

Article

Pyrolytic Conversion of Cellulosic Pulps from “Lignin-First” Biomass Fractionation

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Abstract: Utilization of lignin is among the most pressing problems for biorefineries that convert lignocellulosic biomass to fuels and chemicals. Recently “lignin-first” biomass fractionation has received increasing attention. In most biorefining concepts, carbohydrate portions of the biomass are separated, and their monomeric sugar components released, while the relatively chemically stable lignin rich byproduct remains underutilized. Conversely, in lignin-first processes, a one-pot fractionation and depolymerization is performed, leading to an oil rich in phenolic compounds and a cellulosic pulp. Usually, the pulp is considered as a fermentation feedstock to produce ethanol. Herein, the results of a study where various cellulosic pulps are tested for their potential to produce valuable products via pyrolysis processes, assessed via analytical pyrolysis (py-GC), are presented. Samples of herbaceous (switchgrass) and woody biomass (oak) were subjected to both an acid-catalyzed and a supported-metal-catalyzed reductive lignin-first depolymerization, and the pulps were compared. Fast pyrolysis of the pulps produced levoglucosan in yields of up to about 35 wt %. When normalized for the amount of biomass entering the entire process, performing the lignin-first reductive depolymerization resulted in 4.0–4.6 times the yield of levoglucosan than pyrolysis of raw biomass. Pulps derived from switchgrass were better feedstocks for levoglucosan production compared with pulps from oak, and pulps produced from metal-on-carbon catalyzed depolymerization produced more levoglucosan than those from acid-catalyzed depolymerization. Catalytic pyrolysis over HZSM-5 produced aromatic hydrocarbons from the pulps. In this case, the yields were similar from both feedstocks and catalyst types, suggesting that there is no advantage to lignin fractionation prior to zeolite-catalyzed catalytic pyrolysis for hydrocarbons.

Keywords: levoglucosan; catalytic pyrolysis; lignin-first; depolymerization; pulp



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1. Introduction

The largest share of both energy carriers and chemical industry products are derived from fossil fuels, leading to greenhouse gas emissions and other environmental problems. Efforts to decarbonize the production of chemicals and liquid fuels have focused on lignocellulosic biomass, the largest source of renewable carbon available [1]. While efforts over the last several decades have developed efficient methods for converting carbohydrates to various fuel and chemical products [2], lignin recalcitrance is a major hurdle preventing many biorefinery concepts from achieving economic viability. In biochemical, thermochemical, or hybrid conversion schemes, efficient conversion of lignin to renewable products has proven difficult. In standard biochemical based conversion models, lignin is a co-product released in the pre-fermentation process used to depolymerize complex carbohydrates to sugars [3,4]. Several types of pretreatments can be used, including dilute acid (usually H₂SO₄), alkaline (NaOH, KOH or NH₃), steam, liquid hot water, or organic solvents [5]. Each of these pretreatments modifies the biomass structure so that enzymatic hydrolysis can better release monomeric fermentable sugars. Often, the lignin remaining has little other use than to be burned for process energy. In thermochemical processes, a

large fraction of the lignin carbon often winds up as part of solids (bio-char) or heavy ends of pyrolysis liquids and ultimately is poorly converted to deoxygenated hydrocarbons [6]. This fraction of bio-oil also largely contributes to coking of catalysts during downstream bio-oil upgrading processes.

Recent research has made several advances in the utilization of lignin [7]. Solvent-phase depolymerization of lignins has received a lot of attention as a means to produce phenolic monomers from isolated lignins [8–10]. These methods can be catalyzed by acids, bases, metal oxides, or supported active metals and may also be performed under oxidative or reductive conditions. Reductive depolymerizations have received the most attention recently due to the depolymerization efficiency of this approach. Like other lignin conversion methods, the yield of monomers produced is limited by two main factors: the relative stability of the non- β -O4 type linkages and the tendency for repolymerization reactions to occur. Because most isolation methods also cause structural changes that decrease the concentration of β -O4 type linkages and increase more stable C-C linkages compared with native structures, depolymerization of isolated lignins often has poor yields of monomers even if the average molecular weight is significantly decreased. Therefore, several researchers have recently proposed a “lignin-first” process where whole biomass is subject to solvent liquefaction conditions. Lignin is thereby separated and depolymerized to a monomer-rich phenolic oil via solvolysis and thermocatalytic depolymerization [11–18]. This combines the organic solvent-based pretreatment process mentioned above with lignin depolymerization in one pot. By acting on native lignin, the yield of monomers is generally increased because of the higher concentration of the labile β -O4 linkages. In this case, a cellulose-rich “pulp” is the byproduct.

In this study, we performed an in situ reductive polymerization via hydrogen transfer using Pd/C and Ru/C, without hydrogen gas, on switchgrass and oak biomass. Each of these catalysts has been proven effective for reductive lignin-first depolymerizations. Previously, Van den Bosch et al. reported monomer yields of 50 wt %, 44 wt %, 27 wt % and 21 wt % for Ru/C catalyzed lignin-first depolymerization from birch, poplar, miscanthus, and mixed softwoods, respectively [19]. Similarly, Galkin et al., 2016, reported monomer yields of greater than 30% with high selectivity to propylsyringol and propenylsyringol using Pd/C for reductive lignin-first depolymerization of birch wood [17]. We also tested using acid catalysis to aid in the depolymerization; both a solid (HZSM-5) and a soluble Lewis acid, aluminum triflate ($\text{Al}(\text{OTf})_3$), were selected. Kramarenko et al. reported yields of phenolic monomers of up to 20 wt % using acidic zeolite ($\text{H}\beta$) catalysts for lignin-first depolymerization [14]. Two different types of lignocellulosic biomasses were chosen to compare the efficiency of the lignin fractionation and depolymerization process with the different types of lignin structures found in the woody and herbaceous feedstocks. Hardwoods have previously been found to perform more efficiently than softwoods and herbaceous feedstocks for lignin-first depolymerizations [19].

