ACS Sustainable Chemistry & Engineering

Research Article

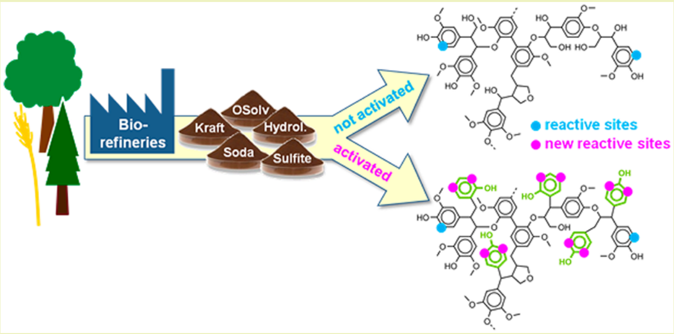
pubs.acs.org/journal/ascecg

Structure−Function Relationships in the Phenolation of Lignins from Different Sources

Jacob Podschun,[†] Alexander Stücker,[‡] Bodo Saake,[†] and Ralph Lehnen*,[‡]

[†]Department of Wood Science and Chemical Wood Technology, University of Hamburg, Leuschnerstraße 91b, 21031 Hamburg, Germany

[‡]Thünen Institute of Wood Research, Leuschnerstraße 91b, 21031 Hamburg, Germany



ABSTRACT: In recent years, significant amounts of various lignins became commercially available. Their technical utilization for thermosets such as phenol formaldehyde resins is widely discussed as an added value. However, the comparably low number of reactive sites is still limiting utilization in higher proportions. To overcome this obstacle, lignins can be activated by phenolation prior to resin synthesis. In this study, the applicability and outcome of phenolation was studied for a set of organosolv lignins from hardwood, softwood, and annual plants and was compared to their counterparts from commercial processes, i.e., kraft, sulfite, soda, and hydrolysis lignin. Thus, structural properties of various raw lignins could be linked to the increase of reactive sites upon phenolation. Large differences were found and could mainly be attributed to the number of aliphatic hydroxyl groups in the raw lignins. Highest activation was achieved for hardwood organosolv and softwood sulfite lignins. With ion-exchanged sulfite lignin in H^+ form the phenolation could even be performed autocatalyzed to a high extent. In contrast, soda grass and softwood kraft lignin showed weak potential for activation. Additionally, the influence of ash and sulfur content, and the changes in molecular weight were elucidated.

KEYWORDS: *Organosolv lignins, Technical lignins, Phenolation, Thermosetting resins, ^{31}P NMR, GPC, Elemental analysis*

■ INTRODUCTION

Despite being one of the most abundant natural polymers, lignin's economic market share is still small. Driven by environmental and technological shortcomings, lignin is gaining increasing attention as a valuable sustainable resource. From the environmental perspective, increased atmospheric CO_2 concentration, its impact on world's climate and the necessity for more severe methods to produce raw oil are the main driving forces for a change in raw materials supply. Simultaneously, technological developments favor this process. On the one hand, improved process efficiency in pulping companies led to a serious availability of lignin (LignoBoost, Sequential Liquid Lignin Recovery and Purification (SLRP), LignoForce).[1−4] Here, the amount of lignin, which might be recovered, could be estimated to be around 50 Mt per year (based on 45% pulp yield and 20% lignin content in biomass).[5] Some key and future producers are Borregaard, Tembec and Aditya Birla Group (lignosulfonate), MeadWestvaco, Domtar/UPM, Stora Enso and Suzano (kraft lignin), as well as ALM India and GreenValue (soda lignin).[6] On the other hand, in recent years, various cellulosic ethanol production facilities started generating ethanol from lignocellulosics on a commercial scale. It is anticipated that at least some producers will follow those who already started recovering lignin since technologies are currently advancing.[7,8] Due to their high ethanol capacity, this industry will additionally generate considerable amounts of lignin. Their potential lignin capacity might be calculated based on the ethanol capacity. In industrial processes, about 200 L ethanol can be generated per ton of biomass.[7] Assuming an average lignin content in biomass of 20%, the lignin capacity in kilotons equals the ethanol capacity in megaliters (Table 1).[7,9−11]

A detailed overview on lignin availability is also given in the 2014 Deep Research Report on global lignin and lignin-based products industry.[12] The actual option to use lignin as fuel, however, might not be viable for long, since lignin's potential

Received: July 18, 2015
Revised: August 24, 2015
Published: August 27, 2015

DOI: 10.1021/acssuschemeng.5b00705
ACS Sustainable Chem. Eng. 2015, 3, 2526−2532

Table 1. Lignocellulosic Biorefineries with Production Capacity of Ethanol >5 ML annually and (potentially) Lignin (based on References 7 and 9−11)

company	location	feedstock	annual capacity EtOH [ML]/lignin [kt][a]	commercial start-up
Dong Energy/Inbicon	Kalundborg, Denmark	wheat straw	6/13	2010
Shengquan	China	corn cob	23	2012
Longlive	Yucheng, China	corn cob	50	2012
CTC	Piracicaba, Brazil	bagasse	40	2012
Beta Renewables	Crescentino, Italy	energy crops, agricultural residue	75	2013
Mascoma	Rome, NY, US	wood, switchgrass	76	2013
Fiberight	Blairstown, IA, US	municipal solid waste	23	2013
INEOS Bio	Vero Beach, FL, US	vegetative, municipal, wood waste	30	2013
Abengoa	Hugoton, KS, US	corn stover, wheat straw, switchgrass	95	2014
POET-DSM	Emmetsburg, IA, US	corn cob, crop residue	95	2014
GranBio	Sao Miguel, Brazil	straw, sugar cane bagasse	82	2014
COFCO-Sinopec	China	N/A	57	2014
Iogen/Raízen	São Paulo, Brasil	straw, sugar cane bagasse	40	2014
Quad County	Galva, IL, US	corn kernel fiber	8	2014
DuPont	Nevada, IA, US	corn stover	114	2014
Beta Renewables	Clinton, NC, US	energy grass	75	2016
M&G Chemicals	Fuyang, China	wheat straw, corn stover	230/610	2016
Canergy	CA, US	sugar cane	95	2016
Stora Enso/Verida	Raceland, LA, US	sugar cane bagasse	N/A	2017
Biocom	Malanje, Angola	sugar cane	28	2019
Renmatix/BASF	N/A	N/A	N/A	N/A
ZeaChem	Boardman, OR, US	hybrid poplar, agricultural waste	95	N/A

