

Optimization of Lignin Extraction from Pine Wood for Fast Pyrolysis by Using #-valerolactone-Based Binary Solvent System

Sureerat Jampa, Allen Puente-Urbina, Zhiqiang Ma, Sujitra Wongkasemjit, Jeremy Scott Luterbacher, and Jeroen A. van Bokhoven

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3 **Optimization of Lignin Extraction from Pine Wood for Fast Pyrolysis by Using γ -valerolactone-**
4 **Based Binary Solvent System**
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9 Sureerat Jampa^{a,b,#}, Allen Puente-Urbina^{a,#}, Zhiqiang Ma^a, Sujitra Wongkasemjit^b, Jeremy S.
10 Luterbacher^c, Jeroen A. van Bokhoven^{a,d,*}
11
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14
15

16 ^aInstitute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH
17 Zurich, HCI E 127, Vladimir-Prelog-Weg 1, 8093 Zurich, Switzerland
18
19

20 ^bThe Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand
21

22 ^cLaboratory of Sustainable and Catalytic Processing, Institute of Chemical Sciences and Engineering,
23 École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland
24
25

26 ^dLaboratory for Catalysis and Sustainable Chemistry, Paul Scherrer Institute, WLG A 135, 5232
27 Villigen, Switzerland
28
29
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35 *Corresponding author: Tel.: +41 44 632 5542. E-mail address: jeroen.vanbokhoven@chem.ethz.ch
36 (Jeroen A. van Bokhoven)
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39 #These authors contributed equally to this work.
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43 **Abstract**
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45 Fast pyrolysis of lignin is a promising method to produce aromatic chemicals and fuels.
46 Lignin structure and pyrolysis conditions determine the liquid yield and product selectivity. Extraction
47 of pine wood using γ -valerolactone (GVL) mixed with water in the presence of diluted sulfuric acid
48 obtains lignin (GVL-lignin) which shows different product yield and selectivity. The composition of
49 the extraction medium influences the yield of GVL-lignin and affects its native structure. The GVL-
50 to-water ratio affects the lignin yield without significantly modifying the structure of the extracted
51 lignin, whereas the sulfuric acid concentration affects both the extraction yield and the extracted
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1 lignin structure. These structural changes influence the products distribution after fast pyrolysis,
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3 which generates phenols and alkoxy phenols as the main products in the liquid fraction. Lignin
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5 extracted with a mixture of 4/1 of GVL/H₂O (w/w) with 0.075 M sulfuric acid solution produces the
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7 highest pyrolysis liquid yield. Pyrolysis of GVL-lignin at 750 °C generates the maximum liquid yield.
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9 The amount of phenols in fast pyrolysis products increases with increasing temperature and sulfuric
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11 acid concentration used in the GVL-lignin extraction. This indicates that the extraction conditions of
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13 GVL-lignin may be optimized to increase the selectivity in fast pyrolysis.
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20 **Keywords:** lignocellulosic biomass, lignin, γ -valerolactone (GVL), fast pyrolysis, bio-oil
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24 **Introduction**

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26 Owing to the increase in worldwide population in recent years, fossil resources consumption
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28 has also increased, leading to concerns about their depletion and negative effects on the environment.
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30 Therefore, processes facilitating the use of alternative sustainable feedstocks receive more and more
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32 consideration. Among the alternative resources, biomass is a promising raw material for producing
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34 value-added chemicals, fuels and energy with a low carbon footprint.¹⁻³
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37 Lignocellulosic biomass is an exceptional renewable feedstock to obtain useful products (e.g.
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39 chemicals and fuels) and energy through biochemical or thermochemical transformations.⁴ The
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41 relevance of a certain type of biomass in a specific region depends on its availability, which often
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43 depends on technical, economic, environmental and other factors.⁵ In Switzerland, there is a
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45 substantial sustainable potential for forest energy wood, wood from landscape maintenance and waste
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47 wood, with softwoods being the majority of domestic wood species produced.^{5,6} In general,
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49 lignocellulosic biomass is mainly composed of cellulose, hemicellulose and lignin, but also has small
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51 amounts of ash and extractives.⁷ Each type of lignocellulosic biomass contains different amounts of
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53 these components. In all cases, lignin is an important fraction that has a high potential to be used as a
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55 renewable source for producing fuels and aromatic compounds.⁸
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58 Lignin has a complex three-dimensional amorphous structure. It has been described
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60 conventionally as a polymer of phenylpropane units (monolignols), namely *p*-coumaryl, coniferyl and

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3 sinapyl alcohols, also called units H, G and S.^{9,10} Each unit in the lignin structure is connected by
4 various ether and carbon-carbon linkages, such as β -O-4, 4-O-5, α -O-4, β - β , β -5, β -1 and 5-5.^{11,12}
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6 Generally, softwood lignin contains coniferyl alcohol and hardwood lignin both coniferyl and sinapyl
7 alcohols as predominant units.¹³ However, lignin properties and its isolation yield depend on its
8 source (e.g. softwood or hardwood) and the extraction technique applied. These factors also influence
9 the products that can be obtained from further processing of such lignin. Thus, it is necessary to use a
10 suitable extraction method to obtain high yields as well as adequate characteristics for the intended
11 use.
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20 The organosolv extraction is one of the most popular processes to isolate cellulose,
21 hemicellulose and lignin from lignocellulosic biomass. This method can solubilize lignin and separate
22 it from the lignocellulosic feedstocks, usually along with hemicellulose, by using a mixture of organic
23 solvents and inorganic acids catalysts such as hydrochloric acid and sulfuric acid.¹⁴ Regular solvents
24 used in this process include methanol, ethanol, acetone, ethylene glycol, triethylene glycol and
25 tetrahydrofurfuryl alcohol.¹⁵ Due to the milder conditions required and the solubilization of the lignin,
26 the lignin's structure can generally be better preserved than using other extraction methods such as
27 Kraft or aqueous methods though some condensation does occur.¹⁶⁻¹⁸ Thus, the organosolv method
28 generates lignin which is more amenable towards depolymerization.¹⁹ However, this method still has
29 some drawbacks, such as the need for solvent recovery, high-pressure operation conditions, associated
30 risks due to high volatility and flammability of the organic solvents used as well as their toxicity to
31 the environment and human health, among others, which contribute to a low economic
32 competitiveness with respect to other fractionation methods.²⁰⁻²² In addition, side reactions such as
33 cleavage of aryl ether linkages, ethoxylation and condensation reactions can take place, resulting in
34 undesired structure modifications.^{22,23}
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51 Trying to minimize these problems, green solvents have attracted attention in recent years for
52 biomass processing.²⁴ Among them, γ -valerolactone (GVL) is a promising solvent for biomass
53 fractionation with the possibility of obtaining the extracted lignin by addition of water.²⁵⁻³¹ It has
54 favorable physical and chemical properties for various applications such as low melting point (-31
55 °C), high boiling point (207 °C) and low volatility (vapor pressure of 0.44 mbar at 25 °C),
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3 renewability, high open cup flash point (96 °C), non-toxicity, stability, biodegradability and also the
4 possibility to be mixed or chemically modified to tailor other specific purposes.³²⁻³⁴
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7 Lignin can be converted into useful liquids (bio-oil), gases and char by pyrolysis as
8 thermochemical decomposition process.⁴ It can be classified as fast pyrolysis or slow pyrolysis
9 depending on its operation conditions.³⁵ Interestingly, fast pyrolysis generates a higher amount of bio-
10 oil, an alternative source of solvents, fuels and other high value chemicals.³⁶⁻³⁸ In fast pyrolysis, lignin
11 is thermally treated using very high heating rates and short vapor residence times, followed by a rapid
12 cooling of the pyrolysis vapors to obtain bio-oil containing important amounts of aromatic
13 compounds.^{39,40} In addition, fast pyrolysis can be developed under catalytic and non-catalytic
14 conditions, which together with the process conditions, determine the products distribution.⁴¹⁻⁴⁵
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24 In this study, pine wood (softwood) was employed as the lignocellulosic biomass source for
25 lignin extraction with GVL/H₂O solvent in the presence of sulfuric acid. The influence of extraction
26 conditions (i.e. time, temperature, sulfuric acid concentration and GVL/H₂O ratio) on the process and
27 lignin structure was analyzed. Then, the extracted lignin underwent fast pyrolysis at various
28 temperatures and the corresponding products were determined. The objective of this work was to find
29 the best conditions for lignin extraction from pine wood by using GVL/H₂O solvent to maximize the
30 organic liquid yield obtained by fast pyrolysis.
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41 **Experimental Section**

42 **Chemicals**

43 All chemicals were obtained as reagent grade and used without further purification. The commercial
44 lignin that was used was softwood alkaline lignin supplied by Tokyo Chemical Industry UK Ltd.
45 (product number: L0082).
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50 **Lignin extraction**

51 Pine wood was dried at 100 °C and then milled to particles of <180 µm by steel ball milling.
52 The milled pine wood was suspended in GVL/H₂O containing sulfuric acid, using a solid-to-solvent
53 ratio of 1/10 w/w. The resulting mixture was heated in a 100 ml teflon reactor with constant stirring,
54 varying temperature (120, 140 and 160 °C), time (1, 3, 5, 15, 21, 24 and 27 h), sulfuric acid
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3 concentration (by addition of 0.025, 0.050, 0.075, 0.125, 0.175, 0.225 and 0.275 M sulfuric acid
4 aqueous solutions, 10 wt% with respect to GVL/H₂O solvent) and initial GVL/H₂O ratio (4/1, 2/1 and
5 1/1 w/w). Table S1 has additional details about the solutions used for lignin extraction. Then, the
6 products were separated by filtration. The lignin contained in the filtrate was precipitated using water
7 and the sludge stirred for 30 min. The resulting solid (i.e. lignin, Table S2) was filtered, washed with
8 water and dried overnight at 100 °C.

15 **Lignin characterization**

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18 Fourier-transform infrared spectroscopy (FTIR) measurements were developed using a Bio-
19 Rad Excalibur Series FTS 3000 spectrometer. The samples were pelletized with KBr, using a
20 proportion of 1 mg of lignin per 40 mg of KBr. Each spectrum was obtained by averaging 256 scans
21 in a wavenumber range of 800-4000 cm⁻¹ with a resolution of 2 cm⁻¹.