There is comparatively little work on the subsequent uses for the carbohydrate pulps, though most have considered this pulp as a feedstock to undergo hydrolysis to release fermentable sugars for subsequent production of ethanol or other fermentation products [11,15,16]. In contrast, there has been little attention towards this product as a potential feedstock for conversion via pyrolysis. Therefore, in this contribution, we report on the pyrolytic conversion of the cellulosic pulps produced from the different feedstock and catalyst combinations described above. The cellulosic pulps from these processes were tested for conversion to levoglucosan and related products via fast pyrolysis and aromatic hydrocarbons via catalytic pyrolysis over HZSM-5. These are two distinct options for thermochemical conversion of the cellulosic residues. Levoglucosan is a dehydrated form of glucose and is the major product of cellulose pyrolysis. Pure cellulose can give high yields (up to 60 wt %) of levoglucosan, but when cellulose remains in the biomass structure, a much less selective thermal depolymerization occurs. Levoglucosan is considered a potential important starting material for many fine chemical applications. In contrast, when catalytic pyrolysis is performed over zeolites such as HZSM-5, the primary oxygenates are converted via a series of reactions to a product

mixture containing aromatic hydrocarbons, largely the important petrochemical BTEX mixture (benzene, toluene, ethyl benzene, and xylenes). The overall process considered in this study is summarized in Figure 1. The effect of the feedstocks and depolymerization catalysts were compared and contrasted for both the composition of the phenolic oils, the properties of the cellulosic pulps, and their pyrolysis products.

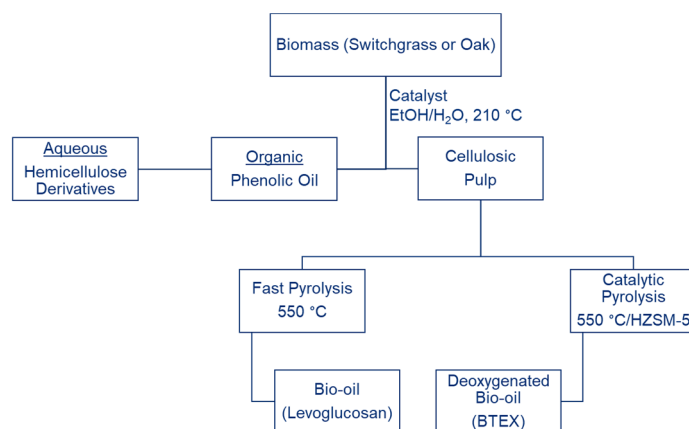


Figure 1. Schematic of biomass conversion process of this study.

2. Materials and Methods

2.1. Materials

Switchgrass was obtained from the McDonnell farm in East Greenville, PA, USA. Oak wood was recovered from a tree removed from the campus of the Eastern Regional Research Center, Wyndmoor, PA, USA. Each biomass was ground to 2 mm particles before use. Pd/C (5 wt %), Ru/C (5 wt %), and aluminum triflate $\text{Al}(\text{OTf})_3$ were purchased from Sigma-Aldrich and used as received in powder form. HZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 23$) was purchased from Zeolyst as $\text{NH}_4\text{ZSM-5}$ and calcined at 600 °C for 24 h before use to obtain the acid form. The same material was used for both lignin depolymerization and catalytic pyrolysis.

2.2. Lignin-First In Situ Depolymerization

A 100 mL stainless steel Parr reactor was loaded with 2 g biomass (switchgrass or oak) and 0.5 g catalyst. A quantity of 25 mL of ethanol and 25 mL of water was added. The reactor was purged of air by flushing with N_2 three times. The reactor was then pressurized to ~3.4 atm with N_2 . The heating was started. When the temperature reached ± 10 °C of the target temperature (210 °C), the reaction time was started. After 120 min, the heater was removed, and the reaction vessel cooled in an ice water bath. After cooling to room temperature, the reactor was opened, and the reaction mixture was filtered through a filter paper. The solid pulp and catalyst mixture was washed with ethanol/water, acetone, and then water, and air-dried. The filtrate was partially concentrated using a rotary evaporator and then underwent an extraction with dichloromethane and water. After separation, the aqueous layer was washed 3X with dichloromethane. The dichloromethane was removed by rotary evaporation to yield the phenolic oil. The dried pulp catalyst mixture (in case of heterogeneous catalysts) was subjected to sieving using a 150-mesh screen. The fine fraction was considered used catalyst and the coarse fraction recovered pulp.

GC/MS on the phenolic oil was performed using a Shimadzu GC-2010 (Columbia, MD, USA). A DB-1701(60 m $\times$ 0.25 mm and 0.25 μm) column was used. The GC oven was held at 45 °C for 4 min, then increased at 3 °C/min to 280 °C, and then held at 280 °C for 20 min. The injector temperature was 250 °C, and the split ratio was set to 30:1. The flow rate of the He carrier gas was 1 mL/min. The phenolic oil samples were prepared as 3 ± 1 wt % solutions in acetone.

Gel permeation chromatography (GPC) of the phenolic oils was performed on an Agilent Infinity 1260 Series HPLC equipped with two identical Agilent Oligopore GPC columns (polystyrene-divinyl-benzene copolymer, 300×7.5 mm) in series heated at 30°C . Tetrahydrofuran (THF) was used as the mobile phase liquid and a flow rate of 1 mL/min was used. Samples were well dissolved (~ 1 mg/mL) in THF. Peak detection was done by a diode array UV detector. Several wavelengths were used but the GPC calculations were based on detection at 273 nm. Polystyrene standards in the MW range of 162–2900 were used for calibration.