[a] Potential lignin capacity was calculated from ethanol capacity. If not otherwise mentioned, numbers are equal.

value as a feedstock for material application will superpower the energetic value.[13] The vast variety of lignins due to differences in plant resources and pulping processes is expected to further increase since continuous advances are made in both areas.[14,15] However, the majority of lignins have in common that their aromatic reactivity is insufficient regarding application as building block in high proportions in polymers such as phenolic resins or other thermosets. To overcome this obstacle, multiple strategies are discussed to activate lignin.[16−18] A preceding activation of lignin by phenolation (Figure 1) is reported to enhance the performance of lignin and have broad potential applications ranging from membranes to surfactants to carbon fibers.[19−25] Various applications were studied by Funaoka[19] including recyclable composites, adsorbents and hydrogels by using phenol and its derivatives. Beech organosolv lignin was phenolated by Podschun et al.[20] toward application in thermosets such as polybenzoxazines, epoxy resins and phenolic resins since high numbers of both free phenolic para/ortho sites and phenolic hydroxyl groups were achieved. The effect of phenolation of Alcell lignin in phenol formaldehyde resins for particleboards was studied by Çetin and Özmen.[21,22] They found that a higher fraction (up to 30%) of lignin could be added to resins upon phenolation giving properties comparable to lignin-free resins. It was also demonstrated that steam-explosion birch lignin yielded improved adhesive properties due to phenolation, especially wet tensile strength, which was correlated to improved cross-linking.[23] Alonso et al.[24] investigated phenolation of lignosulfonate in view of application in novolac resins and optimized reaction parameters. Improved surfactant properties (i.e., Zeta potential and charge density) of LignoBoost spruce lignin were reported when phenolation was performed prior to Mannich reaction.[25]

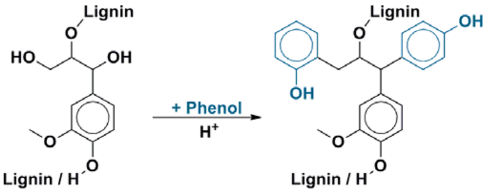


Figure 1. Phenolation of lignin.

The degree of phenolation strongly varied in literature. Ono and Sudo[23] found that their steam explosion birch lignin could be phenolated up to 1.3 phenols per C_9-unit, whereas 0.3 per C_9 was obtained for kraft lignin. In contrast, Funaoka[19] described that a lower degree of phenolation was obtained for softwood (0.7 per C_9) as compared to hardwood lignin (0.9 per C_9). The synthesis of phenolated lignins under alkaline conditions was also reported.[26] However, it was not clearly proven if the phenol residues were covalently bound or if residual phenol was physically attached to lignin. In general, structure−function relationships were not reported. Thus, the influence of the significantly varying properties of different lignins due to type and source still remains unknown. This study presents a comparison of the extent of phenolation for lignins from hardwood, softwood and annual plants, and different pulping methods such as organosolv, kraft, soda, sulfite, and hydrolysis using consistent reaction conditions. The different reactivities were linked to raw lignin properties to deduce structure−function correlations. As reactivity enhancement was achieved for all lignins, the method might serve as a universal route to provide an improved feedstock for lignin-based materials.

■ EXPERIMENTAL SECTION

Materials. Organosolv lignins were produced at the Thünen Institute of Wood Research (Hamburg, Germany) by pulping of beech wood, poplar wood, pine wood and wheat straw. Pulping was performed using ethanol:water (1:1, v/v) with a liquor-biomass-ratio

Table 2. Pulping Conditions for the Production of Organosolv Lignins

feedstock	time [min]	temperature [°C]	H_2SO_4 [% of dry matter]
beech wood	90	170	0.5
poplar wood	90	170	0.7
pine wood	90	170	1.0
wheat straw	120	180	2.0

of 4:1 (w/w). Additional pulping parameters are given in Table 2. Lignins were precipitated in the 2-fold amount of H_2O, filtered and vacuum-dried over P_2O_5.[27]

The industrial lignins were obtained from Stora Enso (spruce/pine kraft, "softwood kraft 1"), Borregaard Lignotech (Curan 100DD, "softwood kraft 2"), Suzano (2 batches of eucalyptus kraft "hardwood kraft 1 + 2"), Tembec (pine sulfite-NH_4), and from an enzymatic hydrolysis pilot plant for ethanol production (wheat straw, "hydrolysis 1"). Since the hydrolysis lignin contained some ashes and residual carbohydrates, it was additionally purified by alkaline extraction at the VTT, Espoo, Finland ("hydrolysis 2"). Soda lignin was purchased from GreenValue (wheat straw). Tembec sulfite lignin was additionally transferred to the acid form by passing an aqueous solution (50 g L^{-1}) over a column packed with 600 g of preacidified Amberlite IR 120 cation exchange resin.