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24 Nuclear magnetic resonance (NMR) spectra were recorded in a Bruker 500 MHz Ultrashield
25 spectrometer at room temperature. Samples were prepared dissolving 30 mg of lignin in 0.9 mL of
26 DMSO-d₆. ¹H NMR experiments were performed using the pulse sequence zg30, 16 scans, 2 dummy
27 scans, 1 s of relaxation delay and 3.27 s of acquisition time. The heteronuclear single quantum
28 correlation (HSQC) spectra were obtained using the pulse program hsqcetgpsisp2.2, 8 scans, 4
29 dummy scans, 0.5 s of relaxation delay, spectral widths of 6010 Hz (12 to 0 ppm) for ¹H dimension
30 (F2) and 27669 Hz (220 to 0 ppm) for ¹³C dimension (F1), 2048 points recorded for ¹H dimension and
31 1024 points for ¹³C dimension, and acquisition times of 0.17 s for ¹H dimension and 0.018 s for ¹³C
32 dimension. The results were analyzed using TopSpin 3.5 software.

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35 Thermogravimetric analyses (TGA) were performed in a Mettler Toledo TGA/SDTA851^e
36 thermogravimetric analyzer. Lignin samples were heated from 30 °C to 760 °C with a heating rate of
37 10 °C min⁻¹ under nitrogen flow (50 cm³ min⁻¹).

38 **Fast pyrolysis and products analyses**

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41 Fast pyrolysis experiments were carried out in a CDS Analytical 5150 pyrolyzer using an
42 open quartz tube resistively heated by a platinum coil. Lignin samples of 1.5-2 mg were immobilized
43 in the middle of the reactor by quartz wool and pyrolyzed at a heating rate of 20 °C/ms, a residence
44 time of 20 s and varying the pyrolysis temperature from 550 to 850 °C.

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3 Pyrolysis products were directly transferred at 300 °C into an Agilent 7890A gas
4 chromatograph using helium at 1.1 mL min⁻¹ as carrier gas, equipped with a thermal conductivity
5 detector (TCD) and an Agilent 5975C mass selective detector (MSD). The oven was programmed to
6 start at 40 °C, hold for 5 min and then heat up to 260 °C at 10 °C min⁻¹, temperature that was held for
7 25 min. An injector temperature of 300 °C and a split ratio of 35:1 were used. The flow was split to
8 analyze condensable pyrolysis products in one stream and gases in another. Condensable pyrolysis
9 products were separated with a HP-5MS column (30 m x 0.25 mm x 0.25 μm) and analyzed by means
10 of the mass spectrometry detector, where peaks were identified using the NIST08 mass spectrum
11 library and the corresponding compounds classified according to their functional groups into seven
12 categories: thiols; non-aromatic esters, ketones, aldehydes, furans and acids; aromatic hydrocarbons;
13 alkoxy aromatic hydrocarbons; phenols; alkoxy phenols and non-identified (typical quantifications
14 with less than ±5 % error). Non-condensable gases were separated with Agilent Plot/Q and molecular
15 sieve capillary columns (both 30 m x 0.53 mm) and quantified using the TCD, which was calibrated
16 for the most predominant gaseous molecules (CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₆ and C₃H₈). In
17 addition, the remaining solid after pyrolysis was measured gravimetrically and the liquid fraction was
18 calculated by mass difference. All the measurements were performed at least in duplicate and reported
19 with 95 % confidence level.
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41 **Results and discussion**

42 **Effect of pyrolysis temperature on pyrolysis yields and liquid product distribution of GVL-lignin**

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44 The pyrolysis temperature is an important operational factor for this type of process. Different
45 temperatures (i.e. 550, 650, 750 and 850 °C) were used to evaluate the fast pyrolysis of GVL-lignin
46 from pine wood using a heating rate of 20 °C/ms and residence time of 20 s. The pyrolysis products can
47 be divided into three phases, namely liquid (bio-oil), solid (char) and gas.⁴¹⁻⁴⁸ Figure 1A illustrates the
48 yields of liquid, char and gaseous products as a function of the pyrolysis temperature of GVL-lignin
49 obtained using a mixture of 4/1 GVL/H₂O (w/w) and 0.075 M sulfuric acid at 160 °C for 24 h. The
50 liquid fraction increased from 550 to (650-850) °C, because of an increase in primary decomposition of
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lignin at higher temperatures.^{49,50} In contrast, the char yield decreased from 550 to (650-850) °C. This reduction originated either from a greater primary decomposition of lignin or from secondary decomposition of the char residue at higher temperatures.⁵¹ Gas yield increased steadily with temperature from 4.6% to 12.6%. The higher gas yields generated at higher temperature came from the secondary cracking of the pyrolysis vapor and secondary decomposition of the char to non-condensable gaseous products.⁵²⁻⁵⁴ These trends obtained confirm that the pyrolysis temperature plays a dominating role in determining product distribution.

Figure 1B presents the liquid product distribution of GVL-lignin using varying pyrolysis temperature (water not included). The compounds are classified into seven groups: thiols; non-aromatic esters, ketones, aldehydes, furans and acids; aromatic hydrocarbons; alkoxy aromatic hydrocarbons; phenols; alkoxy phenols and non-identified. The amount of phenol alkoxy compounds produced decreased with increasing pyrolysis temperature. On the contrary, phenol products increased with increasing pyrolysis temperature. Horne and Williams⁵¹ reported that compounds in the group of alkoxy phenols (methoxyphenol, dimethoxyphenol and their derivatives) form at low temperatures. In addition, using higher temperature increases the extent of secondary reactions in which such large phenolic compounds thermally breakdown to phenol or they undergo alkylation, increasing the quantity of alkylated phenols.⁵¹

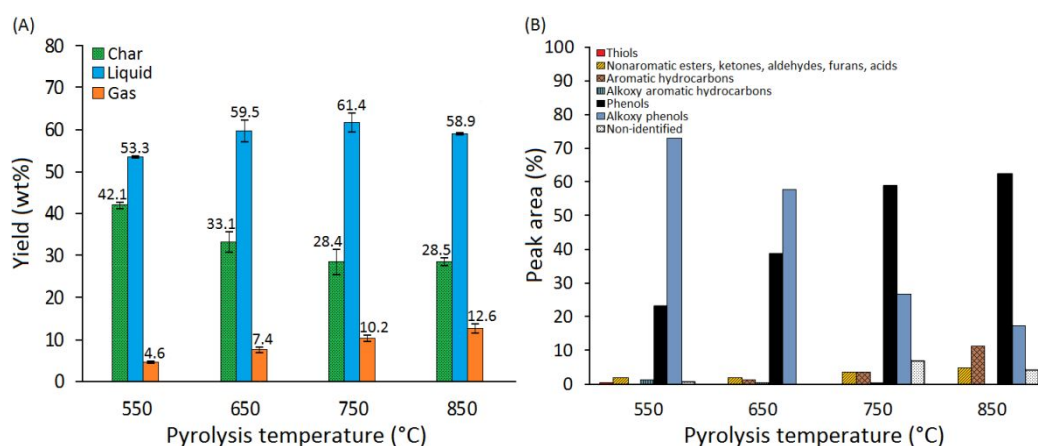


Figure 1 Effect of temperature on pyrolysis of extracted lignin with a mixture of 4/1 GVL/H₂O (w/w) and 0.075 M sulfuric acid at 160 °C for 24 h. (A) Yields of char, liquid and gas and (B) Liquid product distribution.

Effect of GVL/H₂O ratio on GVL-lignin and pyrolysis yield and liquid product distribution

Extracted lignin yields of 19.7, 18.6 and 15.0 wt% were obtained using mixtures of 4/1, 2/1 and 1/1 of GVL/H₂O (w/w) with 0.075 M sulfuric acid solution at 160 °C for 24 h (Tables S1 and S2). During lignin extraction processes, lignin was first released from the complete lignocellulosic material by hydrolytic cleavage of the ether bond in the lignin-carbohydrate complex or between lignin moieties, and then dissolved.⁵⁵ These cleavages are promoted by the presence of acid, either generated in the process, such as acetic acid generated by cleavage of acetyl groups in hemicellulose⁵⁶, or added externally as in our case.

Lignin extraction with GVL/H₂O is a complex process. Lignin solubility in GVL/H₂O is insignificant up to 32 wt% of GVL.⁵⁵ Above this concentration, the mixture tends to split into two phases and lignin solubility greatly increases.⁵⁵ In addition, it depends on the temperature of the medium as well as the presence of acids, which can promote lignin dissolution⁵⁵⁻⁵⁷ and also the establishment of an equilibrium of GVL with its ring opening product 4-hydroxyvaleric acid, which in our study remained at low concentration because of the low concentration of sulfuric acid.⁵⁸ The lowest content of GVL in the solvent mixture was ca. 45 wt% for the combination of 1/1 of GVL/H₂O (w/w) with the different sulfuric acid solutions, and above 50 wt% for the other mixtures (Table S1). For GVL contents above 50 wt%, Xue et al.⁵⁹ explained that the GVL-based binary solvent system can promote the solubility of lignin due to effects such as the breakdown of the strong hydrogen bonds in the lignin structure. Similar results were reported by Fang and co-workers, which found the greatest delignification of birch (a hardwood) sawdust at a GVL concentration between 50 and 65 wt%.²⁶ In mixtures with GVL contents below 50 wt%, water acts as an antisolvent for lignin extraction, because a larger amount of water strongly interacts with GVL molecules, resulting in fewer interactions with lignin, decreasing its solubility.⁵⁹ However, the complexity of the process is advantageous for product handling, considering that lignin is easily precipitated by water addition. Furthermore, a liquid phase split can be used as an effective chemical recovery pathway.⁶⁰

The lignins extracted from pine wood by varying the GVL/H₂O (w/w) ratio were pyrolyzed at 750 °C with a heating rate of 20 °C/ms and a residence time of 20 s (Figure 2A). Initial GVL/H₂O ratios of 4/1 and 2/1 (w/w) presented no significant differences on the liquid yield. However, the use of initial