A thermogravimetric analyzer (TA Instruments Q500 TGA) was used for proximate analysis of the pulp samples. For each material, an approximately 10 mg sample was heated to 800°C at $20^\circ\text{C}/\text{min}$ under N_2 flow (60 mL/min), then the purge gas was switched to air to combust the remaining sample. The moisture, volatile matter, and fixed carbon concentrations were determined by the percent mass loss after heating to 150°C , 800°C under N_2 , and 800°C under air, respectively. The ash content was determined by the residual sample mass after combustion in air. Elemental analysis was performed using a Thermo Flash EA1112 CHNS/O analyzer by complete combustion of the material followed by GC quantification of combustion products. Oxygen was determined by difference after accounting for organic CHNS, ash, and water.

2.3. Pyrolysis-GC-Polyarc-FID

The pyrolysis volatiles were analyzed by means of a micropyrolyzer (Multi-Shot Pyrolyzer EGA/PY 3030D, Frontier Laboratories Ltd., Fukushima, Japan) coupled to a gas chromatograph (Shimadzu GC2010). Compounds from the GC were converted to methane via a catalytic microreactor (Polyarc, Activated Research Company, Eden Prairie, MN, USA) and detected by a flame ionization detector (FID). An identical analysis using Py-GC/MS (Frontier Laboratories, Shimadzu) was used for compound identification. Approximately 500 μg of biomass and 2000 μg of HZSM-5 (for catalytic pyrolysis) was used for each analysis. The micropyrolyzer temperature was 550°C and the GC inlet temperature was 280°C . Helium was the carrier gas (2.5 mL/min) and a split ratio of 30:1 was used. The column (Restek RTX-1701) was held at 45°C for 4 min, heated to 280°C at $3^\circ\text{C}/\text{min}$, then held for 20 min. The Polyarc reactor was held at 300°C and converted organic compounds exiting the GC to methane before detection by FID. The FID was held at 300°C with H_2 flow of 1.5 mL/min and air flow of 350 mL/min. Py-GC-Polyarc-FID analysis was repeated in triplicate for each sample.

3. Results and Discussion

3.1. Lignin-First Fractionation and Depolymerization

The purpose of this study was to compare the fractionation depolymerization process from the two types of feedstocks (herbaceous grass and hardwood), and to test if the catalyst had effects on the composition and pyrolysis behavior of the cellulosic portion. The tests were performed at conditions similar to those previously known to be effective for production of bio-oil with relatively high concentrations of monomeric phenols [14,17,20,21]. The addition of water to the reaction mixture allowed for separation of hemicellulose-derived compounds from the lignin oil [18]. Oak, a hardwood, contained more lignin than switchgrass (Table 1). Additionally, the lignin structures are expected to be different between the two plant species; hardwoods generally have more of the dimethoxylated phenolic rings (syringyl (S)) than do grasses. Grasses contain appreciable levels of non-methoxylated (H) units, and some monomethoxylated (G) units, in addition to the S-units. Grasses are also expected to contain more C-O bonded linkages, and particularly, more $\beta\text{-O}4$ linkages, than hardwoods [22,23].

These differences in the composition of the biomass can be seen in the results of the lignin fractionation depolymerization results. Table 2 presents the mass balance for the solvent-phase lignin depolymerization step. Yields from oil range from 27 wt % to 42 wt % based on biomass input. The yields follow the trend of $\text{Pd/C} < \text{Ru/C} < \text{acids}$; however, the

liquid products can contain impurities not derived from lignin, including solvent-derived products and any carbohydrate-derived products. This explains why some yields based on lignin are greater than 100%. Looking at a comparison of the GC/MS chromatograms of the liquids (Figure 2), one can see that peaks associated with various types of dimerization and oligomerization reactions of ethanol (generally appearing at RT < 32 min) are much more prevalent in the case of the acid catalysts and particularly so in the case of the soluble Lewis acid, Al(OTf)₃. In each case, a small peak for acetic acid can be observed at around a retention time of 10 min. Acetic acid is likely derived from the hydrolysis of acetylated hemicellulose, and much of it is retained in the aqueous phase of the reaction mixture. There appears to be a higher concentration of acetic acid in the oil produced from the combination of oak and Ru/C catalysis; why less of the acetic acid partitioned into the aqueous phase in this case is unclear. For both the switchgrass and oak, the phenolic oil with the narrowest monomer distribution appears to be produced by the Pd/C catalyst. As can be seen in the chromatogram, the most prevalent phenolic monomers produced were 4-propylguaiacol (G3) and 4-propylsyringol (S3). 4-propenylguaiacol (isoeugenol, G3') and 4-propenylsyringol (S3') were also present in the case of the Ru/C, and to a lesser extent over HZSM-5. The Pd/C were more selective for the phenolics with the saturated side chains, suggesting that Pd/C was a more effective transfer hydrogenation catalyst for C=C double bonds outside the aromatic ring. 4-ethylguaiacol (G2) was produced in smaller amounts than the C3 substituted phenolics for oak and switchgrass, while 4-ethylphenol (H2) was also observed for the oils produced from switchgrass with the metal catalysts reflective of the presence of H-type lignin. The Pd/C catalyst was more selective for the phenolic monomers with C2 saturated side chains; compounds with unsaturated side chains (e.g., vinyl phenol and vinyl guaiacol) were not observed in any case. These compounds are common products of thermal decomposition of lignin [24,25], and therefore the lack of their presence in the oil suggest that they are either hydrogenated to the saturated versions (Pd/C) or undergo oligomerization reactions, contributing to the oligomeric fraction of the phenolic oils which makes up the majority of the oil.

