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Abstract

Fast pyrolysis of lignin is a promising method to produce aromatic chemicals and fuels. Lignin structure and pyrolysis conditions determine the liquid yield and product selectivity. Extraction of pine wood using γ-valerolactone (GVL) mixed with water in the presence of diluted sulfuric acid obtains lignin (GVL-lignin) which shows different product yield and selectivity. The composition of the extraction medium influences the yield of GVL-lignin and affects its native structure. The GVL-to-water ratio affects the lignin yield without significantly modifying the structure of the extracted lignin, whereas the sulfuric acid concentration affects both the extraction yield and the extracted

lignin structure. These structural changes influence the products distribution after fast pyrolysis, which generates phenols and alkoxy phenols as the main products in the liquid fraction. Lignin extracted with a mixture of 4/1 of GVL/H_2O (w/w) with 0.075 M sulfuric acid solution produces the highest pyrolysis liquid yield. Pyrolysis of GVL-lignin at 750 °C generates the maximum liquid yield. The amount of phenols in fast pyrolysis products increases with increasing temperature and sulfuric acid concentration used in the GVL-lignin extraction. This indicates that the extraction conditions of GVL-lignin may be optimized to increase the selectivity in fast pyrolysis.

Keywords: lignocellulosic biomass, lignin, γ-valerolactone (GVL), fast pyrolysis, bio-oil

Introduction

Owing to the increase in worldwide population in recent years, fossil resources consumption has also increased, leading to concerns about their depletion and negative effects on the environment. Therefore, processes facilitating the use of alternative sustainable feedstocks receive more and more consideration. Among the alternative resources, biomass is a promising raw material for producing value-added chemicals, fuels and energy with a low carbon footprint.[1-3]

Lignocellulosic biomass is an exceptional renewable feedstock to obtain useful products (e.g. chemicals and fuels) and energy through biochemical or thermochemical transformations.[4] The relevance of a certain type of biomass in a specific region depends on its availability, which often depends on technical, economic, environmental and other factors.[5] In Switzerland, there is a substantial sustainable potential for forest energy wood, wood from landscape maintenance and waste wood, with softwoods being the majority of domestic wood species produced.[5,6] In general, lignocellulosic biomass is mainly composed of cellulose, hemicellulose and lignin, but also has small amounts of ash and extractives.[7] Each type of lignocellulosic biomass contains different amounts of these components. In all cases, lignin is an important fraction that has a high potential to be used as a renewable source for producing fuels and aromatic compounds.[8]

Lignin has a complex three-dimensional amorphous structure. It has been described conventionally as a polymer of phenylpropane units (monolignols), namely *p*-coumaryl, coniferyl and

sinapyl alcohols, also called units H, G and S.[9,10] Each unit in the lignin structure is connected by 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] Generally, softwood lignin contains coniferyl alcohol and hardwood lignin both coniferyl and sinapyl alcohols as predominant units.[13] However, lignin properties and its isolation yield depend on its source (e.g. softwood or hardwood) and the extraction technique applied. These factors also influence the products that can be obtained from further processing of such lignin. Thus, it is necessary to use a suitable extraction method to obtain high yields as well as adequate characteristics for the intended use.

The organosolv extraction is one of the most popular processes to isolate cellulose, hemicellulose and lignin from lignocellulosic biomass. This method can solubilize lignin and separate it from the lignocellulosic feedstocks, usually along with hemicellulose, by using a mixture of organic solvents and inorganic acids catalysts such as hydrochloric acid and sulfuric acid.[14] Regular solvents used in this process include methanol, ethanol, acetone, ethylene glycol, triethylene glycol and tetrahydrofurfuryl alcohol.[15] Due to the milder conditions required and the solubilization of the lignin, the lignin's structure can generally be better preserved than using other extraction methods such as Kraft or aqueous methods though some condensation does occur.[16-18] Thus, the organosolv method generates lignin which is more amenable towards depolymerization.[19] However, this method still has some drawbacks, such as the need for solvent recovery, high-pressure operation conditions, associated risks due to high volatility and flammability of the organic solvents used as well as their toxicity to the environment and human health, among others, which contribute to a low economic competitiveness with respect to other fractionation methods.[20-22] In addition, side reactions such as cleavage of aryl ether linkages, ethoxylation and condensation reactions can take place, resulting in undesired structure modifications.[22,23]

Trying to minimize these problems, green solvents have attracted attention in recent years for biomass processing.[24] Among them, γ-valerolactone (GVL) is a promising solvent for biomass fractionation with the possibility of obtaining the extracted lignin by addition of water.[25-31] It has favorable physical and chemical properties for various applications such as low melting point (-31 °C), high boiling point (207 °C) and low volatility (vapor pressure of 0.44 mbar at 25 °C),

renewability, high open cup flash point (96 ºC), non-toxicity, stability, biodegradability and also the possibility to be mixed or chemically modified to tailor other specific purposes.[32-34]