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3 1/1 GVL/H₂O (w/w) gave a much lower liquid yield. Considering that initial GVL/H₂O ratio of 4/1
4 (w/w) provides high lignin extraction yield (Table S2) while affords high liquid yield in pyrolysis
5 (Figure 2A), this initial ratio seems to be the optimal among those used.
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9 Table 1 compares the liquid yields of the pyrolysis of different lignins under distinct conditions.
10 The liquid yield of GVL-lignin was higher than that of commercial lignin. GVL-lignin pyrolysis results
11 were compared to others previously reported by Custodis *et al.*⁴⁴, which studied similar fast pyrolysis
12 of lignins separated by dioxane-, Klason-, and organosolv-methods. Both softwood and hardwood lignins
13 extracted by the organosolv method (using 60 vol% ethanol with 5 wt% sulfuric acid)⁴⁴ produced lower
14 liquid yields than those obtained from lignin extracted by GVL/H₂O. Furthermore, the liquid yield of
15 GVL-lignin was compared to that of dioxane softwood and hardwood lignin as well as Klason softwood
16 and hardwood lignins. The liquid yield followed the order of Klason hardwood lignin (68 wt%) >
17 dioxane softwood lignin (66 wt%) > dioxane hardwood lignin (65 wt%) > GVL softwood lignin (61
18 wt%) > Klason softwood lignin (56 wt%) > organosolv softwood lignin (55 wt%) > organosolv
19 hardwood lignin (53 wt%) > commercial lignin (40 wt%). For other fast pyrolysis results shown in
20 Table 1, the liquid yield is affected both by the type of lignin and by the conditions of the process.⁶¹⁻⁶⁶
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24 Figure 2B illustrates the pyrolysis liquid product distribution of GVL-lignin extracted with
25 various GVL/H₂O ratios. The two major classes of compounds in the liquid fractions were phenols and
26 alkoxy phenols. All conditions showed similar amounts of phenols and alkoxy phenols in the
27 corresponding pyrolysis liquid fraction of about 60% and 25%, respectively. There was no significant
28 difference in the content of phenols and alkoxy phenols compounds in the pyrolysis liquid product of
29 lignin, because the structures of GVL-lignin extracted by using different initial GVL/H₂O ratios of 4/1,
30 2/1 and 1/1 (w/w) were very similar, as confirmed by 2D HSQC NMR.
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34 Figure 3 shows the 2D HSQC NMR spectra of GVL-lignin (detailed assignments and one ¹H
35 NMR spectrum are presented in Table S3, Table S4 and Figure S1). These were classified into two main
36 cross-signal regions, consisting of a side-chain ($\delta_{\text{H}}/\delta_{\text{C}}$ 2.5-5.8/50-90 ppm) region and an
37 aromatic/unsaturated ($\delta_{\text{H}}/\delta_{\text{C}}$ 6.0-8.0/100-160 ppm) region.⁶⁷⁻⁶⁹ Furthermore, Figure 4 exhibits the main
38 classical substructures of GVL-lignin. In the side-chain region of all GVL-lignins, the C-H correlation
39 in methoxy groups showed a strong cross-signal at $\delta_{\text{H}}/\delta_{\text{C}}$ 3.73/55.6 ppm. The two main substructures
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observed in the HSQC spectra were A_γ and C_γ . The C_γ - H_γ correlation in the β -O-4' substructures (A) was clearly found in the δ_H/δ_C range of 3.21-3.72/60.0-60.7 ppm. The cross-signal at δ_H/δ_C 3.66/63.3 ppm corresponded to the C_γ - H_γ correlation in β -5' (phenylcoumaran) substructures (C). The major cross-signals appearing in the aromatic/unsaturated region of the HSQC spectra corresponded to guaiacyl (G) units, as expected for a softwood.¹³ There were three main C-H correlations in guaiacyl (G) units, causing three different cross-signals. The C_5 - H_5 , C_6 - H_6 and C_2 - H_2 correlations in guaiacyl units (G_5 , G_6 and G_2) were observed at δ_H/δ_C of 6.71/115.0, 6.83/119.5 and 6.98/115.5, respectively. In both side-chain and aromatic/unsaturated regions, the HSQC spectra of all GVL-lignins extracted with various GVL/ H_2O ratios presented the same cross-signal patterns, indicating that the GVL/ H_2O ratio for lignin extraction does not have a significant effect on the structure of GVL-lignin.

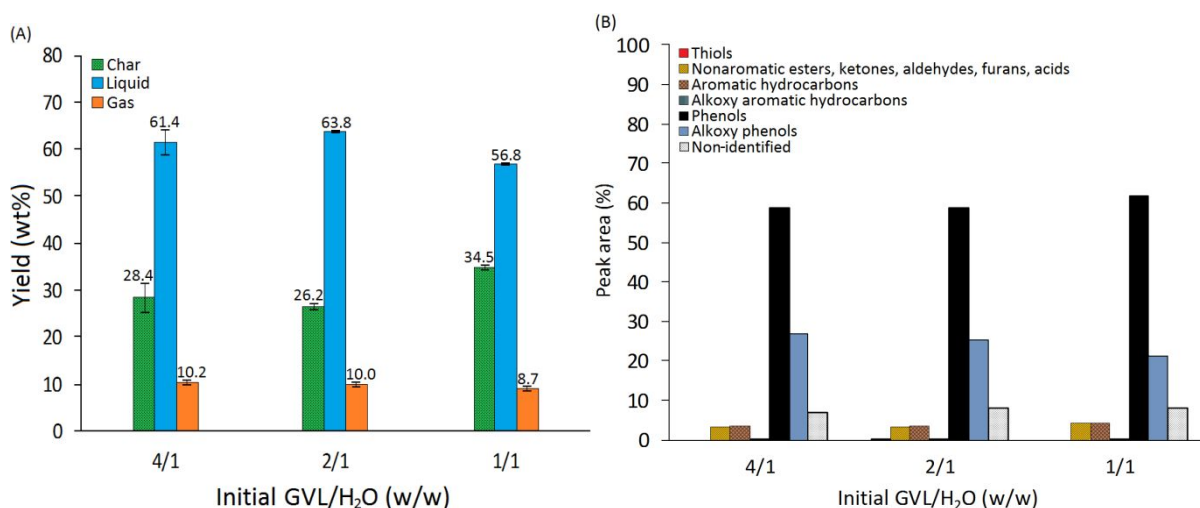


Figure 2 Effect of extracted lignin with various initial GVL/ H_2O ratios (with 0.075 M sulfuric acid at 160 °C for 24 h) on pyrolysis. (A) Yields of char, liquid and gas and (B) Liquid product distribution.

Table 1 Liquid yields comparison of each lignin after fast pyrolysis.

Type of lignin	Pyrolysis temperature (°C)	Liquid yield (wt%)	References
GVL lignin from pine wood	750	61	This study
Commercial lignin	750	40	
Dioxane softwood lignin	750	66	Custodis <i>et al.</i> ⁴⁴
Klason softwood lignin	750	56	
Organosolv softwood lignin	750	55	
Dioxane hardwood lignin	750	65	
Klason hardwood lignin	750	68	
Organosolv hardwood lignin	750	53	
Kraft lignin	650	37.4	
Alkali lignin	650	39.5	Ma <i>et al.</i> ⁴⁵
			Ma <i>et al.</i> ⁴⁷
			Ma <i>et al.</i> ⁴⁸
Alcell lignin	600	17.2	Jiang <i>et al.</i> ⁶¹
Asian lignin	600	15.5	
Lignin (byproduct of fermenting)	500-550	34	Trinh <i>et al.</i> ⁶²
Pyrolytic lignin precipitated from water	600	40	Zhao <i>et al.</i> ⁶³
Pyrolytic lignin separated from the mixture of glycerol and bio-oil	600	37	
Alkali lignin	600	6	
Kraft lignin	600	7	
Alkali lignin A	650	ca. 21.5	Li <i>et al.</i> ⁶⁴
Alkali lignin B	650	ca. 46.7	
Organosolv lignin	600	ca. 22.0	Patwardhan <i>et al.</i> ⁶⁵ Fan <i>et al.</i> ⁶⁶