Table 1. Proximate, ultimate and biochemical analysis (wt %) of oak and switchgrass biomasses used in this study.

	Oak	Switchgrass
Moisture	6.6	6.4
VM, d.b.	81.0	87.7
FC, d.b.	17.4	9.3
Ash, d.b.	1.6	3.1
C	50.52	43.8
H ¹	6.24	4.7
N	0.12	0.5
O ¹	35.04	41.6
Cellulose	29.71	36.77
Hemicellulose	21.62	33.07
Lignin	37.08	27.42

¹ hydrogen and oxygen values are organic only, oxygen by difference.

Table 2. Mass balance (wt %) of lignin-first fractionation/depolymerization experiments in ethanol at 210 °C.

Biomass—Catalyst	Phenolic Oil Yield (from Biomass)	Phenolic Oil Yield (from Lignin)	Pulp Yield (from Biomass)	Pulp Yield (from Cellulose)
Oak—Pd/C	28.0	75.6	27.7	93.2
Oak—Ru/C	34.2	92.2	38.5	129.5
Oak—HZSM-5	39.5	106.6	36.3	122.3
SWG—Pd/C	27.1	98.9	31.1	84.6
SWG—Ru/C	41.6	151.9	33.4	90.8
SWG—Al(OTf) ₃	37.0	135.0	24.5	66.7

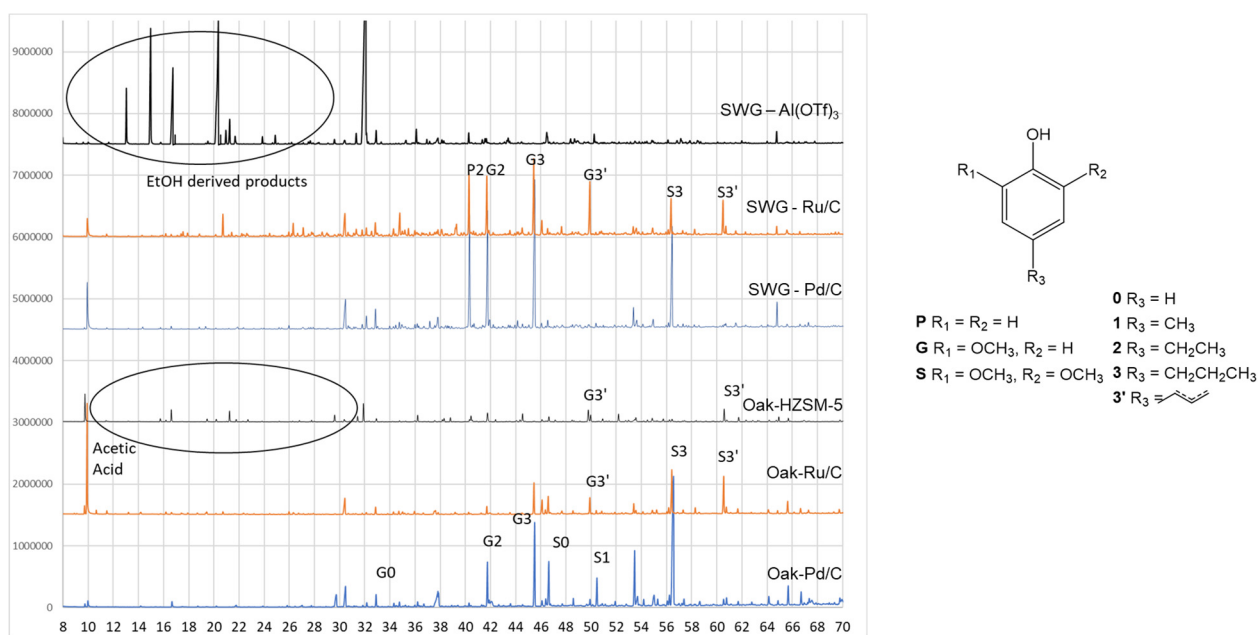


Figure 2. GC/MS chromatograms of phenolic oils produced from lignin-first fractionation and depolymerization in ethanol at 210 °C.

To understand the effect of the biomass and catalyst choices on the overall depolymerization rates of the lignin, the oils were analyzed by GPC analysis. The number average molecular weight (Mn) and weight average molecular weight (Mw) of the bio-oils are presented in Table 3. For lignin oils from oak, the Pd/C catalyst provided the lowest average MW, with those produced with Ru/C exhibiting a higher average MW. With HZSM-5, the average MW was in a similar range to the metal catalysts, despite a lower apparent production of monomers. For switchgrass, the Ru/C actually produced bio-oil with a lower MW than Pd/C did, but the MWs were more similar than for the oak lignin oils. The soluble Al(OTf)₃ acidic catalyst produced oils with a high average MW, indicating that it was either a poor depolymerization catalyst or was also a catalyst for repolymerization reactions. Given that it also produced a number of oligomerized products from ethanol, it is possible that some of those products such as diols acted as crosslinkers for phenolics, resulting in an increase in the observed average MW [10]. In general, for comparable catalyst/biomass combinations (Ru/C and Pd/C), the oak lignin oils had higher average molecular weights, which may be a reflection of fewer labile β-O4 linkages and more recalcitrant C-C linkages in their structures than in switchgrass lignin.

Table 3. The number average molecular weight (Mn) and weight average molecular weight (Mw) of phenolic oils produced via lignin-first fractionation/depolymerization experiments in ethanol/water at 210 °C.

