Group[27,37-38] **Reductive Catalytic Fractionation**	Ni/Al_2O_3	Solvent: MeOH Feeds: Birch wood	Batch reactor 250ºC 435 psig initial H_2	44% monomers, 9 wt% dimers, and 87 wt% lignin oil yield from birch	Tunable to products 34% to 4-propylsyringol to be converted into potential BPA replacement Carbohydrates remain after reaction as a pulp

Román-Leshkov and Beckham Groups[28,39] Reductive Catalytic Fractionation	Ni/C 50/50 SiO_2	Solvent: MeOH Feeds: Poplar wood and model β-O-4 compound	Semi-continuous flow reactor 190ºC 870 psig	16.9 wt% monomers and 45 wt% lignin oil yield from poplar	Demonstrated as semi-continuous flow process Carbohydrates remain after reaction as a pulp
Rinaldi Group[41,44] Catalytic Upstream Biorefining (CUB) + Catalytic Upgrading or Lignin Hydrotreating	1. Raney Ni 2. Ni2P/SO_2	Solvent: IPA/ H_2O Feeds: Poplar or spruce wood	Batch reactor 1. 160-220ºC autogenous pressure 2. 300ºC 725 psig H_2 for aliphatic production or 350ºC 72.5-145 psig H_2 for aromatic production	1. 25 wt% lignin oil yield 2. 10 wt% cumulative yield to aromatic or aliphatic rich products	Carbohydrates remain after reaction as a holocellulose pulp Tunable for aromatic or aliphatic production

Conclusions

SCM-DHDO converts lignin into aromatic and cyclohexyl monomers, dimers and trimers. SCM-DHDO of maple wood results in greater than two times higher yield of lignin monomers than SCM-DHDO of GVL extracted lignin while the dimer and trimer yields were similar at longer reaction times. SCM-DHDO of physical mixtures of GVL extracted lignin and cellulose and SCM-DHDO of GVL lignin had similar lignin monomer yields indicating that the higher yield in the maple wood is not due to an interaction with the cellulose products such as cellulose products forming protection groups. The higher yield with the maple wood is likely because higher concentrations of lignin occur with the extracted lignin than the maple wood which results in undesired condensation reactions. This higher concentration is likely a result of the higher solubility of the GVL lignin in the methanol and the higher lignin density in the starting materials.

The initial lignin products (15 min) include guaiacols and syringols with and without deoxygenated 1 to 3-carbon alkyl tails, which is evidence of C–C cleavage and deoxygenation during depolymerization. The 15 min maple wood products also showed increased demethoxylation with S/G/P ratios of 1.0/4.2/1.2 vs 1.0/1.0/0.1 for the GVL extracted lignin products. The products from SCM-DHDO of the GVL extracted lignin had higher amounts of dimers and trimers than the products from SCM-DHDO of the maple wood as determined by GPC. The quantitative ^{13}C NMR revealed high amounts of hydrodeoxygenation, demethoxylation, and saturation of aromatics with the aromatic and C–O aliphatic regions and the methoxyl subregion decreasing from 69%, 24%, and 13% in GVL extracted lignin to 20%, 8%, and 1% respectively after a 4 h reaction. The FT-ICR MS supported this by highlighting a decrease in the O/C ratio from 0.32 in GVL extracted lignin to 0.06 and 0.04 in the 4 h SCM-DHDO GVL extracted lignin products and the 4 h SCM-DHDO maple wood products. Additionally, the FT-ICR MS heteroatom class distribution and C number versus DBE plots showed that 19% of the SCM-DHDO GVL extracted lignin products and 41% of the SCM-DHDO maple wood products contained no O. Some of the products contained up to 60 C, highlighting the formation of new C–C linkages during SCM-DHDO chemistry.

Acknowledgements

This work was supported by ExxonMobil. The authors would like to thank John Ralph for helpful discussions on lignin depolymerization, the Magnetic Resonance Facility in the Chemistry Department of the University of Wisconsin-Madison for use of the Bruker Avance III 500 gifted by Paul J. Bender, the Center for Laser-Assisted NMR for use of the Bruker Avance III 600 (NIH S10 OD012245), and the DOE Great Lakes Bioenergy Research Center (DOE BER Office of Science DE-SC0018409).

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