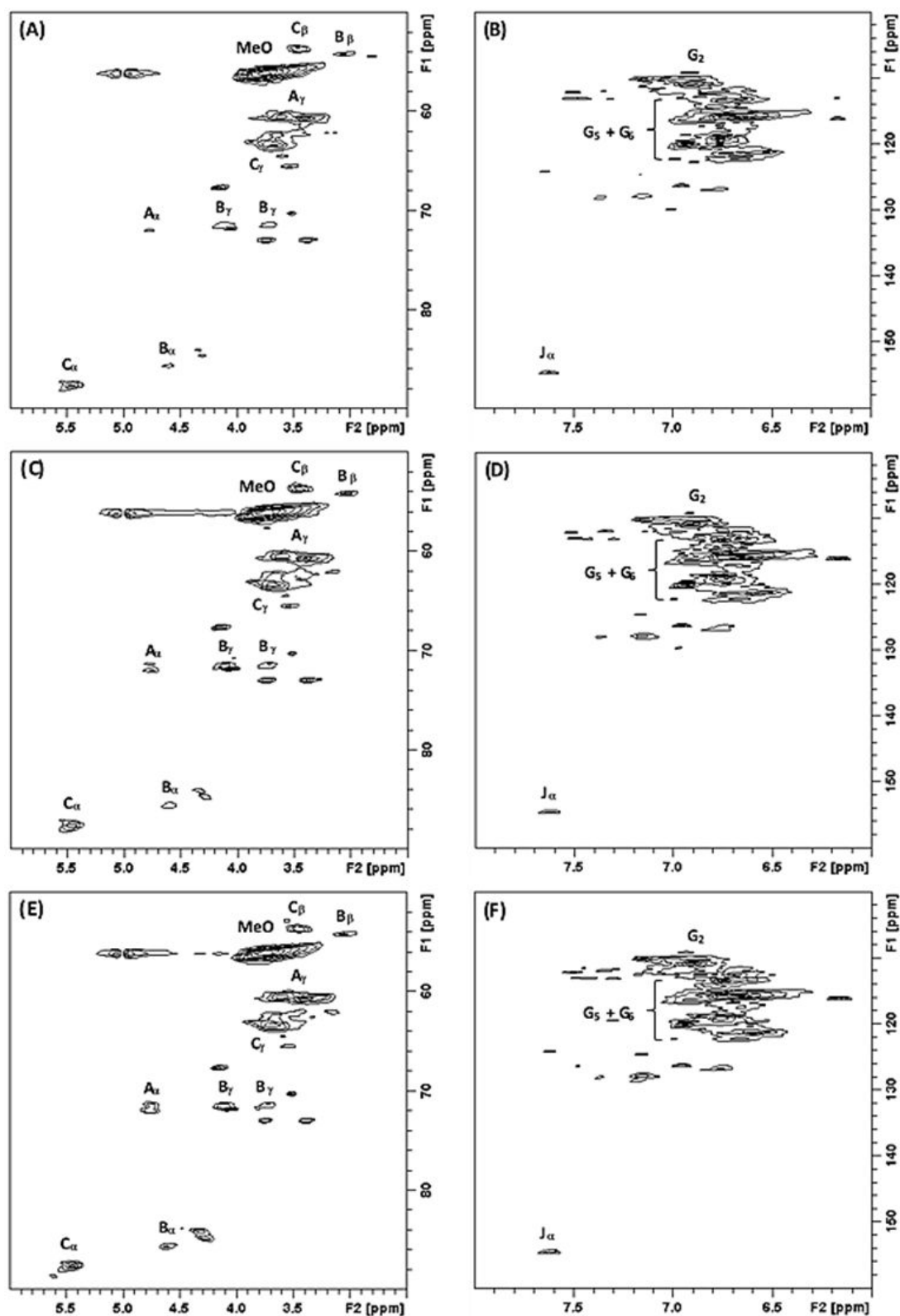


Figure 3 Side-chain ($\delta_{\text{H}}/\delta_{\text{C}}$ 2.5-5.8/50-90) and aromatic/unsaturated ($\delta_{\text{H}}/\delta_{\text{C}}$ 6.0-8.0/100-160) regions in the 2D HSQC NMR spectra of extracted lignin with mixtures of various initial GVL/H₂O ratios and 0.075 M sulfuric acid at 160 °C for 24 h. (A, B) initial GVL/H₂O of 4/1 (w/w); (C, D) initial GVL/H₂O of 2/1 (w/w) and (E, F) initial GVL/H₂O of 1/1 (w/w).

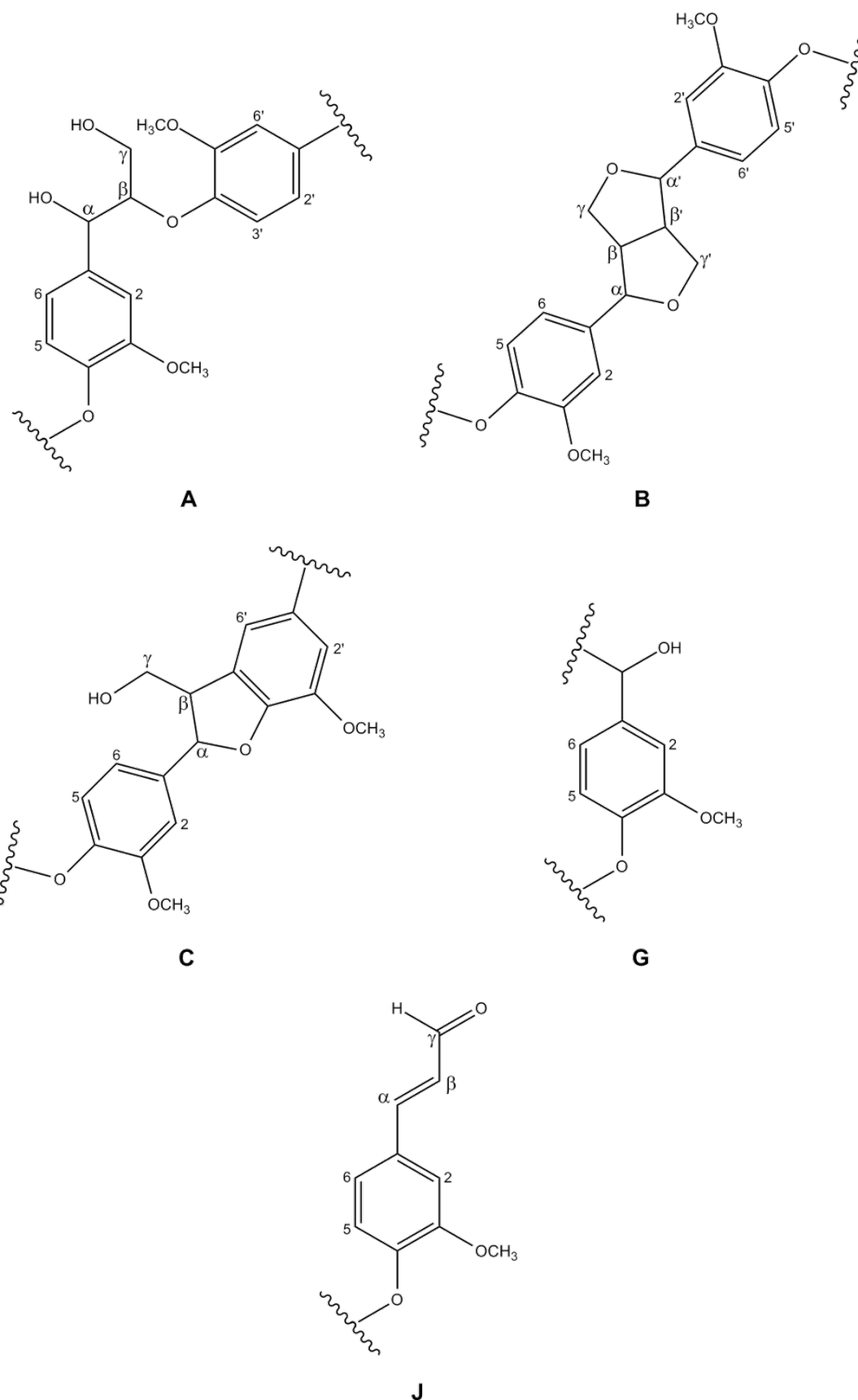


Figure 4 Main classical substructures, involving different side-chain linkages and aromatic units, identified by 2D HSQC NMR in extracted lignin from pine wood: (A) β -O-4' substructure; (B) resinol substructure, formed by β - β' coupling and α -O- γ' and γ -O- α' bonding during quinone methide rearomatization; (C) phenylcoumaran, formed by β -5' coupling and subsequent α -O-4' bonding; (G) guaiacyl unit; (J) cinnamaldehyde end-groups.

Effect of sulfuric acid concentration on GVL-lignin and pyrolysis yield and liquid product distribution

Figure 5A shows the extracted lignin yields with various sulfuric acid concentrations. In the concentration range provided by the addition of 0.025-0.175 M sulfuric acid solutions (see Table S1 for detailed information about specific concentrations), the extracted lignin yield increased with increasing concentration. The extracted lignin yields remained almost constant for higher concentrations. The concentration of sulfuric acid also influenced pyrolysis yield and liquid product distribution of GVL-lignin (Figure 5A and 5B). The increase of sulfuric acid concentration provided by the addition of solutions from 0.075 to 0.175 M caused obvious changes in liquid and char yields. The liquid yield decreased and the char yield increased with increasing sulfuric acid concentration in this range, while stable behaviors appeared outside of it. Thus, the maximum liquid yield of GVL-lignin of around 61% was obtained by using 0.075 M sulfuric acid solution mixed with the GVL/H₂O binary solvent for lignin extraction. Finally, gaseous products obtained from GVL-lignin pyrolysis did not seem to be influenced by sulfuric acid concentration.

Figure 5B presents the fast pyrolysis liquid product distribution of extracted GVL-lignin with various sulfuric acid concentrations, with phenols as the dominant group. With an increasing sulfuric acid concentration used during extraction, the amount of phenols continuously increased, but at sulfuric acid concentrations provided by the addition of solutions with concentrations higher than 0.175 M, the phenols contents remained constant. On the contrary, the alkoxy phenols compounds in the liquid fraction decreased with increasing sulfuric acid concentration. The structures of GVL-lignin extracted with various sulfuric acid concentrations characterized by 2D HSQC NMR can explain these different liquid product distributions. Figure 6 illustrates the 2D HSQC NMR spectra of GVL-lignin extracted with various sulfuric acid concentrations. The major cross-signal in the side-chain (δ_H/δ_C 2.5-5.8/50-90 ppm) region of the HSQC spectra of the GVL-lignins corresponded to the methoxy groups. This cross-signal decreased in intensity with increasing sulfuric acid concentration. The high sulfuric acid concentration induces dissociation of O-CH₃ bond located in the substructures of GVL-lignin⁷⁰, decreasing the phenol alkoxy compounds in the liquid fraction at high sulfuric acid concentration.