	Mn (g/mol)	Mw (g/mol)
Oak—Pd/C	484	953
Oak—Ru/C	556	1128
Oak—HZSM-5	533	994
SWG—Pd/C	400	802
SWG—Ru/C	384	741
SWG—Al(OTf) ₃	1141	1659

For oak, the yield of pulp ranged from 27.7 wt %, with the Pd/C catalyst to 38.5% for oak processed in the presence of Ru/C. Based on the estimated amount of cellulose contained in the oak, the obtained yields range from 93 to 122% of the theoretical cellulose recovery. For switchgrass, the yield of pulp ranged from 24.5% for that produced in the

presence of $\text{Al}(\text{OTf})_3$ to 31.1–33.4% for the metal catalysts, or 66.7% of theoretical cellulose from the acid and about 85–90% of possible cellulose with the metal catalysts. Yields of pulp above the theoretical maximum may be due to incomplete fractionation of lignin or hemicellulose or contamination with catalyst not separated during the sieving process. The comparably lower yield of pulp when $\text{Al}(\text{OTf})_3$ is used is likely due to hydrolysis reactions providing breakdown of the cellulose into monomeric sugars and other water-soluble products that are lost to the aqueous phase.

The pulps were analyzed for proximate and ultimate analysis (Table 4). Interestingly, for oak, the fixed carbon amount of the pulps produced under the reductive conditions was similar to that of the parent biomass, but when the solid acid was used, the fixed carbon increased. However, for switchgrass, the fixed carbon rose dramatically in every case, with the largest increase coming from the use of $\text{Al}(\text{OTf})_3$. This suggests that dehydration and polymerization reactions can occur to the point of producing a char-like structure, which can be initiated by the presence of the homogeneous acid. For the metal catalysts, since they are supported on carbon, this increase in fixed carbon could be related to catalyst contamination or a higher propensity for switchgrass to undergo dehydration and char-forming reactions compared with oak. Ash is concentrated in the pulp during the lignin separation process, with ash content of the pulps increasing from that of the parent biomass. Thereby, the ash content of the switchgrass pulps was higher than that of the oak pulps. The use of $\text{Al}(\text{OTf})_3$ produced the pulp with the highest ash content. This is likely related to the lower yield and loss of additional organic material to the aqueous phase as mentioned above. The pulps generally contained more carbon, less oxygen, and less hydrogen than pure cellulose, which is consistent with the presence of some char-type materials or unfractionated lignin remaining with the pulp.

Table 4. Proximate and ultimate analysis (wt %) of cellulosic pulps isolated after lignin fractionation/depolymerization in ethanol at 210 °C using the biomass and catalyst combinations listed.

	Oak Pd/C	Oak Ru/C	Oak HZSM-5	SWG Pd/C	SWG Ru/C	SWG $\text{Al}(\text{OTf})_3$
Moisture	3.2	3.2	5.6	2.6	2.4	5.3
VM, d.b.	80.9	76.9	70.98	66.8	76.5	42.9
FC, d.b.	16.6	19.4	28.0	28.0	17.9	47.4
Ash, d.b.	2.5	3.7	4.1	5.2	5.6	9.7
C	55.79	52.50	40.52	55.79	50.05	58.95
H ¹	5.72	3.82	4.03	3.88	3.58	3.84
N	0.63	0.55	0.25	0.62	0.20	0.20
O ¹	32.15	36.23	45.5	31.91	38.17	22.01
C/O (mol)	2.33	1.92	1.19	2.33	1.74	3.57
H/C (mol)	1.23	0.87	1.06	0.83	0.85	0.78

¹ hydrogen and oxygen values are organic only, oxygen by difference.

3.2. Pyrolysis of the Cellulosic Pulps

The main product of the pyrolysis of pure cellulose is levoglucosan, a dehydrated form of glucose. Thermal decomposition of isolated cellulose can provide levoglucosan in up to 60 wt % yield [26]. However, the yield of levoglucosan from cellulose during raw biomass pyrolysis is generally low, due to the interference of lignin, acid from decomposition of other biomass components, and especially the catalytic action of alkalis present in biomass. In biomass pyrolysis, more fragmentation reactions occur, producing compounds such as hydroxyacetaldehyde, along with various furans and cyclopentanone derivatives, at the expense of levoglucosan [26,27]. Pyrolysis of the two parent biomasses used in this study resulted in 1.3 wt % and 2.8 wt % yields of levoglucosan from oak and switchgrass, respectively, at 550 °C. Using this pyrolysis methodology, pyrolysis of pure cellulose resulted in an average levoglucosan yield of about 50 wt %.

Contained in Figure 3 are the pyrolysis-gas chromatograms (pyrograms) from the pyrolysis of the pulps at 550 °C, allowing for the qualitative comparison of each pulp/catalyst

combination and commercial cellulose. It is clear from the pyrograms that, much like the commercial cellulose, levoglucosan is the major product produced from most of the residual pulps, and many of the minor products are the same for pyrolysis of the different pulps. The obvious exception is the pulp produced from switchgrass over the soluble acid catalyst. Its levoglucosan peak is significantly smaller, and it also exhibits the production of phenolics, indicating that lignin is still present within this pulp.