For ash removal, kraft lignins were dissolved in the 10-fold amount of acetone−water (8:2, v/v) and the solution was precipitated into the 4-fold amount of acidified water (pH 1 with H_2SO_4). The precipitate was collected on a PES membrane (pore size 0.45 μm), washed with water until neutral and vacuum-dried over P_2O_5.

For the reduction of sulfur content in kraft lignin, 2 g softwood kraft lignin was dissolved in 50 mL of 1 M NaOH and treated for 24 h with 200 mg (5.3 mmol) of $NaBH_4$ under nitrogen at RT. Precipitation and filtration was performed as mentioned above.

Technical grade ethanol and acetone, phenol (≥99.5%, Chem-Solute), sulfuric acid (≥95%, Fisher Scientific), and DMSO-d_6 (99.8%, Deutero GmbH) were used as received.

Phenolation of Lignins. Phenolation of lignins was performed by dissolving 1 g of lignin in 2 g (21 mmol) phenol. The homogeneous mixture was treated with 108 μL (2 mmol) conc. H_2SO_4 at 110 °C for 20 min. The reaction mixture was quenched and dissolved with 25 mL of acetone−H_2O (9:1, v/v) and precipitated into the 4-fold amount of dilute H_2SO_4 (pH 1). The precipitate was collected on a PES membrane (pore size 0.45 μm), washed with water until neutral, and vacuum-dried over P_2O_5. All lignins had excellent solubility in phenol with the exception of raw NH_4-sulfite lignin. Here, 0.8 mL of water was required to obtain a homogeneous mixture. Further adaptations were necessary including a reduction of reaction temperature to 90 °C, quenching with water, precipitation, and washing with 2-propanol and filtration over regenerated cellulose (pore size 0.45 μm).

Characterization. ^{31}P NMR spectroscopy was recorded on a Varian Mercury and a Bruker Avance III HD 400 MHz spectrometer following a published procedure.[28] Phosphitylation was performed with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane and cholesterol or endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide was used as IS.[28,29] Acquisition parameters included: 25 °C, 11 990 Hz spectral window (23 000 Hz for thiol detection), 256 scans, acquisition time 1.0 s, and a 20 s delay between pulses. Processing was performed with ACD/Labs NMR processor (version 12, lb = 3 Hz, phase and baseline correction). Signal intensities were corrected for ash and sugar content. For the raw lignosulfonate, DMF/DMF-d_7/pyridine (450/100/100 μL) was used as solvent, and acquisition time was set to 4.0 s.

Methoxy group (OMe) content was determined following a procedure of Vieböck and Schwappach.[30] The mean of three measurements was calculated after calibration with vanillic acid.

Elemental analysis of the dry lignin samples was accomplished using an Elementar vario EL cube. The elements C, H, N, and S were measured in duplicate. The remaining percentage was associated with oxygen after correcting for ash content.

Gel permeation chromatography (GPC) was conducted using dimethyl sulfoxide with 0.1% LiBr as eluent. A set of three PolarGel-M columns (Agilent) was used (two 7.5 mm × 300 mm columns and a 7.5 mm × 50 mm guard column). The flow rate was 0.5 mL min^{-1} at 60 °C. Glucose and polyethylene glycol standards (180−82 250 g mol^{-1}, Agilent) were used for calibration using an RI detector (RI-71, Shodex). Samples were dissolved (c = 1 mg mL^{-1}) and shaken in the eluent for 24 h at room temperature. Sample detection was performed using an UV detector (UV-2077, Jasco) at 280 nm, and phenol red was used to match detectors. The data was recorded and evaluated using WinGPC Unichrom V8.10 software from polymer standards service.

Carbohydrate and lignin contents were analyzed by a two-stage acid hydrolysis as described earlier.[31] In brief, 200 mg lignin was treated with 2 mL of H_2SO_4 (72%) at 30 °C for 1 h. After dilution to a concentration of 4% H_2SO_4 the samples were autoclaved at 120 °C for 40 min. Precipitations in the cold samples were removed over glass frits (P4, Schott). The content of acid-soluble lignin was determined spectrophotometrically at 205 nm according to a TAPPI standard.[32] The hydrolyzed carbohydrates were analyzed by borate-complex anion-exchange chromatography with spectrophotometric detection at 560 nm upon derivatization.

■ RESULTS AND DISCUSSION

Comparison of Structural Features of Organosolv Lignins. Prior to chemical modification, structural features of the four organosolv lignins prepared were compared (Table 3). The methoxy contents (OMe) were in line with the lignin source thus lowest for wheat and highest for hardwood lignins. It was found that the higher the molecular weights and dispersities, the lower was the amount of aromatic hydroxyl groups, which could be related to cleavage of ethers in the biopolymers. The number of aliphatic hydroxyl groups however decreased with increasing acid concentration during pulping showing the dependence on pulping severity as found earlier.[33] The increased dehydration of pine and wheat lignin could also be found in reduced oxygen and increased carbon contents.[34] Variations in acid-soluble lignin and carbohydrate concentration were as described for other organosolv lignins, in which sugar contents were related to sugars from residual organosolv liquor adhering to lignin, and lignin carbohydrate bonds.[33]

Degree of Phenolation of Different Lignins. The approach to increase the number of reactive sites was studied for three different lignin sources: hardwood, softwood and annual plants. In each category, an organosolv lignin was compared to the typical technical lignins. The results in

Table 3. Structural Characteristics of Organosolv Lignins from Different Sources[a]

feedstock	OMe [%]	$\sum$ OH_{arom} [mmol g^{-1}]	OH_{aliph} [mmol g^{-1}]	M_w [g mol^{-1}]	D	C/H/O/N [%]	ASL[b] [%]	$\sum$ sugars [%]
beech wood	21.2	2.0	4.1	4100	4.1	62.0/6.2/31.5/0.3	2.3	4.5
poplar wood	17.0	1.3	3.5	6300	4.6	62.3/6.1/30.6/1.0	2.0	5.2
pine wood	12.6	2.6	2.0	3200	2.9	68.1/6.4/25.2/0.2	1.9	0.7
wheat straw	11.3	1.5	1.9	4300	4.6	64.4/6.3/27.1/2.1	3.0	3.2

[a] Ash and sulfur contents were negligible for all samples except for wheat straw lignin, which contained 0.6% ash. [b] Acid-soluble lignin.