Lignin can be converted into useful liquids (bio-oil), gases and char by pyrolysis as thermochemical decomposition process.[4] It can be classified as fast pyrolysis or slow pyrolysis depending on its operation conditions.[35] Interestingly, fast pyrolysis generates a higher amount of bio-oil, an alternative source of solvents, fuels and other high value chemicals.[36-38] In fast pyrolysis, lignin is thermally treated using very high heating rates and short vapor residence times, followed by a rapid cooling of the pyrolysis vapors to obtain bio-oil containing important amounts of aromatic compounds.[39,40] In addition, fast pyrolysis can be developed under catalytic and non-catalytic conditions, which together with the process conditions, determine the products distribution.[41-45]

In this study, pine wood (softwood) was employed as the lignocellulosic biomass source for lignin extraction with GVL/H_2O solvent in the presence of sulfuric acid. The influence of extraction conditions (i.e. time, temperature, sulfuric acid concentration and GVL/H_2O ratio) on the process and lignin structure was analyzed. Then, the extracted lignin underwent fast pyrolysis at various temperatures and the corresponding products were determined. The objective of this work was to find the best conditions for lignin extraction from pine wood by using GVL/H_2O solvent to maximize the organic liquid yield obtained by fast pyrolysis.

Experimental Section

Chemicals

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

Lignin extraction

Pine wood was dried at 100 ºC and then milled to particles of <180 μm by steel ball milling. The milled pine wood was suspended in GVL/H_2O containing sulfuric acid, using a solid-to-solvent ratio of 1/10 w/w. The resulting mixture was heated in a 100 ml teflon reactor with constant stirring, varying temperature (120, 140 and 160 ºC), time (1, 3, 5, 15, 21, 24 and 27 h), sulfuric acid

concentration (by addition of 0.025, 0.050, 0.075, 0.125, 0.175, 0.225 and 0.275 M sulfuric acid

aqueous solutions, 10 wt% with respect to GVL/H_2O solvent) and initial GVL/H_2O ratio (4/1, 2/1 and

1/1 w/w). Table S1 has additional details about the solutions used for lignin extraction. Then, the

products were separated by filtration. The lignin contained in the filtrate was precipitated using water

and the sludge stirred for 30 min. The resulting solid (i.e. lignin, Table S2) was filtered, washed with

water and dried overnight at 100 ºC.

Lignin characterization

Fourier-transform infrared spectroscopy (FTIR) measurements were developed using a Bio-

Rad Excalibur Series FTS 3000 spectrometer. The samples were pelletized with KBr, using a

proportion of 1 mg of lignin per 40 mg of KBr. Each spectrum was obtained by averaging 256 scans

in a wavenumber range of 800-4000 cm^{-1} with a resolution of 2 cm^{-1}.

Nuclear magnetic resonance (NMR) spectra were recorded in a Bruker 500 MHz Ultrashield

spectrometer at room temperature. Samples were prepared dissolving 30 mg of lignin in 0.9 mL of

DMSO-d_6. ^1H NMR experiments were performed using the pulse sequence zg30, 16 scans, 2 dummy

scans, 1 s of relaxation delay and 3.27 s of acquisition time. The heteronuclear single quantum

correlation (HSQC) spectra were obtained using the pulse program hsqcetgpsisp2.2, 8 scans, 4

dummy scans, 0.5 s of relaxation delay, spectral widths of 6010 Hz (12 to 0 ppm) for ^1H dimension

(F2) and 27669 Hz (220 to 0 ppm) for ^{13}C dimension (F1), 2048 points recorded for ^1H dimension and

1024 points for ^{13}C dimension, and acquisition times of 0.17 s for ^1H dimension and 0.018 s for ^{13}C

dimension. The results were analyzed using TopSpin 3.5 software.

Thermogravimetric analyses (TGA) were performed in a Mettler Toledo TGA/SDTA851^e

thermogravimetric analyzer. Lignin samples were heated from 30 ºC to 760 ºC with a heating rate of

10 ºC min^{-1} under nitrogen flow (50 cm^3 min^{-1}).

Fast pyrolysis and products analyses

Fast pyrolysis experiments were carried out in a CDS Analytical 5150 pyrolyzer using an

open quartz tube resistively heated by a platinum coil. Lignin samples of 1.5-2 mg were immobilized

in the middle of the reactor by quartz wool and pyrolyzed at a heating rate of 20 °C/ms, a residence

time of 20 s and varying the pyrolysis temperature from 550 to 850 °C.