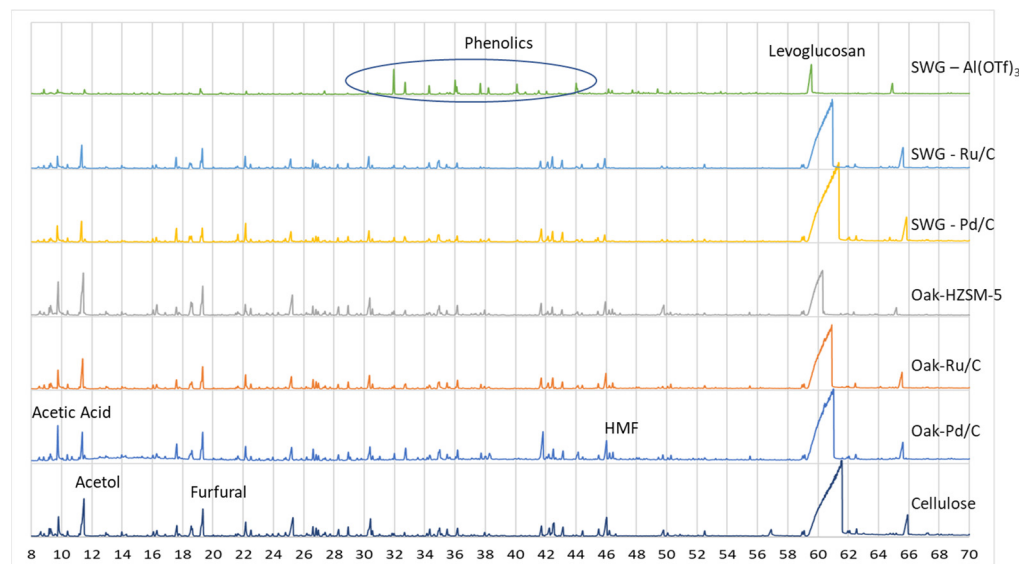


Figure 3. Pyrogram from Py-GC-FID of cellulosic pulps from lignin-first fractionation in ethanol at 210 °C. Pyrolysis at 550 °C.

Figure 4 presents the quantitative yields of levoglucosan based on the input mass of the pulps. Figure 5 presents this data normalized to the total amount of biomass, including the fractionation/lignin depolymerization step. As can be seen from both figures, the pulps generated in the presence of the metal catalyst (and, to a lesser extent, HZSM-5) produce a higher yield of levoglucosan upon pyrolysis than the raw biomass. While the yield is lower than that obtained from commercial cellulose, a significant amount of levoglucosan can be generated. The pulps produced from switchgrass using either metal catalyst produced greater than 30 wt % yield of levoglucosan or about 11–12 wt % yield after normalization to raw biomass. As discussed above, the pulp produced in the presence of the soluble acid catalyst has a significantly different composition, and therefore the yield of levoglucosan is predictably low. For oak, there was a bigger difference between the pulp produced in the presence of Pd or Ru, and the yields were lower compared with switchgrass. However, for both biomasses, the yield of levoglucosan (based on total biomass input) via pyrolysis of the pulps produced after lignin-first conversion was increased by about 4.0–4.7 times over the pyrolysis of raw biomass.

Table 5 presents the yields of some other selected pyrolysis products. Hydroxyacetaldehyde is a breakdown product that results from further fragmentation of cellulosic pyrolysis products and is often formed at the expense of levoglucosan [27]. Generally, the switchgrass pulps produced less hydroxyacetaldehyde than did commercial cellulose, while the oak pulps produced more, particularly that produced with HZSM-5. All of the pulps produced significantly less acetic acid than their parent biomass, which may make isolation or further conversion of the produced levoglucosan easier, as acid content and bio-oil stability tend to be negatively correlated. The pulp produced with $\text{Al}(\text{OTf})_3$ produced the greatest concentration of phenolics, other than trace amounts of phenol. As mentioned above, it appears that that catalyst was less effective at net removal of lignin from the remaining solids.

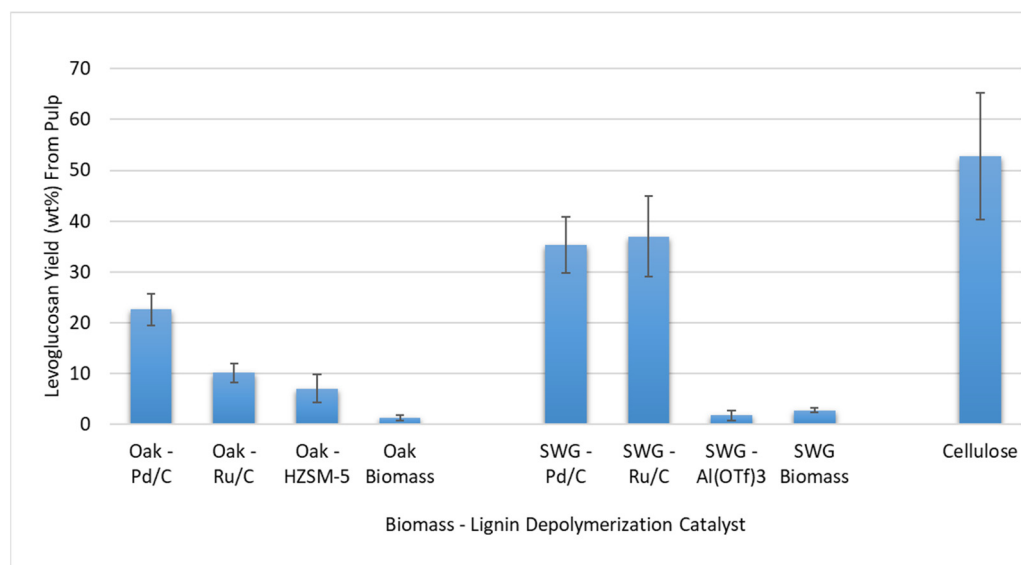


Figure 4. Levoglucosan yield (wt %) from pyrolysis of cellulosic pulps isolated after lignin-first fractionation in ethanol at 210 °C. Pyrolysis at 550 °C. Error bars are one standard deviation.