2D HSQC NMR also revealed other structural changes in GVL-lignin as a result of the influence of sulfuric acid. The C_7-H_7 in β -O-4' substructures (A) and C_7-H_7 in β -5' (phenylcoumaran) substructures (C) decreased with increasing sulfuric acid concentration, because sulfuric acid can break down the hydroxy group (-OH) in these substructures. In addition, considering the aromatic/unsaturated (δ_H/δ_C 6.0-8.0/100-160 ppm) region of the HSQC spectra, the cross-signals of G₂, G₅ and G₆ decreased with increasing sulfuric acid concentration, because sulfuric acid decomposes these substructures. Furthermore, the loss of methoxy groups due to high sulfuric acid concentrations strongly influenced the C₂-H₂ correlation in guaiacyl units since methoxy groups in G substructure were the closest to the C₂-H₂ position, resulting in the disappearance of the G₂ cross-signal. In contrast, G₅ and G₆ cross-signals still weakly emerged. The dissociation of methoxy groups lightly affected the C₅-H₅ and C₆-H₆ correlations compared to C₂-H₂ correlation in guaiacyl units. Moreover, using high sulfuric acid concentration in the lignin extraction process can lead to irreversible condensation of lignin. Rapid lignin condensation systematically occurs during most lignin extraction processes but is greatly accelerated by increasing acid concentrations. Under these conditions, a benzylic cation on G substructures of lignin is easily generated, which reacts with another part of lignin, forming condensed structures via new stable carbon-carbon (C-C) bonds and decreasing G units.⁷¹

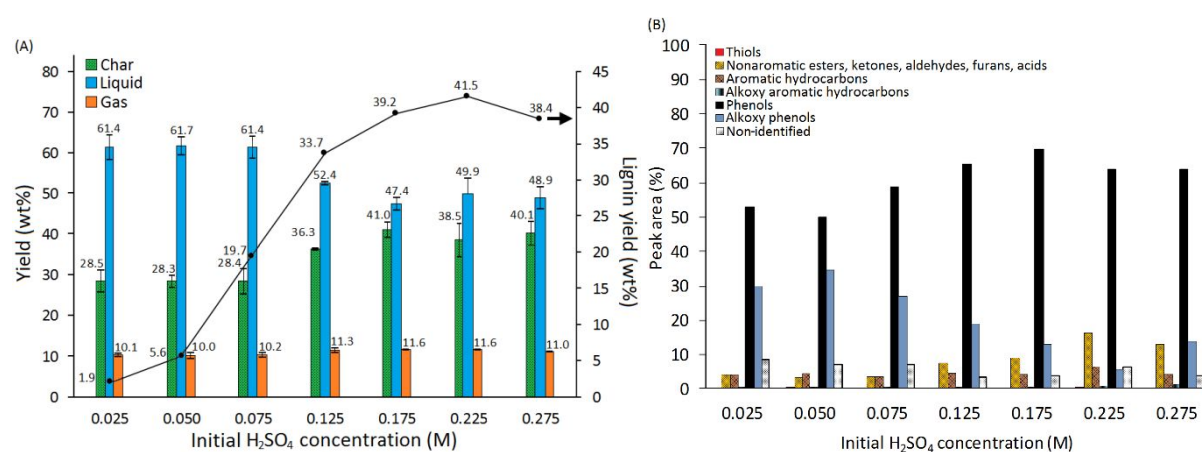


Figure 5 Effect of extracted lignin with various initial sulfuric acid concentrations [initial GVL/H₂O of 4/1 (w/w), at 160 °C for 24 h] on pyrolysis and extracted lignin yields. (A) Lignin extraction yield (curve) and pyrolysis yields of char, liquid and gas (columns) and (B) Liquid product distribution.

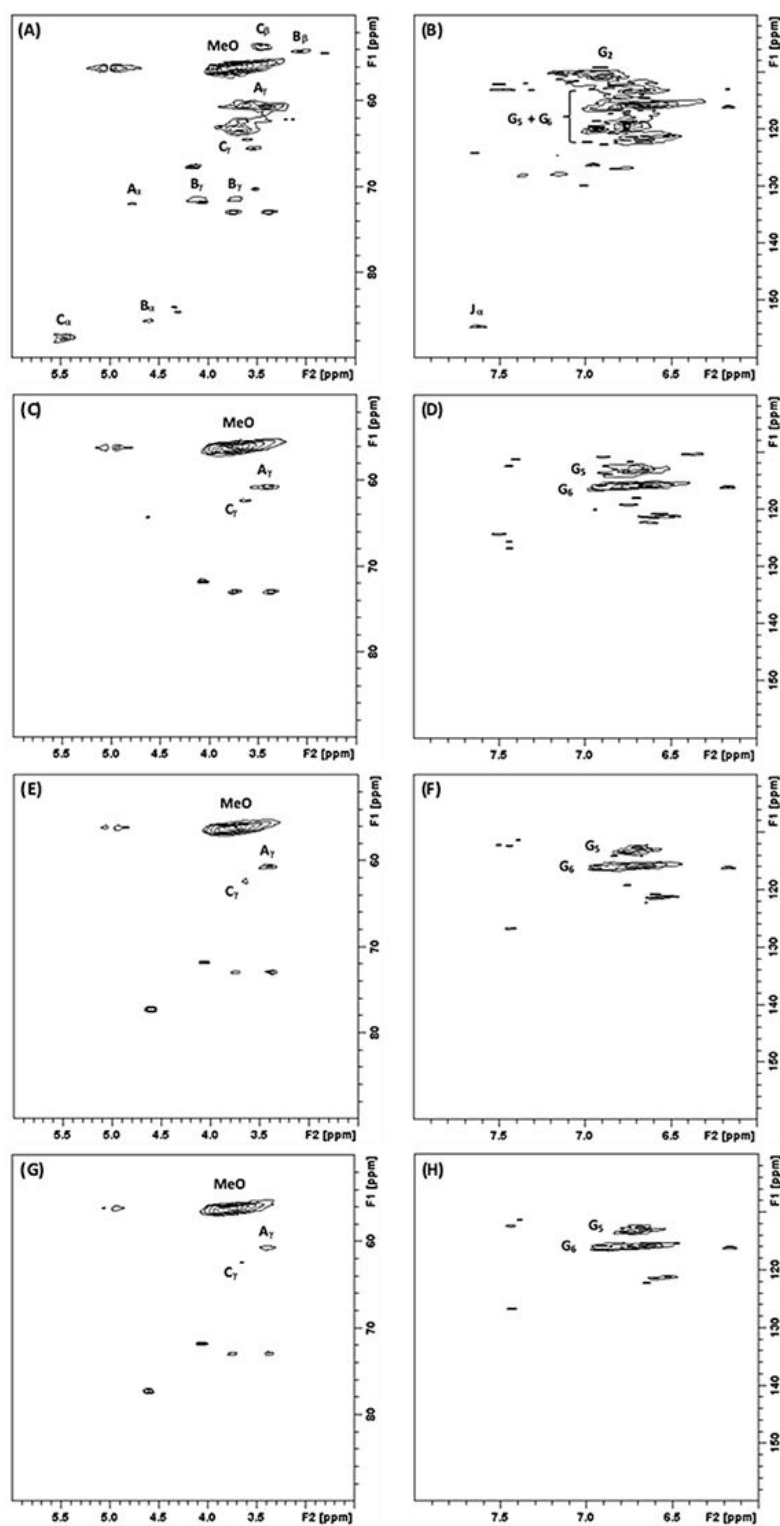


Figure 6 Side-chain ($\delta_{\text{H}}/\delta_{\text{C}}$ 2.5-5.8/50-90) and aromatic/unsaturated ($\delta_{\text{H}}/\delta_{\text{C}}$ 6.0-8.0/100-160) regions in the 2D HSQC NMR spectra of extracted lignin with GVL/H₂O [initial GVL/H₂O of 4/1 (w/w)] and various sulfuric acid concentrations at 160 °C for 24 h. (A, B) initial 0.075 M sulfuric acid; (C, D) initial 0.125 M sulfuric acid; (E, F) initial 0.175 M sulfuric acid and (G, H) initial 0.225 M sulfuric acid.

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3 FTIR analyses (spectra in Figure S2 and interpretation in Table S5) were carried out to identify
4 the functional groups existing in the structures of GVL-lignin extracted with various sulfuric acid
5 concentrations. The characteristic bands presented in all spectra correspond to the ones reported in
6 previous works.^{70,72-76} The characteristic bands at 2839 and 1210 cm^{-1} , attributed to the C-H stretching
7 in $-\text{OCH}_3$ and the C-O stretching, respectively, can be used to analyze the structural changes of the
8 GVL-lignins. The bands at 1595 cm^{-1} , assigned to aromatic skeleton vibrations and independent of
9 sulfuric acid concentration, were used to normalize those two peaks. The ratio of absorption value at
10 2849 cm^{-1} to 1595 cm^{-1} and the ratio of absorption value at 1210 cm^{-1} to 1595 cm^{-1} were identified as
11 representative of $-\text{OCH}_3$ and C-O, respectively.⁷⁰ Table 2 shows the relative absorbance values at
12 different sulfuric acid concentrations. For higher sulfuric acid concentrations, there is a decrease in the
13 values related to $-\text{OCH}_3$ groups while the corresponding values for C-O increase. These results
14 correspond to the 2D HSQC NMR involving the loss of methoxy groups while using high sulfuric acid
15 concentration during GVL-lignin extraction and previous reports of Nikafshar and co-workers that
16 found that the intensity of the signal at 1210 cm^{-1} increases after demethylation reactions.⁷⁶ Moreover,
17 the functional groups of GVL-lignin were confirmed by ^1H NMR (Figure S1). The ^1H NMR results
18 showed that GVL-lignin consists of six major functional groups, in accordance with other lignins⁷⁷:
19 formyl (10.08-9.47 ppm), phenolic (9.28-8.02 ppm), aromatic and vinyl (8.06-6.11 ppm), aliphatic CH-
20 O, C- CH_2 -O (5.80-4.28 ppm), methoxy (4.28-3.05 ppm) and aliphatic C- CH_3 , C- CH_2 -C (2.16-0.00
21 ppm).

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43 Structural changes occur in lignin due to mild acidic conditions during extraction.⁷⁸ This is
44 noted from the signals related to the side-chains of lignin obtained with different sulfuric acid
45 concentrations (Figure 6) in accordance with loss of β -O-4 structures, producing more condensed
46 structures. TGA analysis and its first derivative representation (DTG) confirm these changes in lignins
47 structures. TGA and DTG results (Figure S3 and Table S6) show one main event centered around 400
48 $^\circ\text{C}$ associated with lignin decomposition. The temperature of maximum devolatilization rate increases
49 for higher concentration of sulfuric acid used in the extraction process. This trend suggests that more
50 stable lignin structures form at higher sulfuric acid concentrations due to greater extent of condensation
51 and the presence of strong C-C bonds.^{57,79,80} In addition, there is an important decrease in the maximum
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devolatilization rate of GVL-lignins extracted with mixtures containing solutions of initial concentration of 0.125-0.275 M sulfuric acid with respect to 0.075 M sulfuric acid, which is consistent with previous results reported by Gardner and co-workers, who demonstrated a significant decrease in the rate of weight loss for more condensed lignins.⁷⁹

The results evidence that the extraction conditions affect the lignin and then the products distribution in fast pyrolysis. However, GVL-lignin remains more similar to native lignin compared to other extraction methods, especially those involving aqueous conditions with high acid concentration, as demonstrated Luterbacher and co-workers.²⁸ Therefore, a fine-tuning of the conditions may enable improved control of the selectivity in fast pyrolysis.