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Pyrolysis products were directly transferred at 300 °C into an Agilent 7890A gas chromatograph using helium at 1.1 mL min⁻¹ as carrier gas, equipped with a thermal conductivity detector (TCD) and an Agilent 5975C mass selective detector (MSD). The oven was programmed to 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 25 min. An injector temperature of 300 °C and a split ratio of 35:1 were used. The flow was split to analyze condensable pyrolysis products in one stream and gases in another. Condensable pyrolysis products were separated with a HP-5MS column (30 m x 0.25 mm x 0.25 μm) and analyzed by means of the mass spectrometry detector, where peaks were identified using the NIST08 mass spectrum library and the corresponding compounds classified according to their functional groups into seven categories: thiols; non-aromatic esters, ketones, aldehydes, furans and acids; aromatic hydrocarbons; alkoxy aromatic hydrocarbons; phenols; alkoxy phenols and non-identified (typical quantifications with less than ±5 % error). Non-condensable gases were separated with Agilent Plot/Q and molecular sieve capillary columns (both 30 m x 0.53 mm) and quantified using the TCD, which was calibrated for the most predominant gaseous molecules (CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6 and C_3H_8). In addition, the remaining solid after pyrolysis was measured gravimetrically and the liquid fraction was calculated by mass difference. All the measurements were performed at least in duplicate and reported with 95 % confidence level.

Results and discussion

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

The pyrolysis temperature is an important operational factor for this type of process. Different temperatures (i.e. 550, 650, 750 and 850 °C) were used to evaluate the fast pyrolysis of GVL-lignin from pine wood using a heating rate of 20 °C/ms and residence time of 20 s. The pyrolysis products can be divided into three phases, namely liquid (bio-oil), solid (char) and gas.[41-48] Figure 1A illustrates the yields of liquid, char and gaseous products as a function of the pyrolysis temperature of GVL-lignin obtained using a mixture of 4/1 GVL/H_2O (w/w) and 0.075 M sulfuric acid at 160 ºC for 24 h. The liquid fraction increased from 550 to (650-850) °C, because of an increase in primary decomposition of

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 Williams[51] 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]
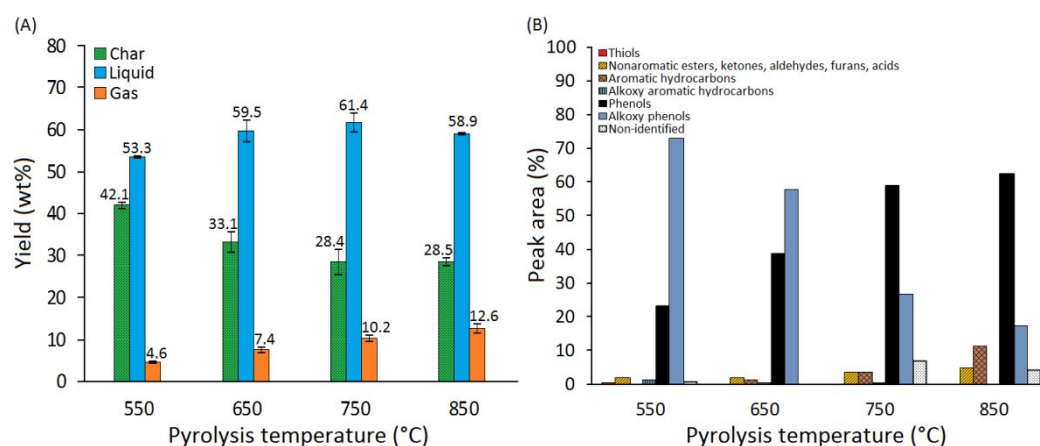
Figure 1 Effect of temperature on pyrolysis of extracted lignin with a mixture of 4/1 GVL/H_2O (w/w) and 0.075 M sulfuric acid at 160 °C for 24 h. (A) Yields of char, liquid and gas and (B) Liquid product distribution.

Effect of GVL/H$_2$O 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/H$_2$O (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 hemicellulose[56], or added externally as in our case.

Lignin extraction with GVL/H$_2$O is a complex process. Lignin solubility in GVL/H$_2$O 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 dissolution[55-57] 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/H$_2$O (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/H$_2$O (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/H$_2$O ratios of 4/1 and 2/1 (w/w) presented no significant differences on the liquid yield. However, the use of initial

1/1 GVL/H_2O (w/w) gave a much lower liquid yield. Considering that initial GVL/H_2O ratio of 4/1 (w/w) provides high lignin extraction yield (Table S2) while affords high liquid yield in pyrolysis (Figure 2A), this initial ratio seems to be the optimal among those used.