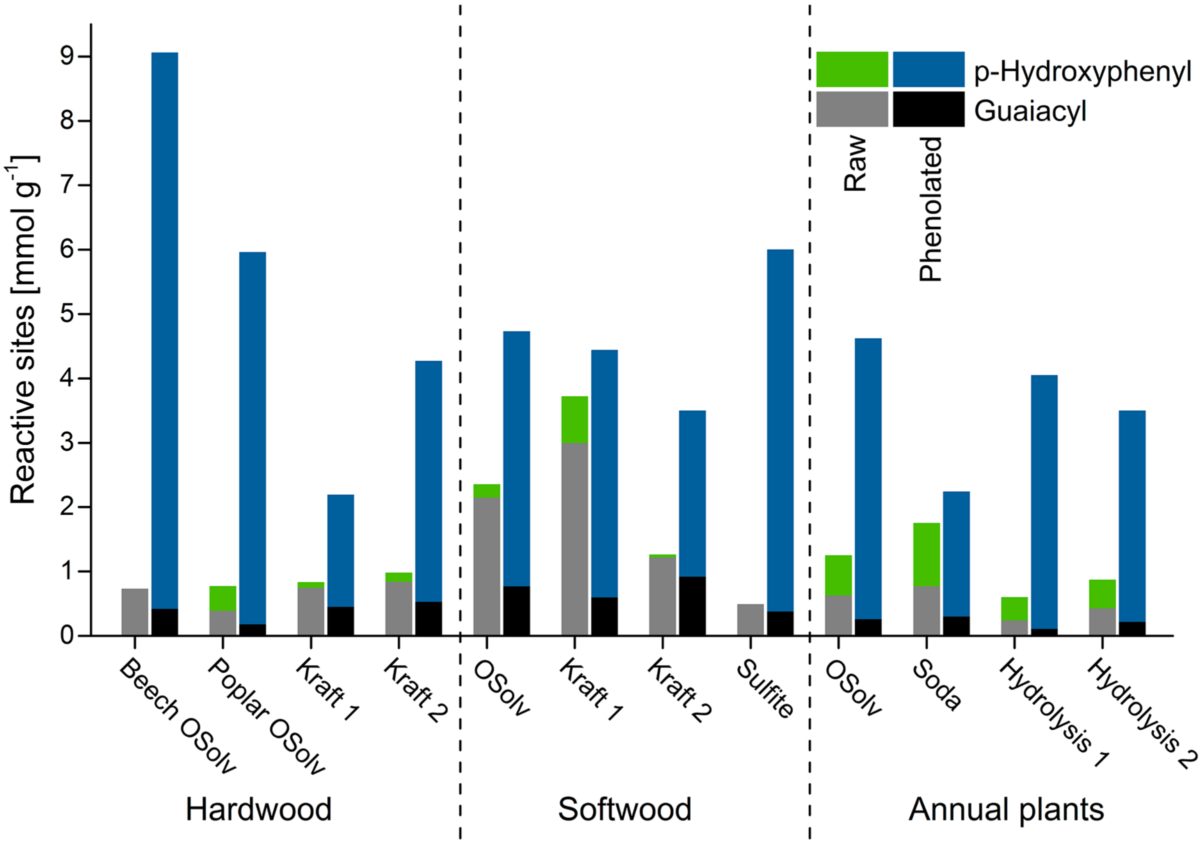


Figure 2. Comparison of number of reactive sites of raw and phenolated lignins based on ^{31}P NMR measurement.

Figure 2 show the number of reactive sites of the raw lignins in comparison to the phenolated lignin products. The data was deduced from ^{31}P NMR measurements of the hydroxyl groups counting one reactive site for guaiacyl OH and two for *p*-hydroxyphenyl OH with regard to ortho/para-directing substitution due to the aromatic hydroxyl group. The good correlation between the number of hydroxyl groups from ^{31}P NMR and the number of aromatic protons from ^{1}H NMR was already shown in a previous paper.[20] Thus, the activation by phenolation resulted for all lignins in an increased number of free aromatic ortho and para reactive sites. Among all organosolv lignins, beech wood lignin showed the highest degree of phenolation with 9.0 mmol reactive sites per gram. Thus, the number was significantly increased by the factor of 12.9 compared to the raw lignin. The achieved number was 45% of the number of reactive sites in bisphenol F, a highly reactive constituent of PF resin having 20.0 mmol g^{-1} reactive sites. Compared to the other lignins, sulfite, poplar organosolv and hydrolysis lignin no. 1 showed the highest increase factors with 12.2, 7.7, and 6.8, respectively. Softwood kraft lignin no. 1 was less prone for activation by phenolation (increase factor 1.2). This relatively small increase could be attributed to the high content of G and H units in the raw kraft lignin, which decreased for all lignins probably due to acid-catalyzed condensation reactions during phenolation.