Table 2 Relative absorbance values of functional groups presented in GVL-lignin obtained by FTIR.

Wavenumber (cm ⁻¹)	Relative absorbance values at various initial sulfuric acid concentrations					Assignment
	0.075 M	0.125 M	0.175 M	0.225 M	0.275 M	
2839	0.438	0.350	0.335	0.333	0.329	C-H stretching in -OCH ₃
1595	1.000	1.000	1.000	1.000	1.000	Aromatic skeleton vibrations
1210	1.242	1.285	1.347	1.354	1.372	C-O stretching

Conclusions

The precise composition of the extraction medium influences the extraction yield of GVL-lignin and subtly affects its resulting structure. The GVL-to-water ratio affects the lignin yield, while minimally affecting the lignin structure. In contrast, the sulfuric acid concentration during the extraction affects both the extraction yield and the lignin structure, resulting in higher yields and more modified lignins for higher acid concentrations. These structural changes influence the products distribution after fast pyrolysis. Further fine-tuning of the extraction conditions could facilitate selectivity control in fast pyrolysis of lignin.

Author Information

*Corresponding author: Tel.: +41 44 632 5542. E-mail address: jeroen.vanbokhoven@chem.ethz.ch

(Jeroen A. van Bokhoven)

#These authors contributed equally to this work.

ORCID

Allen Puente-Urbina: <https://orcid.org/0000-0001-5328-2142>

Zhiqiang Ma: <https://orcid.org/0000-0003-3713-3926>

Sujitra Wongkasemjit: <https://orcid.org/0000-0003-4501-8848>

Jeremy S. Luterbacher: <http://orcid.org/0000-0002-0967-0583>

Jeroen A. van Bokhoven: <http://orcid.org/0000-0002-4166-2284>

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Supporting Information

Additional information about the solutions used for lignin extraction, lignin extraction yields and characterization (NMR, FTIR TGA and DTG).

References

- (1) Wang, S.; Dai, G.; Yang, H.; Luo, Z. Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review. *Prog. Energ. Combust.* **2017**, *62*, 33 – 86, DOI 10.1016/j.pecs.2017.05.004.
- (2) Qi, Z.; Jie, C.; Tiejun, W.; Ying, X. Review of biomass pyrolysis oil properties and upgrading research. *Energ. Convers. Manage.* **2007**, *48* (1), 87 – 92, DOI 10.1016/j.enconman.2006.05.010.

- 1
2
3 (3) Gallezot, P. Conversion of biomass to selected chemical products. *Chem. Soc. Rev.* **2012**, *41*, 1538
4 – 1558, DOI 10.1039/C1CS15147A.
5
- 6
7 (4) Shen, D.; Jin, W.; Hu, J.; Xiao, R.; Luo, K. An overview on fast pyrolysis of the main constituents
8 in lignocellulosic biomass to valued-added chemicals: Structures, pathways and interactions.
9
10 *Renew. Sust. Energ. Rev.* **2015**, *51*, 761 – 774, DOI 10.1016/j.rser.2015.06.054.
11
- 12
13 (5) Steubing B., Zah R., Waeger P., Ludwig, C. Bioenergy in Switzerland: Assessing the domestic
14 sustainable biomass potential. *Renew. Sust. Energ. Rev.*, **2010**, *14* (8), 2256 – 2265, DOI
15 10.1016/j.rser.2010.03.036.
16
- 17
18 (6) Swiss National Forest Inventory; Swiss Federal Institute for Forest, Snow and Landscape Research
19 and Federal Office for the Environment: Switzerland, 2018; <http://www.lfi.ch/>.
20
- 21
22 (7) Stefanidis, S. D.; Kalogiannis, K. G.; Iliopoulou, E. F.; Michailof, C. M.; Pilavachi, P. A.; Lappas
23 A. A. A study of lignocellulosic biomass pyrolysis via the pyrolysis of cellulose, hemicellulose
24 and lignin. *J. Anal. Appl. Pyrol.* **2014**, *105*, 143 – 150, DOI 10.1016/j.jaap.2013.10.013.
25
- 26
27 (8) Kabir, G.; Hameed, B. H. Recent progress on catalytic pyrolysis of lignocellulosic biomass to high
28 grade bio-oil and bio-chemicals. *Renew. Sust. Energ. Rev.* **2017**, *70*, 945 – 967, DOI
29 10.1016/j.rser.2016.12.001.
30
- 31
32 (9) Kumar, P.; Barrett, D. M.; Delwiche, M. J.; Stroeve, P. Methods for pretreatment of lignocellulosic
33 biomass for efficient hydrolysis and biofuel production. *Ind. Eng. Chem. Res.* **2009**, *48* (8), 3713
34 – 3729, DOI 10.1021/ie801542g.
35
- 36
37 (10) Crestini, C.; Melone, F.; Sette, M.; Saladino, R. Milled wood lignin: A linear oligomer.
38 *Biomacromolecules* **2011**, *12* (11), 3928 – 3935, DOI 10.1021/bm200948r.
39
- 40
41 (11) Lapierre, C.; Pollet, B.; Rolando, C. New insights into the molecular architecture of hardwood
42 lignins by chemical degradative methods. *Res. Chem. Intermediat.* **1995**, *21*, 397 – 412, DOI
43 10.1007/BF03052266.
44
- 45
46 (12) Neutelings, G. Lignin variability in plant cell walls: Contribution of new models. *Plant Sci.* **2011**,
47 *181* (4), 379 – 386, DOI 10.1016/j.plantsci.2011.06.012.
48
- 49
50 (13) Dhyani, V.; Bhaskar, T. A comprehensive review on the pyrolysis of lignocellulosic biomass.
51 *Renew. Energ.* **2018**, *129*, 695 – 716, DOI 10.1016/j.renene.2017.04.035.
52
53
54
55
56
57
58
59
60