Table 1 compares the liquid yields of the pyrolysis of different lignins under distinct conditions. The liquid yield of GVL-lignin was higher than that of commercial lignin. GVL-lignin pyrolysis results were compared to others previously reported by Custodis *et al.*[44], which studied similar fast pyrolysis of lignins separated by dioxane-, Klason-, and organsolv-methods. Both softwood and hardwood lignins extracted by the organosolv method (using 60 vol% ethanol with 5 wt% sulfuric acid)[44] produced lower liquid yields than those obtained from lignin extracted by GVL/H_2O. Furthermore, the liquid yield of GVL-lignin was compared to that of dioxane softwood and hardwood lignin as well as Klason softwood and hardwood lignins. The liquid yield followed the order of Klason hardwood lignin (68 wt%) > dioxane softwood lignin (66 wt%) > dioxane hardwood lignin (65 wt%) > GVL softwood lignin (61 wt%) > Klason softwood lignin (56 wt%) > organolsolv softwood lignin (55 wt%) > organolsolv hardwood lignin (53 wt%) > commercial lignin (40 wt%). For other fast pyrolysis results shown in Table 1, the liquid yield is affected both by the type of lignin and by the conditions of the process.[61-66]

Figure 2B illustrates the pyrolysis liquid product distribution of GVL-lignin extracted with various GVL/H_2O ratios. The two major classes of compounds in the liquid fractions were phenols and alkoxy phenols. All conditions showed similar amounts of phenols and alkoxy phenols in the corresponding pyrolysis liquid fraction of about 60% and 25%, respectively. There was no significant difference in the content of phenols and alkoxy phenols compounds in the pyrolysis liquid product of lignin, because the structures of GVL-lignin extracted by using different initial GVL/H_2O ratios of 4/1, 2/1 and 1/1 (w/w) were very similar, as confirmed by 2D HSQC NMR.

Figure 3 shows the 2D HSQC NMR spectra of GVL-lignin (detailed assignments and one ^{1}H NMR spectrum are presented in Table S3, Table S4 and Figure S1). These were classified into two main cross-signal regions, consisting of a side-chain (δ_H/δ_C 2.5-5.8/50-90 ppm) region and an aromatic/unsaturated (δ_H/δ_C 6.0-8.0/100-160 ppm) region.[67-69]. Furthermore, Figure 4 exhibits the main classical substructures of GVL-lignin. In the side-chain region of all GVL-lignins, the C-H correlation in methoxy groups showed a strong cross-signal at δ_H/δ_C 3.73/55.6 ppm. The two main substructures

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.
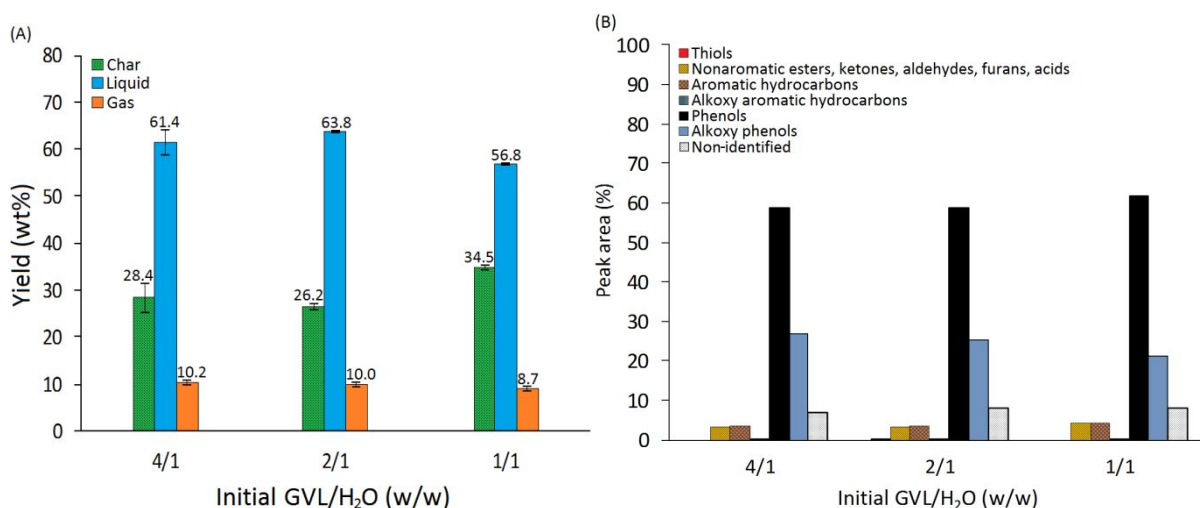

Figure 2 Effect of extracted lignin with various initial GVL/H_2O ratios (with 0.075 M sulfuric acid at 160 °C for 24 h) on pyrolysis. (A) Yields of char, liquid and gas and (B) Liquid product distribution.