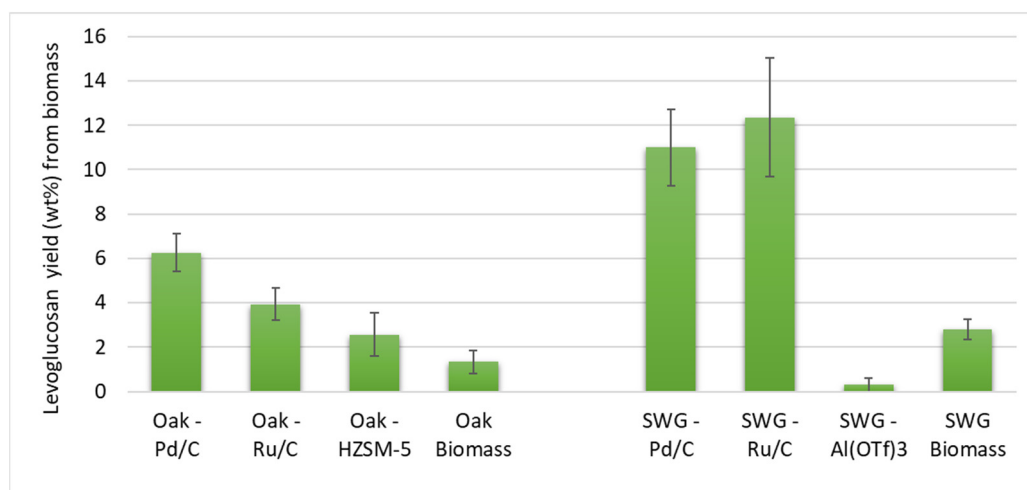


Figure 5. Levoglucosan yield (wt %) from pyrolysis of cellulosic pulps isolated after lignin-first fractionation in ethanol at 210 °C, based on total biomass input. Pyrolysis at 550 °C. Error bars are one standard deviation.

Table 5. Yields of selected compounds from pyrolysis of cellulosic pulps isolated after lignin-first fractionation in ethanol at 210 °C.

(wt % Yield)	Oak-Pd/C	Oak-Ru/C	Oak—HZSM-5	Oak—Biomass	SWG—Pd/C	SWG—Ru/C	SWG—Al(OTf) ₃	SWG—Biomass	Cellulose
Hydroxy-acetaldehyde	2.95	1.29	5.28	2.41	0.55	1.51	0.08	1.63	1.98
Acetic Acid	0.47	0.37	1.10	6.76	0.69	0.54	0.17	3.60	0.32
Acetol	0.81	0.28	1.63	2.20	0.28	1.08	0.21	3.22	0.88
2-Cyclopenten-1-one	0.41	0.08	0.18	0.15	0.00	0.18	0.04	0.20	0.13
Furfural	0.82	0.38	0.86	0.76	0.35	0.86	0.13	0.75	0.52
Hydroxymethyl-furfural (HMF)	0.63	0.17	0.46	0.13	0.09	0.29	0.15	0.11	0.34
Phenol	0.03	0.08	0.08	0.06	0.00	0.07	0.20	0.14	0.01
Guaiacol	0.18	0.09	0.10	0.22	0.00	0.11	0.13	0.18	nd
Syringol	0.14	0.07	0.15	0.38	0.00	0.11	0.07	0.00	nd

3.3. Catalytic Pyrolysis over HZSM-5

Catalytic pyrolysis of biomass over HZSM-5 to produce aromatic hydrocarbons is another thermochemical conversion option for the cellulosic pulps [28]. At high temperatures, the microporous zeolite initiates a series of reactions, including decarbonylation, dehydration, oligomerization of alkenes, and aromatization via dehydrogenation. For pyrolysis vapors containing large molecules such as levoglucosan, cracking reactions occur on the surface of the zeolite, producing smaller molecules that can penetrate the pores. The specific shape selectivity of ZSM-5 makes it highly selective for aromatic hydrocarbons, specifically the BTEX compounds (benzene, toluene, ethyl benzene, xylenes). Although the yield of BTEX from biomass is generally low, the deoxygenated mixture is much easier and more efficient for refinement to finished fuels. Specifically, the aromatic compounds are a small but necessary fraction in gasoline and jet fuels, in addition to their many industrial uses. Aromatics from biomass via catalytic pyrolysis, combined with alkanes from vegetable oil processing, is a pathway to a 100% renewable sustainable aviation fuel.

Figures 6 and 7 show the yields of BTEX generated from catalytic pyrolysis of the pulps over HZSM-5 at a biomass-to-catalyst ratio of approximately 5:1, from the pulp and total input biomass, respectively. Under these conditions, BTEX yields ranged from 4.5–6 wt % for both the pulps and the raw biomasses. The exception was pulp generated with the $\text{Al}(\text{OTf})_3$ catalyst. This was likely due to the high fixed carbon of this pulp, due to charring-like reactions with the soluble strong acid during the first step. Comparing both the pulps and the raw biomass, the normalized values show that the yield of BTEX is actually decreased by removing and depolymerizing the lignin first. This is because, in contrast to conversion to levoglucosan by fast pyrolysis, where lignin is not a viable feedstock, lignin can contribute to the production of BTEX via catalytic pyrolysis. Although not captured by this study, there may be an advantage to utilizing the pulps over raw biomass over time because lignin and hemicellulose are both strong sources of catalyst-deactivating coke [29,30].