- 1
2
3 (14) Behera, S.; Arora, R.; Nandhagopal, N.; Kumar, S. Importance of chemical pretreatment for
4 bioconversion of lignocellulosic biomass. *Renew. Sust. Energ. Rev.* **2014**, *36*, 91 – 106, DOI
5 10.1016/j.rser.2014.04.047.
6
7
8
9 (15) Taherzadeh, M. J.; Karimi, K. Pretreatment of lignocellulosic wastes to improve ethanol and
10 biogas production: A review. *Int. J. Mol. Sci.* **2008**, *9* (9), 1621 – 1651, DOI
11 10.3390/ijms9091621.
12
13
14 (16) Shuai, L.; Talebi Amiri, M.; Luterbacher, J. S. The influence of interunit carbon-carbon linkages
15 during lignin upgrading. *Curr. Opin. Green Sustain. Chem.* **2016**, *2*, 59 – 63, DOI
16 10.1016/j.cogsc.2016.10.001.
17
18
19 (17) Schutyser, W.; Renders, T.; Van den Bosch, S.; Koelewijn, S.-F.; Beckham, G. T.; Sels, B. F.
20 Chemicals from lignin: An interplay of lignocellulose fractionation, depolymerisation, and
21 upgrading. *Chem. Soc. Rev.* **2018**, *47*, 852 – 908, DOI 10.1039/C7CS00566K.
22
23
24 (18) Sun, Z.; Fridrich, B.; de Santi, A.; Elangovan, S.; Barta, K. Bright side of lignin depolymerization:
25 Toward new platform chemicals. *Chem. Rev.* **2018**, *118* (2), 614 – 678, DOI
26 10.1021/acs.chemrev.7b00588.
27
28
29 (19) Rinaldi, R.; Jastrzebski, R.; Clough, M. T.; Ralph, J.; Kennema, M.; Bruijninx, P. C. A.;
30 Weckhuysen, B. M. Paving the way for lignin valorisation: Recent advances in bioengineering,
31 biorefining and catalysis. *Angew. Chemie Int. Ed.* **2016**, *55* (29), 8164 – 8215, DOI
32 10.1002/anie.201510351.
33
34
35 (20) Sun, F.; Chen, H. Organosolv pretreatment by crude glycerol from oleochemicals industry for
36 enzymatic hydrolysis of wheat straw. *Bioresource Technol.* **2008**, *99* (13), 5474 – 5479, DOI
37 10.1016/j.biortech.2007.11.001.
38
39
40 (21) Agbor, V. B.; Cicek, N.; Sparling, R.; Berlin, A.; Levin D. B. Biomass pretreatment: Fundamentals
41 toward application. *Biotechnol. Adv.* **2011**, *29* (6), 675 – 685, DOI
42 10.1016/j.biotechadv.2011.05.005.
43
44
45 (22) Zhao, X.; Li, S.; Wu, R.; Liu, D. Organosolv fractionating pre-treatment of lignocellulosic biomass
46 for efficient enzymatic saccharification: Chemistry, kinetics, and substrate structures. *Biofuel.*
47 *Bioprod. Bior.* **2017**, *11* (3), 567 – 590, DOI 10.1002/bbb.1768.
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 (23) Wen, J.-L.; Sun, S.-L.; Yuan, T.-Q.; Xu, F.; Sun, R.-C. structural elucidation of lignin polymers of
4 *Eucalyptus Chips* during organosolv pretreatment and extended delignification. *J. Agric. Food*
5 *Chem.* **2013**, *61* (46), 11067 – 11075, DOI 10.1021/jf403717q.
6
7
8
9 (24) Soh, L.; Eckelman, M. J. Green solvents in biomass processing. *ACS Sustain. Chem. Eng.* **2016**, *4*
10 (11), 5821 – 5837, DOI 10.1021/acssuschemeng.6b01635.
11
12
13 (25) Lê, H. Q.; Ma, Y.; Borrega, M.; Sixta, H. Wood biorefinery based on γ -valerolactone/water
14 fractionation. *Green Chem.* **2016**, *18*, 5466 – 5476, DOI 10.1039/C6GC01692H.
15
16
17 (26) Fang, W.; Sixta, H. Advanced biorefinery based on the fractionation of biomass in γ -valerolactone
18 and water. *ChemSusChem* **2015**, *8* (1), 73 – 76, DOI 10.1002/cssc.201402821.
19
20
21 (27) Li, S.-X.; Li, M.-F.; Yu, P.; Fan, Y.-M.; Shou, J.-N.; Sun, R.-C. Valorization of bamboo by γ -
22 valerolactone/acid/water to produce digestible cellulose, degraded sugars and lignin. *Bioresource*
23 *Technol.* **2017**, *230*, 90 – 96, DOI 10.1016/j.biortech.2017.01.041.
24
25
26 (28) Luterbacher, J. S.; Azarpira, A.; Motagamwala, A. H.; Lu, F.; Ralph, J.; Dumesic, J. A. Lignin
27 monomer production integrated into the γ -valerolactone sugar platform. *Energ. Environ. Sci.* **2015**,
28 *8*, 2657 – 2663, DOI 10.1039/C5EE01322D.
29
30
31 (29) Angelini, S.; Ingles, D.; Gelosia, M.; Cerruti, P.; Pompili, E.; Scarinzi, G.; Cavalaglio, G.; Cotana,
32 F.; Malinconico, M. One-pot lignin extraction and modification in γ -valerolactone from steam
33 explosion pre-treated lignocellulosic biomass. *J. Clean. Prod.* **2017**, *151*, 152 – 162, DOI
34 10.1016/j.jclepro.2017.03.062.
35
36
37 (30) Tang, X.; Zeng, X.; Li, Z.; Hu, L.; Sun, Y.; Liu, S.; Lei, T.; Lin, L. Production of γ -valerolactone
38 from lignocellulosic biomass for sustainable fuels and chemicals supply. *Renew. Sust. Energ. Rev.*
39 **2014**, *40*, 608 – 620, DOI 10.1016/j.rser.2014.07.209.
40
41
42 (31) Alonso, D. M.; Wettstein, S. G.; Mellmer, M. A.; Gurbuz, E. I.; Dumesic, J. A. Integrated
43 conversion of hemicellulose and cellulose from lignocellulosic biomass. *Energ. Environ. Sci.*
44 **2013**, *6*, 76 – 80, DOI 10.1039/C2EE23617F.
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4 (32) Horvath, I. T.; Mehdi, H.; Fabos, V.; Boda, L.; Mika, L. T. γ -Valerolactone-a sustainable liquid
5 for energy and carbon-based chemicals. *Green Chem.* **2008**, *10*, 238 – 242, DOI
6 10.1039/B712863K.
7
8
9 (33) Fegyverneki, D.; Orha, L.; Láng, G.; Horváth, I. T. Gamma-valerolactone-based solvents.
10 *Tetrahedron* **2010**, *66* (5), 1078 – 1081, DOI 10.1016/j.tet.2009.11.013.
11
12 (34) Emelyanenko, V. N.; Kozlova, S. A.; Verevkin, S. P.; Roganov, G. N. Vapour pressures and
13 enthalpies of vapourization of a series of the γ -lactones. *J. Chem. Thermodyn.* **2008**, *40* (6), 911 –
14 916, DOI 10.1016/j.jct.2008.02.002.
15
16
17 (35) Sharma, A.; Pareek, V.; Zhang, D. Biomass pyrolysis-A review of modelling, process parameters
18 and catalytic studies. *Renew. Sust. Energ. Rev.* **2015**, *50*, 1081 – 1096, DOI
19 10.1016/j.rser.2015.04.193.
20
21 (36) Laurichesse, S.; Avérous, L. Chemical modification of lignins: Towards biobased polymers. *Prog.*
22 *Polym. Sci.* **2014**, *39* (7), 1266 – 1290, DOI 10.1016/j.progpolymsci.2013.11.004.
23
24 (37) Bu, Q.; Lei, H.; Ren, S. J.; Wang, L.; Holladay, J.; Zhang, Q.; Tang, J.; Ruan, R. Phenol and
25 phenolics from lignocellulosic biomass by catalytic microwave pyrolysis. *Bioresource Technol.*
26 **2011**, *102* (13), 7004 – 7007, DOI 10.1016/j.biortech.2011.04.025.
27
28 (38) Yaman, S. Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energ. Convers.*
29 *Manage.* **2004**, *45* (5), 651 – 671, DOI 10.1016/S0196-8904(03)00177-8.
30
31 (39) Li, C.; Zhao, X.; Wang, A.; Huber, G. W.; Zhang, T. Catalytic transformation of lignin for the
32 production of chemicals and fuels. *Chem. Rev.* **2015**, *115* (21), 11559 – 11624, DOI
33 10.1021/acs.chemrev.5b00155.
34
35 (40) Bridgwater, A. V. Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenerg.*
36 **2012**, *38*, 68 – 94, DOI 10.1016/j.biombioe.2011.01.048.
37
38 (41) Hemberger, P.; Custodis, V. B. F.; Bodi, A.; Gerber, T.; van Bokhoven, J. A. Understanding the
39 mechanism of catalytic fast pyrolysis by unveiling reactive intermediates in heterogeneous
40 catalysis. *Nat. Commun.* **2017**, *8*, DOI 10.1038/ncomms15946.
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 (42) Ma, Z.; Ghosh, A.; Asthana, N.; van Bokhoven, J. A. Optimization of the reaction conditions for
4 catalytic fast pyrolysis of pretreated lignin over zeolite for the production of phenol.
5 *ChemCatChem* **2017**, *9* (6), 954 – 961, DOI 10.1002/cctc.201601674.
6
7
8
9 (43) Custodis, V. B. F.; Karakoulia, S. A.; Triantafyllidis, K. S.; van Bokhoven, J. A. Catalytic Fast
10 Pyrolysis of Lignin over High-Surface-Area Mesoporous Aluminosilicates: Effect of Porosity and
11 Acidity. *ChemSusChem* **2016**, *9* (10), 1134 – 1145, DOI 10.1002/cssc.201600105.
12
13
14 (44) Custodis, V. B. F.; Bährle, C.; Vogel, F.; van Bokhoven, J. A. Phenols and aromatics from fast
15 pyrolysis of variously prepared lignins from hard- and softwoods. *J. Anal. Appl. Pyrol.* **2015**, *115*,
16 214 – 223, DOI 10.1016/j.jaap.2015.07.018.
17
18
19 (45) Ma, Z.; Troussard, E.; van Bokhoven, J. A. Controlling the selectivity to chemicals from lignin via
20 catalytic fast pyrolysis. *Appl. Catal. A-Gen.* **2012**, *423-424*, 130 – 136, DOI
21 10.1016/j.apcata.2012.02.027.
22
23
24 (46) Bährle, C.; Custodis, V.; Jeschke, G.; van Bokhoven, J. A., Vogel, F. The influence of zeolites on
25 radical formation during lignin pyrolysis. *ChemSusChem* **2016**, *9* (17), 2397 – 2403, DOI
26 10.1002/cssc.201600582.
27
28
29 (47) Ma, Z.; Custodis, V.; van Bokhoven, J. A. Selective deoxygenation of lignin during catalytic fast
30 pyrolysis. *Catal. Sci. Technol.* **2014**, *4*, 766 – 772, DOI 10.1039/C3CY00704A.
31
32
33 (48) Ma, Z.; van Bokhoven, J. A. Deactivation and regeneration of H-USY zeolite during lignin
34 catalytic fast pyrolysis. *ChemCatChem* **2012**, *4* (12), 2036 – 2044, DOI 10.1002/cctc.201200401.
35
36
37 (49) Kim, Y. M.; Jae, J.; Myung, S.; Sung, B. H.; Dong, J. I.; Park, Y. K. Investigation into the lignin
38 decomposition mechanism by analysis of the pyrolysis product of *Pinus radiata*. *Bioresource*
39 *Technol.* **2016**, *219*, 371 – 377, DOI 10.1016/j.biortech.2016.08.001.
40
41
42 (50) Onay, O. Influence of pyrolysis temperature and heating rate on the production of bio-oil and char
43 from safflower seed by pyrolysis, using a well-swept fixed-bed reactor. *Fuel Process. Technol.*
44 **2007**, *88* (5), 523 – 531, DOI 10.1016/j.fuproc.2007.01.001.
45
46
47 (51) Horne, P. A.; Williams, P. T. Influence of temperature on the products from the flash pyrolysis of
48 biomass. *Fuel* **1996**, *75* (9), 1051 – 1059, DOI 10.1016/0016-2361(96)00081-6.
49
50
51
52
53
54
55
56
57
58
59
60