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 et al.[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	Ma et al.[42]
Alkali lignin	650	39.5	Ma et al.[45] Ma et al.[47] Ma et al.[48]
Alcell lignin	600	17.2	Jiang et al.[61]
Asian lignin	600	15.5	
Lignin (byproduct of fermenting)	500-550	34	Trinh et al.[62]
Pyrolytic lignin precipitated from water	600	40	Zhao et al.[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 et al.[64]
Alkali lignin B	650	ca. 46.7	
Organosolv lignin	600	ca. 22.0	Patwardhan et al.[65] Fan et al.[66]
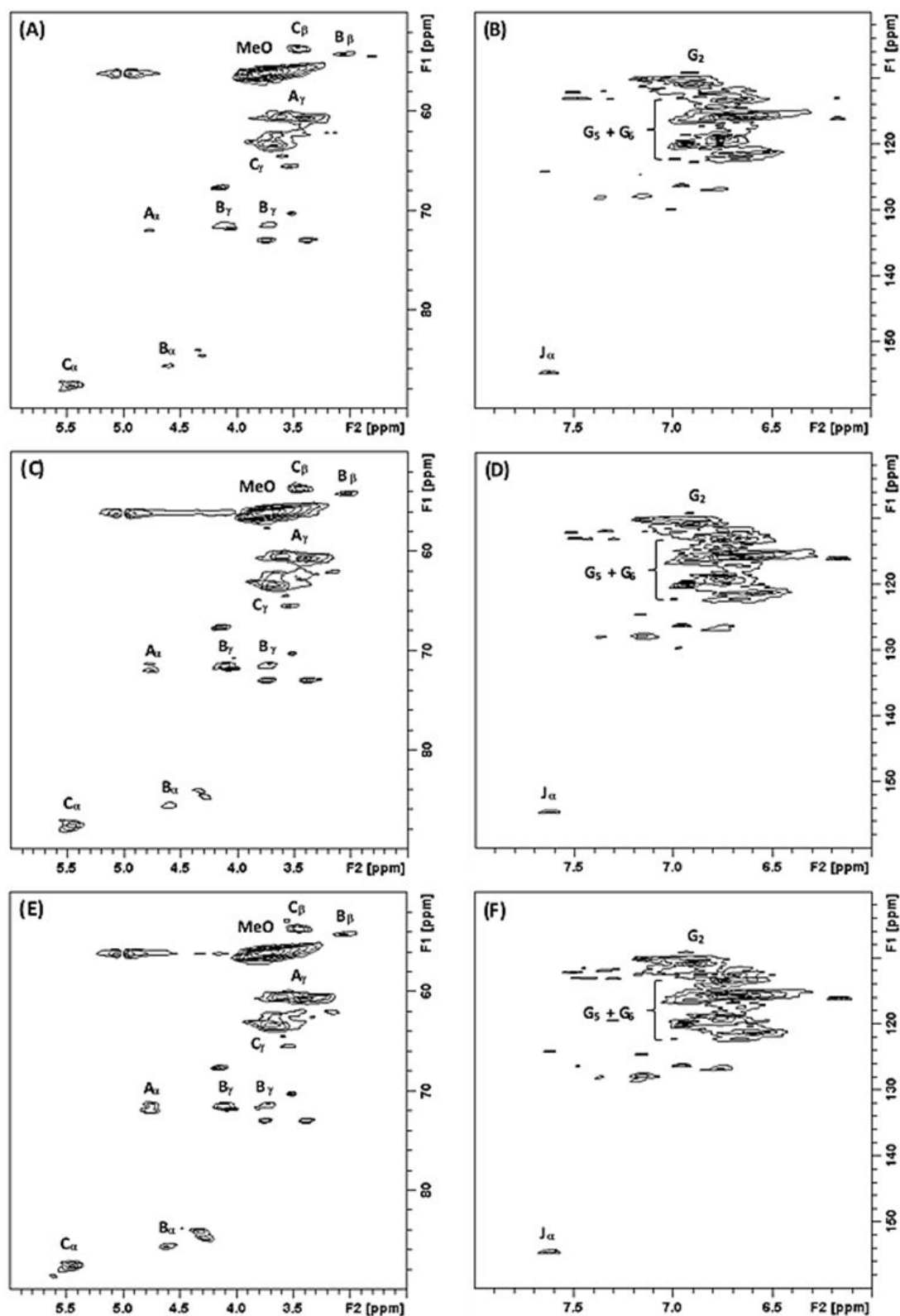
Figure 3 Side-chain (δ_H/δ_C 2.5-5.8/50-90) and aromatic/unsaturated (δ_H/δ_C 6.0-8.0/100-160) regions in the 2D HSQC NMR spectra of extracted lignin with mixtures of various initial GVL/H_2O ratios and 0.075 M sulfuric acid at 160 °C for 24 h. (A, B) initial GVL/H_2O of 4/1 (w/w); (C, D) initial GVL/H_2O of 2/1 (w/w) and (E, F) initial GVL/H_2O of 1/1 (w/w).
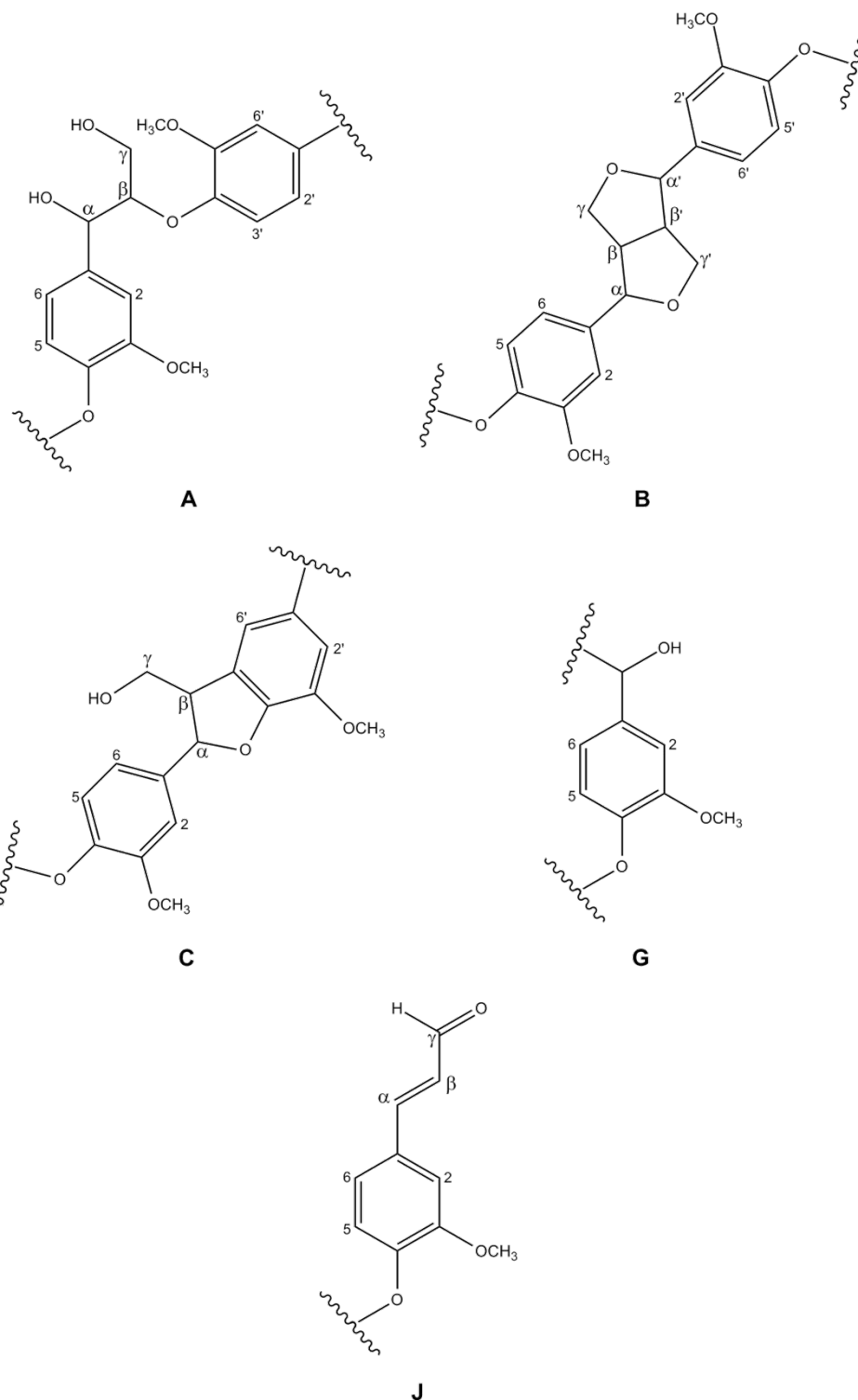
**Figure 4** Main classical substructures, involving different side-chain linkages and aromatic units, identified by 2D HSQC NMR in extracted lignin from pine wood: (A) β-O-4' substructure; (B) resinol substructure, formed by β-β' coupling and α-O-γ' and γ-O-α' bonding during quinone methide rearomatization; (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/H_2O 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-CH_3 bond located in the substructures of GVL-lignin[70], 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_γ-H_γ in β-O-4' substructures (A) and C_γ-H_γ 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 G_2, G_5 and G_6 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 C_2-H_2 correlation in guaiacyl units since methoxy groups in G substructure were the closest to the C_2-H_2 position, resulting in the disappearance of the G_2 cross-signal. In contrast, G_5 and G_6 cross-signals still weakly emerged. The dissociation of methoxy groups lightly affected the C_5-H_5 and C_6-H_6 correlations compared to C_2-H_2 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]
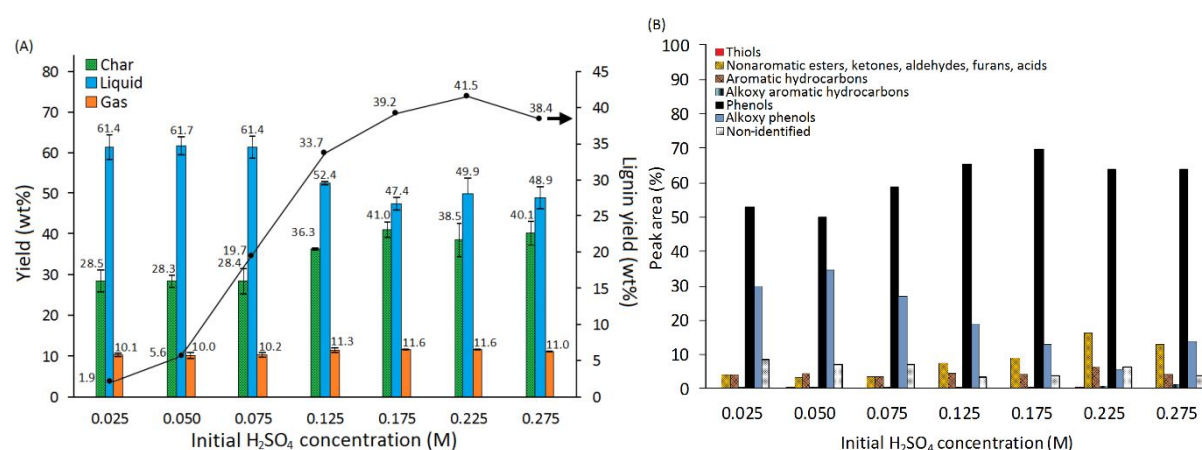
Figure 5 Effect of extracted lignin with various initial sulfuric acid concentrations [initial GVL/H_2O of 4/1 (w/w), at 160 °C for 24 h] on pyrolysis and extracted lignin yields. (A) Lignin extraction yield (curve) and pyrolysis yields of char, liquid and gas (columns) and (B) Liquid product distribution.