By comparison, Mansouri et al.[34] and Gosselink et al.[35] evaluated the reactivity of multiple lignins in view of their application in phenol−formaldehyde resins. The reactive sites of the lignins studied ranged from 0.81 to 2.27 mmol g^{-1} with highest values for softwood kraft lignin, which could be found for the raw lignins in our study as well. Hence, it can be assumed that raw softwood kraft lignin no. 1 is most suitable for application in phenol formaldehyde resin formulations since lignins with high number of reactive sites performed best in wood failure test of LPF-bonded plywood.[35] In our study (Figure 2), all of the lignins activated by phenolation exceeded the reactivity found for technical lignins reported in the literature.[34,35] After activation, the degree of phenolation was reported per C_9-unit and in millimoles per gram[20] and could approximately be converted using a C_9-mass of 200 g mol^{-1}. Thus, the degree of phenolation reported by Ono and Sudo[23] can be given for steam explosion lignin as 4.0 mmol g^{-1} and for kraft lignin as 1.3 mmol g^{-1}. The values reported by Funaoka et al.[19] can be approximated to 2.6 mmol g^{-1} for softwood and 3.2 mmol g^{-1} for hardwood lignin. However, the resulting trends were not consistent with our study (Figure 2). Thus, structure−function relationships were investigated to clarify how structural differences of the lignins influence derivatization.

Factors Affecting the Degree of Phenolation. To elucidate the factors affecting the reactivity, the number of aliphatic hydroxyl groups of the raw lignins was compared to the number of *p*-hydroxyphenyl aromatic hydroxyl groups after phenolation. The results illustrated in Figure 3 showed that for both functional groups similar values were measured. The data of the variety of lignins can be summarized by a linear fit, which showed a slope close to one. Deviations from the linear correlation might be attributed to *p*-hydroxyphenyl units that were already present in the raw lignin and could not be differentiated from newly introduced *p*-hydroxyphenyl unit equivalents after phenolation. Furthermore, it should be noted that the ^{31}P NMR results are given per gram, thus higher values for phenol−OH are realistic when correlated to a lignin-C_9 unit. Additionally, new aliphatic reactive sites are generated upon cleavage of e.g. aromatic aliphatic ethers and C_β−C_γ

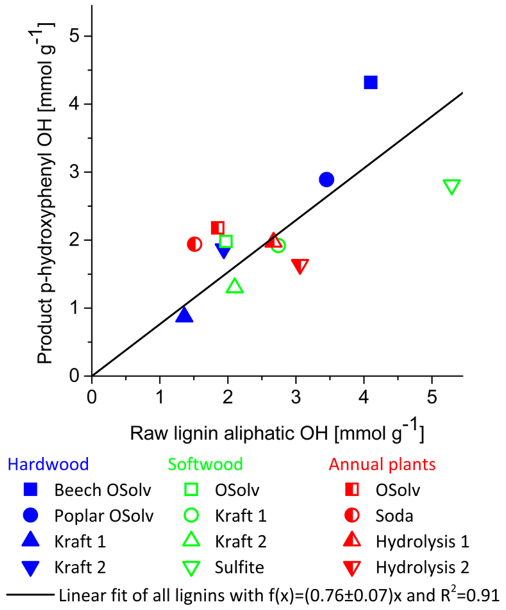


Figure 3. Correlation of *p*-hydroxyphenyl OH in phenolated lignins with aliphatic OH in raw lignins.

bonds as found in our previous study.[20] It can however be assumed that the large differences in the degree of phenolation shown in Figure 2 were mainly related to variations of the amount of aliphatic hydroxyl groups in the raw lignins, which in turn depends on the intensity of pulping. Thus, the major mechanism of lignin phenolation was in accordance with the results found for model compounds.[36,37]

Since phenolation does not exclusively originate from the substitution of aliphatic hydroxyl groups but also from phenolysis,[20] the correlation of weight-average molecular weight of raw and phenolated lignin was linked to the degree of phenolation (Figure 4). It was found that the molecular weight of the phenolated product decreased with increasing degree of phenolation. Furthermore, the molecular weight of the phenolated product was reduced more extensively when the raw lignin had a higher molecular weight. This effect could be related to an increased concentration of hydrolyzable bonds (e.g., aliphatic-aromatic ethers like β-O-4) in high molecular weight lignins, as shown by Koda et al.[38] The majority of lignins showed a decreased dispersity as found earlier.[20,24] Furthermore, the weight-average molecular weights of phenolated lignins were in a narrower range as compared to the raw lignins. Hardwood kraft lignin no. 1 was the only exception since the molecular weight increased, which might partially be attributed to less pronounced phenolysis, thus M_W increased due to phenolation. Overall, an increased suitability for application in thermosetting resin can be expected, which might additionally be favored by enhanced solubility characteristics.[20]

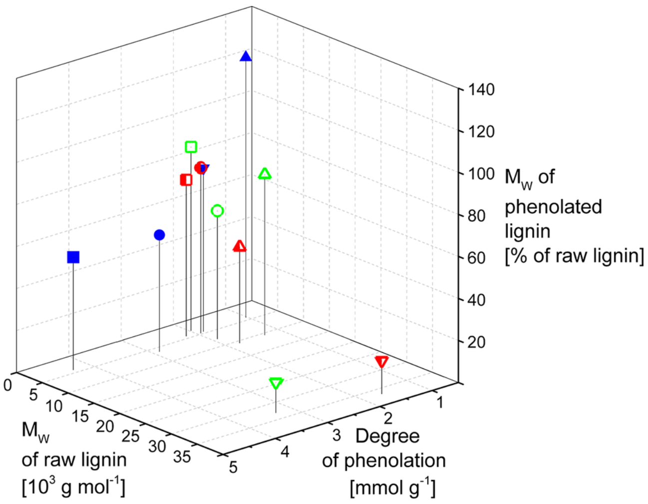


Figure 4. Relation of weight-average molecular weight of raw lignins, degree of phenolation, and decrease of weight-average molecular weight during phenolation (legend as in Figure 3).