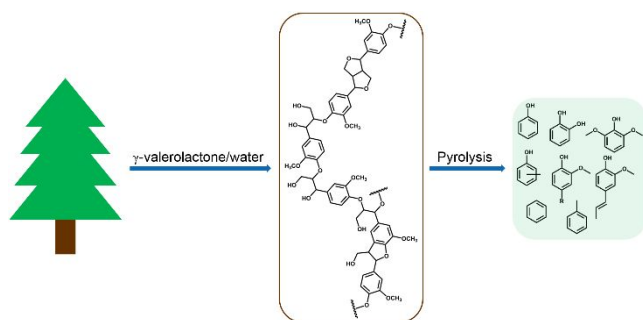
- 1
2
3 (52) Heo, H. S.; Park, H. J.; Dong, J. I.; Park, S. H.; Kim, S.; Suh, D. J.; Suh, Y. W.; Kim, S. S.; Park,
4
5 Y. K. Fast pyrolysis of rice husk under different reaction conditions. *J. Ind. Eng. Chem.* **2010**, *16*
6
7 (1), 27 – 31, DOI 10.1016/j.jiec.2010.01.026.
8
9 (53) Naqvi, S. R.; Uemura, Y.; Yusup S. B. Catalytic pyrolysis of paddy husk in a drop type pyrolyzer
10
11 for bio-oil production: The role of temperature and catalyst. *J. Anal. Appl. Pyrol.* **2014**, *106*, 57 –
12
13 62, DOI 10.1016/j.jaap.2013.12.009.
14
15 (54) Imam, T.; Capareda, S. Characterization of bio-oil, syn-gas and bio-char from switchgrass
16
17 pyrolysis at various temperatures. *J. Anal. Appl. Pyrol.* **2012**, *93*, 170 – 177, DOI
18
19 10.1016/j.jaap.2011.11.010.
20
21 (55) Lê, H. Q.; Zaitseva, A.; Pokki, J.-P.; Ståhl, M.; Alopaeus, V.; Sixta, H. Solubility of organosolv
22
23 lignin in γ -valerolactone/water binary mixtures. *ChemSusChem* **2016**, *9* (20), 2939 – 2947, DOI
24
25 10.1002/cssc.201600655.
26
27 (56) Brasch, D. J.; Free, K. W. Prehydrolysis-Kraft pulping of *Pinus radiata* grown in New Zealand.
28
29 *Tappi* **1965**, *48*, 245 – 248.
30
31 (57) Pepper, J. M.; Siddiqueullah, M. The effect of initial acid concentration on the lignin isolated by
32
33 the acidolysis of aspen wood. *Cana. J. Chem.* **1961**, *39* (7), 1454 – 1461, DOI 10.1139/v61-185.
34
35 (58) Wong, C. Y. Y.; Choi, A. W.-T.; Lui, M. Y.; Fridrich, B.; Horváth, A. K.; Mika, L. T.; Horváth, I.
36
37 T. Stability of gamma-valerolactone under neutral, acidic, and basic conditions. *Struct. Chem.*
38
39 **2017**, *28* (2), 423 – 429, DOI 10.1007/s11224-016-0887-6.
40
41 (59) Xue, Z.; Zhao, X.; Sun, R. C.; Mu, T. Biomass-derived γ -valerolactone-based solvent systems for
42
43 highly efficient dissolution of various lignins: dissolution behavior and mechanism study. *ACS*
44
45 *Sustain. Chem. Eng.* **2016**, *4* (7), 3864 – 3870, DOI 10.1021/acssuschemeng.6b00639.
46
47 (60) Luterbacher, J. S.; Rand, J. M.; Alonso, D. M.; Han, J.; Youngquist, J. T.; Maravelias, C. T.;
48
49 Pflieger, B. F.; Dumesic, J. A. Nonenzymatic sugar production from biomass using biomass-
50
51 derived γ -valerolactone. *Science* **2014**, *343* (6168), 277 – 280, DOI 10.1126/science.1246748.
52
53 (61) Jiang, G.; Nowakowski, D. J.; Bridgwater, A. V. Effect of the temperature on the composition of
54
55 lignin pyrolysis products. *Energ. Fuel.*, **2010**, *24* (8), 4470 – 4475, DOI 10.1021/ef100363c.
56
57
58
59
60

- 1
2
3 (62) Trinh, T. N.; Jensen, P. A.; Sárossy, Z.; Dam-Johansen, K.; Knudsen, N. O.; Sørensen, H. R.;
4
5 Egsgaard, H. Fast pyrolysis of lignin using a pyrolysis centrifuge reactor. *Energ. Fuel.*, **2013**, *27*
6
7 (7), 3802 – 3810, DOI 10.1021/ef400527k.
8
9 (63) Zhao, Y.; Deng, L.; Liao, B.; Fu, Y.; Guo, Q. X. Aromatics production via catalytic pyrolysis of
10
11 pyrolytic lignins from bio-oil. *Energ. Fuel.*, **2010**, *24* (10), 5735 – 5740, DOI 10.1021/ef100896q.
12
13 (64) Li, X.; Su, L.; Wang, Y.; Yu, Y.; Wang, C.; Li, X.; Wang, Z. Catalytic fast pyrolysis of Kraft lignin
14
15 with HZSM-5 zeolite for producing aromatic hydrocarbons. *Front. Env. Sci. Eng.* **2012**, *6* (3), 295
16
17 – 303, DOI 10.1007/s11783-012-0410-2.
18
19 (65) Patwardhan, P. R.; Brown, R. C.; Shanks, B. H. Understanding the fast pyrolysis of lignin.
20
21 *ChemSusChem* **2011**, *4* (1), 1629 – 1636, DOI 10.1002/cssc.201100133.
22
23 (66) Fan, L.; Zhang, Y.; Liu, S.; Zhou, N.; Chen, P.; Cheng, Y.; Addy, M.; Lu, Q.; Omar, M. M.; Liu,
24
25 Y.; Wang, Y.; Dai, L.; Anderson, E.; Peng, P.; Lei, H.; Ruan, R. Bio-oil from fast pyrolysis of
26
27 lignin: Effects of process and upgrading parameters. *Bioresource Technol.* **2017**, *241*, 1118 – 1126,
28
29 DOI 10.1016/j.biortech.2017.05.129.
30
31 (67) Lourenço, A.; Rencoret, J.; Chemetova, C.; Gominho, J.; Gutiérrez, A.; del Río, J. C.; Pereira, H.
32
33 Lignin composition and structure differs between xylem, phloem and phellemen *Quercussuber L.*
34
35 *Front. Plant Sci.* **2016**, *7*, DOI 10.3389/fpls.2016.01612.
36
37 (68) Rencoret, J.; Marques, G.; Gutiérrez, A.; Nieto, L.; Santos, J. I.; Jimenez-Barbero, J.; Martínez, A.
38
39 T., del Río J. C. HSQC-NMR analysis of lignin in woody (*Eucalyptus globulus* and *Picea abies*)
40
41 and non-woody (*Agave sisalana*) ball-milled plant materials at the gel state. *Holzforschung* **2009**,
42
43 *63* (6), 691 – 698, DOI 10.1515/HF.2009.070.
44
45 (69) Martínez, A. T.; Rencoret, J.; Marques, G.; Gutiérrez, A.; Ibarra, D.; Jiménez-Barbero, J.; del Río
46
47 J. C. Monolignol acylation and lignin structure in some nonwoody plants: A 2D NMR study.
48
49 *Phytochemistry* **2008**, *69* (16), 2831 – 2843, DOI 10.1016/j.phytochem.2008.09.005.
50
51 (70) Li, J.; Wang, W.; Zhang, S.; Gao, Q.; Zhang, W.; Li, J. Preparation and characterization of lignin
52
53 demethylated at atmospheric pressure and its application in fast curing biobased phenolic resins.
54
55 *RSC Adv.* **2016**, *6*, 67435 – 67443, DOI 10.1039/C6RA11966B.
56
57
58
59
60

- 1
2
3 (71) Shuai, L.; Amiri, M. T.; Questell-Santiago, Y. M.; Héroguel, F.; Li, Y.; Kim, H.; Meilan, R.;
4 Chapple, C.; Ralph, J.; Luterbacher, J. S. Formaldehyde stabilization facilitates lignin monomer
5 production during biomass depolymerization. *Science* **2016**, *354* (6310), 329 – 333, DOI
6 10.1126/science.aaf7810.
7
8
9
10
11 (72) Hage, R. E.; Brosse, N.; Chrusciel, L.; Sanchez, C.; Sannigrahi, P.; Ragauskas, A. Characterization
12 of milled wood lignin and ethanol organosolv lignin from *miscanthus*. *Polym. Degrad. Stabil.*
13 **2009**, *94* (10), 1632 – 1638, DOI 10.1016/j.polymdegradstab.2009.07.007.
14
15
16
17 (73) Azadfar, M.; Gao, A. H.; Bule, M. V.; Chen, S. Structural characterization of lignin: A potential
18 source of antioxidants guaiacol and 4-vinylguaiacol. *Int. J. Biol. Macromol.* **2015**, *75*, 58 – 66,
19 DOI 10.1016/j.ijbiomac.2014.12.049.
20
21
22
23 (74) Jahan, M. S.; Chowdhury, D. A. N.; Islam, M. K.; Moeiz, S. M. I. Characterization of lignin
24 isolated from some nonwood available in Bangladesh. *Bioresource Technol.* **2007**, *98* (2), 465 –
25 469, DOI 10.1016/j.biortech.2006.01.005.
26
27
28
29 (75) Wu, M.; Liu, J.-K.; Yan, Z.-Y.; Wang, B.; Zhang, X.-M.; Xu, F.; Sun, R.-C. Efficient recovery and
30 structural characterization of lignin from cotton stalk based on a biorefinery process using a γ -
31 valerolactone/water system. *RSC Adv.*, **2016**, *6*, 6196 – 6204, DOI 10.1039/C5RA23095K.
32
33
34
35 (76) Nikafshar, S.; Zabihi, O.; Moradi, Y.; Ahmadi, M.; Amiri, S.; Naebe, M. Catalyzed synthesis and
36 characterization of a novel lignin-based curing agent for the curing of high-performance epoxy
37 resin. *Polymers*. **2017**, *9* (7), 266, DOI 10.3390/polym9070266.
38
39
40
41 (77) Cheng, Y.; Zhao, P. X.; Alma, M. H.; Sun, D. F.; Li, R.; Jiang, J. X. Improvement of direct
42 liquefaction of technical alkaline lignin pretreated by alkaline hydrogen peroxide. *J. Anal. Appl.*
43 *Pyrol.* **2016**, *122*, 277 – 281, DOI 10.1016/j.jaap.2016.07.022.
44
45
46
47 (78) Santos, R. B.; Harte, P. W.; Jameel, H.; Chang, H. Wood based lignin reactions important to the
48 biorefinery and pulp and paper industries. *Bioresources* **2013**, *8*, 1456 – 1477.
49
50
51
52 (79) Gardner, D. J.; Schultz, T. P.; McGinnis, G. D. The pyrolytic behavior of selected lignin
53 preparations. *J. Wood Chem. Technol.* **1985**, *5* (1), 85 – 110, DOI 10.1080/02773818508085182.
54
55
56
57
58
59
60

- 1
2
3 (80) Kim J.-Y., Hwang H., Oh S., Kim Y.-S., Kim U.-J., Choi, J. W. Investigation of structural
4 modification and thermal characteristics of lignin after heat treatment. *Int. J. Biol. Macromol.*
5
6
7 **2014**, *66*, 57 – 65, DOI 10.1016/j.ijbiomac.2014.02.013.
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
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Abstract Graphic



Synopsis

The extraction conditions of lignin using a solvent system containing γ -valerolactone and water affect the selectivity in fast pyrolysis.