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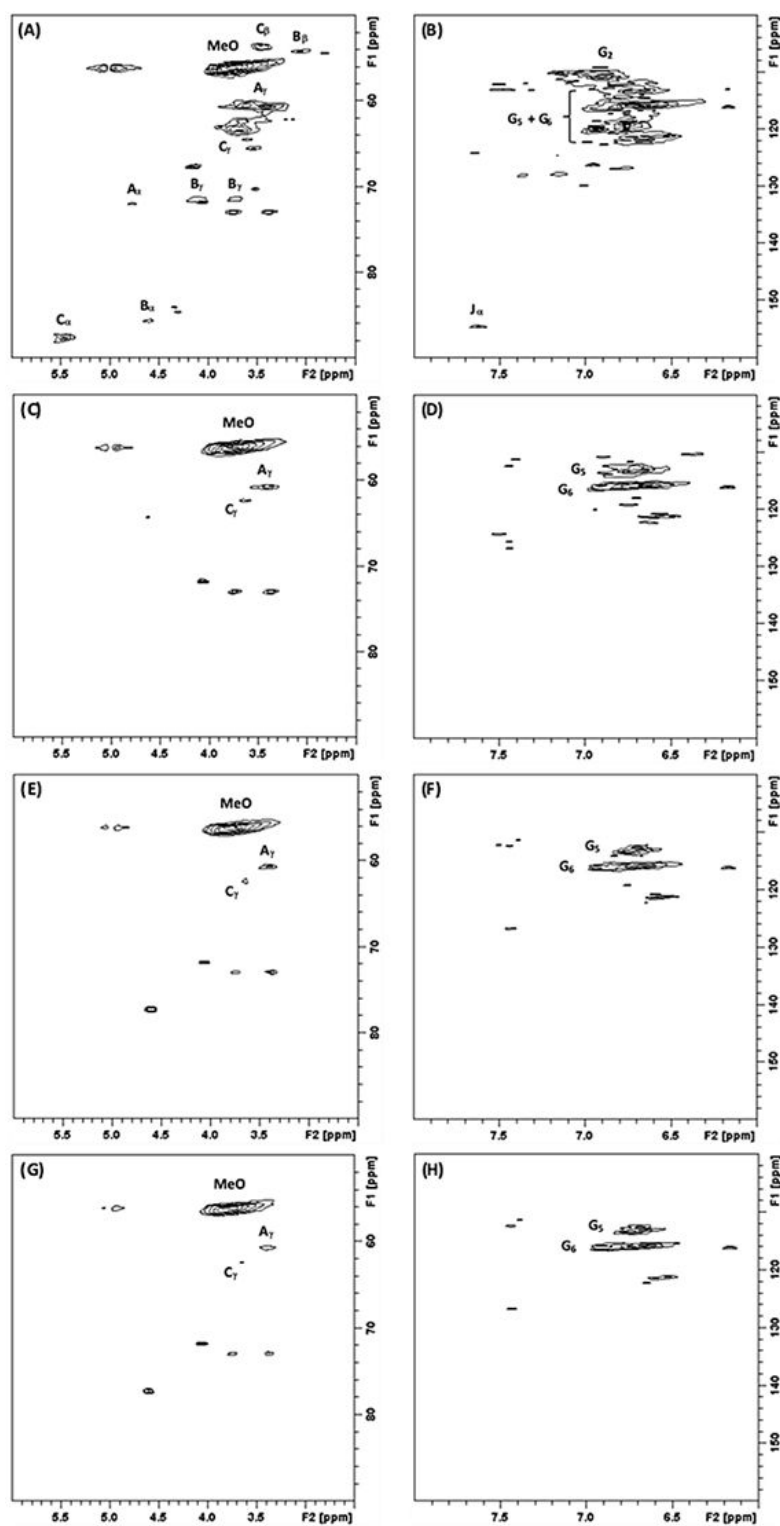
Figure 6 Side-chain (δ_H/δ_C 2.5-5.8/50-90) and aromatic/unsaturated (δ_H/δ_C 6.0-8.0/100-160) regions in the 2D HSQC NMR spectra of extracted lignin with GVL/H_2O [initial GVL/H_2O of 4/1 (w/w)] and various sulfuric acid concentrations at 160 °C for 24 h. (A, B) initial 0.075 M sulfuric acid; (C, D) initial 0.125 M sulfuric acid; (E, F) initial 0.175 M sulfuric acid and (G, H) initial 0.225 M sulfuric acid.