Beside aliphatic hydroxyl groups and molecular weight, the influences of two major differences between kraft and organosolv lignin were investigated, namely ash and sulfur content (Figure 5).

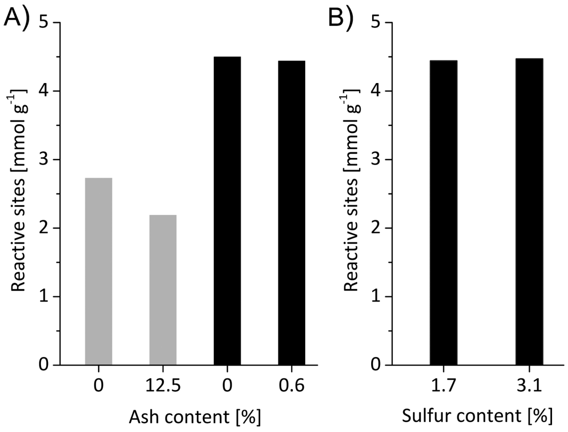


Figure 5. Effect of ash (A) and sulfur content (B) of raw lignins on the degree of phenolation for hardwood kraft no. 2 (gray) and softwood kraft no. 1 (black).

For hardwood kraft lignin, it was found that the large reduction in the ash content resulted in an increased degree of phenolation. In contrast, softwood kraft lignin no. 1 already showed low ash content, thus purification had a negligible effect. It can be assumed that the alkaline ash present in the samples from pulping inhibited the sulfuric acid catalyst during phenolation. The large decrease in sulfur content from 3.1% to 1.7% by $NaBH_4$ reduction did not result in a significant change in the degree of phenolation. In contrast to the correlation of aliphatic OH groups and degree of phenolation, it was found that SH groups were not replaced by phenol since the signals in the range of 200−225 ppm in the ^{31}P NMR spectrum remained unchanged (Figure 6).[39] By comparison of raw and phenolated lignin, the elemental analysis revealed that the sulfur content was slightly decreased from 3.1% to 2.7%. This result was most certainly related to a mass increase upon phenolation.

Phenolation of Sulfite Lignin. Initially, the sulfite lignin showed the lowest degree of phenolation (Figure 7), which could be related to the low solubility of ammonium lignosulfonate in phenol. By ion exchange to the proton form, the sulfite lignin showed excellent solubility in phenol and thus a tremendous increase in the degree of phenolation was obtained. Surprisingly, when omitting the sulfuric acid catalyst during phenolation of sulfite lignin in H^+ form, the same degree of phenolation could be obtained, thus the activation could also be performed autocatalyzed. This result was certainly achieved due to the high content of sulfonic acid groups in the sulfite

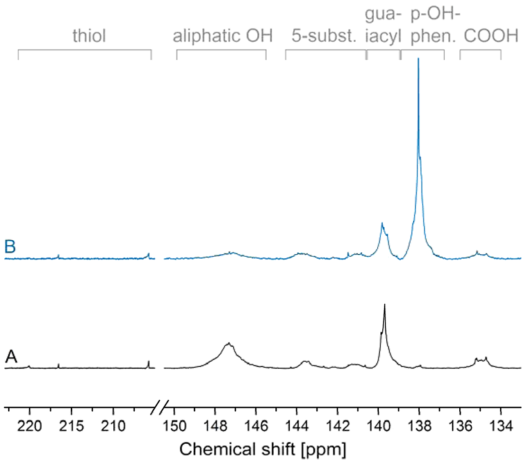


Figure 6. ^{31}P NMR spectra of unmodified (A) and phenolated (B) softwood kraft lignin no. 1 including thiol signals from 200−225 ppm.

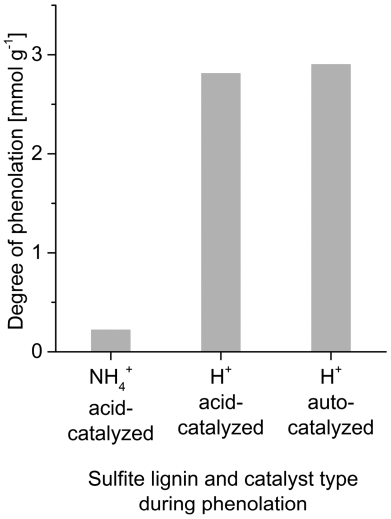


Figure 7. Influence of counterion and exclusion of additional catalyst in sulfite lignin phenolation.

lignin (2.6 mmol g^{-1}, based on 8.2% sulfur content). Hence, the relevance of additional sulfuric acid catalyst was reduced. Previously, it could be shown that the effect of increasing acid concentrations was reduced at higher catalyst levels.[20] The autocatalytic phenolation presents high potential for application since purification efforts can be reduced and the sulfonic acid functionality might even operate as catalyst for thermoset cross-linking or in applications such as lignin based ion-exchange resin.[40]