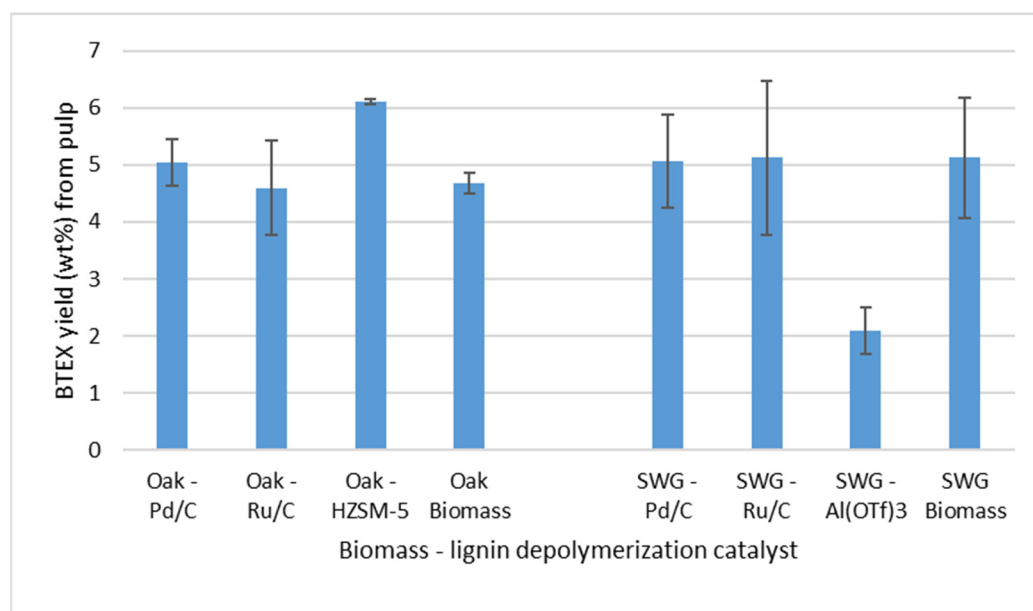


Figure 6. BTEX yield (wt %) from HZSM-5-catalyzed pyrolysis of cellulosic pulps isolated after lignin-first fractionation in ethanol at 210 °C. Pyrolysis at 550 °C, catalyst:biomass ratio of 5:1 (*w/w*). Error bars are one standard deviation.

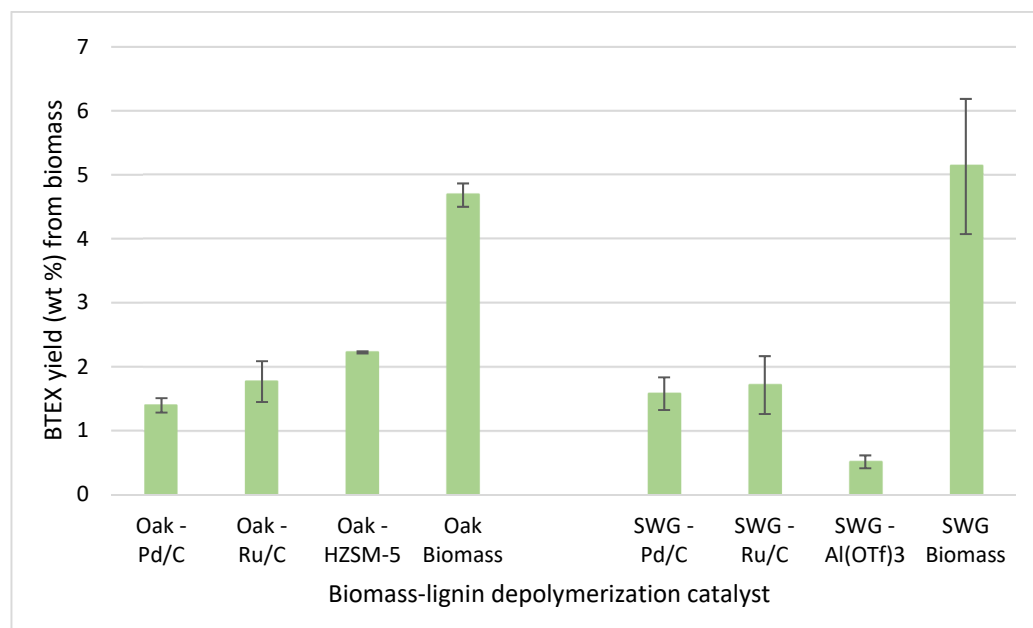


Figure 7. BTEX yield (wt %) from HZSM-5-catalyzed pyrolysis of cellulosic pulps isolated after lignin-first fractionation in ethanol at 210 °C based on total biomass input. Pyrolysis at 550 °C, catalyst:biomass ratio of 5:1 (*w/w*). Error bars are one standard deviation.

4. Conclusions

Oak and switchgrass were used in a lignin-first type biorefinery scheme where lignin was fractionated and depolymerized in a solvent phase reaction, and then the cellulosic pulps were tested for conversion to levoglucosan and BTEX via fast and catalytic pyrolysis over HZSM-5, respectively. For the initial step, reductive depolymerization catalyzed by both Pd/C or Ru/C with hydrogen transfer from ethanol and acid catalyzed depolymerizations (using HZSM-5 or Al(OTf)₃) were tested. Production of phenolic monomers and overall depolymerization rate, as measured by average molecular weight of the lignin oil, was better for the reductive conditions over the acidic conditions. Use of a soluble Lewis acid, Al(OTf)₃, led to particularly heavy lignin oil and also pulps containing both residual lignin and a high level of fixed carbon, making it a poor substrate for further conversion. The pulps from the reductive conditions proved to be a better feedstock for fast pyrolysis to produce levoglucosan. After normalizing for removal of lignin, the overall yield of levoglucosan was 4.0 to 4.6 times higher compared with pyrolysis of the raw biomasses. On the contrary, in catalytic pyrolysis over HZSM-5, the yield of BTEX was decreased compared with conversion of the raw biomass. The results show that initial solvent phase fractionation of lignin from biomass may be advantageous for thermal conversion of cellulosic portions of biomass to oxygenated chemicals such as levoglucosan, but, for selective catalytic conversion pathways for deoxygenated products, raw biomass may be a better feedstock.

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