FTIR analyses (spectra in Figure S2 and interpretation in Table S5) were carried out to identify the functional groups existing in the structures of GVL-lignin extracted with various sulfuric acid concentrations. The characteristic bands presented in all spectra correspond to the ones reported in previous works.[70,72-76] The characteristic bands at 2839 and 1210 cm^{-1}, attributed to the C-H stretching in -OCH$_3$ and the C-O stretching, respectively, can be used to analyze the structural changes of the GVL-lignins. The bands at 1595 cm^{-1}, assigned to aromatic skeleton vibrations and independent of sulfuric acid concentration, were used to normalize those two peaks. The ratio of absorption value at 2849 cm^{-1} to 1595 cm^{-1} and the ratio of absorption value at 1210 cm^{-1} to 1595 cm^{-1} were identified as representative of -OCH$_3$ and C-O, respectively.[70] Table 2 shows the relative absorbance values at different sulfuric acid concentrations. For higher sulfuric acid concentrations, there is a decrease in the values related to -OCH$_3$ groups while the corresponding values for C-O increase. These results correspond to the 2D HSQC NMR involving the loss of methoxy groups while using high sulfuric acid concentration during GVL-lignin extraction and previous reports of Nikafshar and co-workers that found that the intensity of the signal at 1210 cm^{-1} increases after demethylation reactions.[76] Moreover, the functional groups of GVL-lignin were confirmed by ^{1}H NMR (Figure S1). The ^{1}H NMR results showed that GVL-lignin consists of six major functional groups, in accordance with other lignins[77]: formyl (10.08-9.47 ppm), phenolic (9.28-8.02 ppm), aromatic and vinyl (8.06-6.11 ppm), aliphatic CH-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 ppm).