■ CONCLUSION

Increasing industrial availability and diversity of lignin make it necessary to compare the lignins in terms of reactivity and potential applicability. In our study, lignins originating from different sources (hardwood, softwood and annual plants) and technical processes (organosolv, kraft, soda, and sulfite pulping as well as hydrolysis) were compared with regard to their reactivity in phenolation and thus application in thermosetting resins. The chemical activation was successfully shown for all lignins as the number of reactive sites was improved compared to raw lignins. Differences in the degree of phenolation could be generalized since all lignins had in common that the number of aromatic hydroxyl groups introduced by phenolation was nearly equivalent with the number of aliphatic hydroxyl groups of the raw lignins. Highest increase of reactive sites was obtained with beech and poplar organosolv as well as sulfite and hydrolysis lignin with increase factors ranging from 6.8 to 12.9. In addition, the changes in molecular weight as well as ash and sulfur/thiol content were clarified. Surprisingly, an ammonium sulfite lignin, which initially had weak solubility in phenol could even be phenolated autocatalytically to a high degree after conversion to the H$^+$ form. By means of phenolation, the enhanced applicability of all lignins in thermosets is expectable since a more intense integration and a higher cross-link density will be favored. Moreover, it was found that predictable reactivity existed over a broad range of lignin types.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +49 40 73962-526. Fax: +49 40 73962-599. E-mail: ralph.lehnen@ti.bund.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The research was funded by the Federal Ministry of Food and Agriculture (BMEL) and supported by the Fachagentur Nachwachsende Rohstoffe e.V. (FNR project ProLignin, no.: 22020811). The authors gratefully acknowledge Rosanna Buchholz (Thünen Institute of Wood Research, TI) and Martina Heitmann (University of Hamburg, UH) for experimental support, Andreas Schreiber (UH) and Carlos Vila Babarro (TI) for the isolation of lignins, and Florian Mosdzen (UH) for methoxy group determination. We also like to thank Stora Enso, Tembec, and Suzano for provision of lignins as well as Heimo Kanerva and Tiina Liitiä from VTT (Espoo, Finland) for purification of the hydrolysis lignin.

■ REFERENCES

(1) Tomani, P. The lignoboost process. *Cellul. Chem. Technol.* **2010**, *44*, 53−58.

(2) Nagy, M.; Kosa, M.; Theliander, H.; Ragauskas, A. J. Characterization of CO2 precipitated Kraft lignin to promote its utilization. *Green Chem.* **2010**, *12* (1), 31−34.

(3) Velez, J.; Thies, M. C. Solvated liquid-lignin fractions from a Kraft black liquor. *Bioresour. Technol.* **2013**, *148*, 586−590.

(4) Kouisni, L.; Holt-Hindle, P.; Maki, K.; Paleologou, M. The Lignoforce System: A new process for the production of high-quality lignin from black liquor. *J. Sci. Technol. For. Prod. Proc.* **2012**, *2* (4), 6−10.

(5) FAO. *Pulp and Paper Capacities 2013−2018*; Rome, 2014.

(6) Lora, J. H. Industrial commercial lignins: Sources, properties and applications. In *Monomers, Polymers and Composites from Renewable Resources*; Belgacem, M. N., Gandini, A., Eds.; Elsevier Ltd., 2008; pp 225−241.

(7) Larsen, J.; Haven, M. Ø.; Thirup, L. Inbicon makes lignocellulosic ethanol a commercial reality. *Biomass Bioenergy* **2012**, *46*, 36−45.

(8) Leskinen, T.; Kelley, S. S.; Argyropoulos, D. S. Refining of Ethanol Biorefinery Residues to Isolate Value Added Lignins. *ACS Sustainable Chem. Eng.* **2015**, *3* (7), 1632−1641.

(9) McCoy, M. Enzymes poised for cellulosic success. *Chem. Eng. News Arch.* **2012**, *90* (41), 22−25.

(10) Environmental Entrepreneurs. *E2 Advanced biofuel market report*; 2015.

(11) www.demoplants.bioenergy2020.eu; www.iowarfa.org/resources_ethanol_refineries.php and company homepages www.

betarenewables.com; www.abengoabioenergy.com; www.iogen.ca; www.ineos.com; www.zeachem.com (accessed May 11, 2015), www.adityabirla.com, www.asianlignin.com (accessed July 27, 2015).

(12) Deep Research Report on Global and China Lignin and Lignin-Based Products Industry. www.deepresearchreports.com/112435.html (accessed May 11, 2015).

(13) Strassberger, Z.; Tanase, S.; Rothenberg, G. The pros and cons of lignin valorisation in an integrated biorefinery. *RSC Adv.* **2014**, *4* (48), 25310−25318.

(14) Ragauskas, A. J.; Beckham, G. T.; Biddy, M. J.; Chandra, R.; Chen, F.; Davis, M. F.; Davison, B. H.; Dixon, R. A.; Gilna, P.; Keller, M.; et al. Lignin valorization: improving lignin processing in the biorefinery. *Science* **2014**, *344* (6158), 1246843.

(15) Strassberger, Z.; Prinsen, P.; Van Der Klis, F.; Van Es, D. S.; Tanase, S.; Rothenberg, G. Lignin solubilisation and gentle fractionation in liquid ammonia. *Green Chem.* **2015**, *17*, 325−334.

(16) Hu, L.; Pan, H.; Zhou, Y.; Zhang, M. Methods to improve lignin's reactivity as a phenol substitute and as replacement for other phenolic compounds: A brief review. *BioResources* **2011**, *6* (3), 3515−3525.

(17) Duval, A.; Lawoko, M. A review on lignin-based polymeric, micro- and nano-structured materials. *React. Funct. Polym.* **2014**, *85*, 78−96.

(18) Laurichesse, S.; Avérous, L. Chemical modification of lignins: Towards biobased polymers. *Prog. Polym. Sci.* **2014**, *39* (7), 1266−1290.

(19) Funaoka, M. Sequential transformation and utilization of natural network polymer "LIGNIN". *React. Funct. Polym.* **2013**, *73* (2), 396−404.

(20) Podschun, J.; Saake, B.; Lehnen, R. Reactivity enhancement of organosolv lignin by phenolation for improved bio-based thermosets. *Eur. Polym. J.* **2015**, *67*, 1−11.

(21) Çetin, N. S.; Özmen, N. Use of organosolv lignin in phenol-formaldehyde resins for particleboard production: I. Organosolv lignin modified resins. *Int. J. Adhes. Adhes.* **2002**, *22*, 477−480.

(22) Çetin, N. S.; Özmen, N. Use of organosolv lignin in phenol-formaldehyde resins for particleboard production: II. Particleboard production and properties. *Int. J. Adhes. Adhes.* **2002**, *22*, 481−486.

(23) Ono, H.; Sudo, K. Wood adhesives from phenolysis lignin: A way to use lignin from steam-explosion process. In *Lignin Properties and Materials*; ACS symposium series 397; Glasser, W. G., Sarkanen, S., Eds.; American Chemical Society: Washington DC, 1989; pp 334−345.

(24) Alonso, M. V.; Oliet, M.; Rodríguez, F.; García, J.; Gilarranz, M. A.; Rodríguez, J. J. Modification of ammonium lignosulfonate by phenolation for use in phenolic resins. *Bioresour. Technol.* **2005**, *96* (9), 1013−1018.

(25) Du, X.; Li, J.; Lindström, M. E. Modification of industrial softwood kraft lignin using Mannich reaction with and without phenolation pretreatment. *Ind. Crops Prod.* **2014**, *52*, 729−735.

(26) Yang, S.; Wen, J.-L.; Yuan, T.-Q.; Sun, R.-C. Characterization and phenolation of biorefinery technical lignins for lignin−phenol−formaldehyde resin adhesive synthesis. *RSC Adv.* **2014**, *4* (101), 57996−58004.

(27) Puls, J.; Schreiber, A.; Saake, B. Conversion of Beechwood into Platform Chemicals after Organosolv Treatment. *Proceedings of the 15th ISWFPC*; Oslo, Norway, June 15−18, 2009.

(28) Granata, A.; Argyropoulos, D. S. 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, a reagent for the accurate determination of the uncondensed and condensed phenolic moieties in lignins. *J. Agric. Food Chem.* **1995**, *43*, 1538−1544.

(29) Zawadzki, M.; Ragauskas, A. N-hydroxy compounds as new internal standards for the 31P-NMR determination of lignin hydroxy functional groups. *Holzforschung* **2001**, *55* (3), 283−285.

(30) Vieböck, F.; Schwappach, A. Eine neue Methode zur maßanalytischen Bestimmung der Methoxyl- und Äthoxylgruppe. *Ber. Dtsch. Chem. Ges. A/B* **1930**, *63* (10), 2818−2823.

(31) Willför, S.; Pranovich, A.; Tamminen, T.; Puls, J.; Laine, C.; Suurnäkki, A.; Saake, B.; Uotila, K.; Simolin, H.; Hemming, J.; et al. Carbohydrate analysis of plant materials with uronic acid-containing polysaccharides-A comparison between different hydrolysis and subsequent chromatographic analytical techniques. *Ind. Crops Prod.* **2009**, *29* (2−3), 571−580.

(32) *TAPPI UM 250. Acid-soluble lignin in wood and pulp*; Atlanta, GA, 1985.

(33) Huijgen, W. J. J.; Telysheva, G.; Arshanitsa, A.; Gosselink, R. J. A.; de Wild, P. J. Characteristics of wheat straw lignins from ethanol-based organosolv treatment. *Ind. Crops Prod.* **2014**, *59*, 85−95.

(34) Mansouri, N. E. El; Salvadó, J. Structural characterization of technical lignins for the production of adhesives: Application to lignosulfonate, kraft, soda-anthraquinone, organosolv and ethanol process lignins. *Ind. Crops Prod.* **2006**, *24*, 8−16.

(35) Gosselink, R. J. A.; van Dam, J. E. G.; de Jong, E.; Scott, E. L.; Sanders, J. P. M.; Li, J.; Gellerstedt, G. Fractionation, analysis, and PCA modeling of properties of four technical lignins for prediction of their application potential in binders. *Holzforschung* **2010**, *64* (2), 193−200.

(36) Lin, B. L.; Yao, Y.; Shiraishi, N. Liquefaction Mechanism of β-O-4 Lignin Model Compound in the Presence of Phenol under Acid Catalysis Part 1. Identification of the Reaction Products. *Holzforschung* **2001**, *55*, 617−624.

(37) Lin, L.; Nakagame, S.; Yao, Y.; Yoshioka, M.; Shiraishi, N. Liquefaction Mechanism of β-O-4 Lignin Model Compound in the Presence of Phenol under Acid Catalysis Part 2. Reaction Behavior and Pathways. *Holzforschung* **2001**, *55*, 625−630.

(38) Koda, K.; Gaspar, A. R.; Yu, L.; Argyropoulos, D. S. Molecular weight-functional group relations in softwood residual kraft lignins. *Holzforschung* **2005**, *59*, 612−619.

(39) Wroblewski, A. E.; Lensink, C.; Markuszewski, R.; Verkade, J. G. 31P NMR Spectroscopic Analysis of Coal Pyrolysis Condensates and Extracts for Heteroatom Functionalities Possessing Labile Hydrogen. *Energy Fuels* **1988**, *2* (6), 765−774.

(40) Liang, F. B.; Song, Y. L.; Huang, C. P.; Li, Y. X.; Chen, B. H. Synthesis of novel lignin-based ion-exchange resin and its utilization in heavy metals removal. *Ind. Eng. Chem. Res.* **2013**, *52* (3), 1267−1274.