Structural changes occur in lignin due to mild acidic conditions during extraction.[78] This is noted from the signals related to the side-chains of lignin obtained with different sulfuric acid concentrations (Figure 6) in accordance with loss of β-O-4 structures, producing more condensed structures. TGA analysis and its first derivative representation (DTG) confirm these changes in lignins structures. TGA and DTG results (Figure S3 and Table S6) show one main event centered around 400 °C associated with lignin decomposition. The temperature of maximum devolatilization rate increases for higher concentration of sulfuric acid used in the extraction process. This trend suggests that more stable lignin structures form at higher sulfuric acid concentrations due to greater extent of condensation and the presence of strong C-C bonds.[57,79,80] In addition, there is an important decrease in the maximum

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.

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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).

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Abstract Graphic
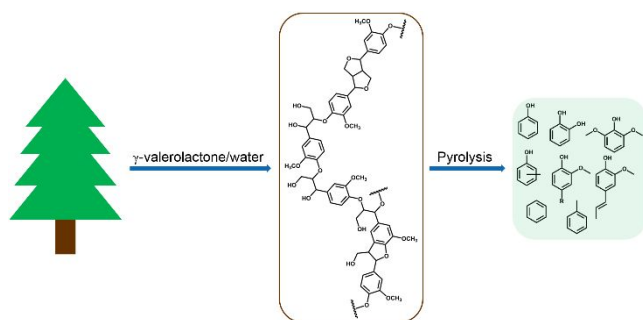
Synopsis

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