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PURIFICATION OF BIOREFINERY LIGNIN WITH ALCOHOLS

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After hydrothermal pretreatment and enzymatic hydrolysis of wheat straw, a slurry rich in lignin but with a high content of inorganic substances, especially silica, and residual carbohydrates is produced. This slurry was used to develop an ethanol organosolv separation method to produce silica-free lignin fractions. The addition of para toluene sulphonic acid (PTSA) and the use of two alternative long-chain alcohols, oleyl alcohol or nonylphenol, were tested. In every reaction, two lignin fractions were produced and their molecular size and elemental composition were characterized. The yield of each fraction and the change in MWD were studied as a function of temperature and solid to liquid ratio. At 100, 150, and 200°C and with the use of PTSA, high-purity lignin fractions were obtained. After lignin fractionation with nonylphenol, a liquid silica-free product with high lignin content was obtained in yields between 17 and 72%.

KEYWORDS. Wheat straw lignin, biorefinery concept, organosolv, silica-free lignin

INTRODUCTION

The processing of lignocellulose to ethanol has renewed interest in developing novel products from lignin, the biggest by-product of the process.^[1] Currently, the major lignin use is as a fuel, and only a few other products like vanillin are produced.^[2] The low applicability of lignin is due to its complex and variable structure, depending on the biomass source, and the process used for its separation, just as there may be high levels of residual carbohydrates and ashes. Additionally, lignin has strong intermolecular forces,^[3] which adds to its low solubility and the difficulty of modifying it further. To obtain novel lignin products, all of these variables and difficulties need to be overcome.

The catalyzed depolymerization of lignin has been extensively studied.^[4] Hydrothermal, solvolytic, and oxidative pathways have been

developed, many of them on model substances due to the high complexity of lignin.^[5] Unfortunately, to the best of our knowledge, none of these processes are industrially feasible due to low conversion yields, energy-demanding process parameters, as well as expensive or unstable catalysts.

Contrary to the Kraft process, in second-generation bioethanol production, a lignin with low sulfur content can be produced when hydrothermal pretreatment and enzymatic hydrolysis of the carbohydrates are used without acid addition. This is an advantageous starting point for further lignin conversion, but the solubility of biorefinery lignin is lower than that of the Kraft analogue due to the higher molecular weight and reduced hydroxyl groups of biorefinery lignin.^[6] A method to partially dissolve lignin is the use of ethanol/water mixtures with or without catalysts at temperatures

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between 80–220°C. Several ethanol organosolv processes have been proposed both as a pretreatment before bioconversion of straw to ethanol as well as pulping processes.^[7] The produced lignin is regarded as a less degraded form of lignin in comparison to traditional chemical pulping processes, although chemical breakdown of the lignin molecule does occur during organosolv treatments.^[8] Despite the extensive research done on the processes, none of the organosolv treatments is the preferred method to delignify pulp or pretreat biomass, due to the relatively high cost of processes in comparison to traditional pulping or more conventional pretreatment methods.^[9] These processes, however, can be scaled up and integrated in biorefineries, as alcohol is already a major product.

The exact mechanism for lignin solubilization, however, is not fully understood in ethanol organosolv processes since, besides the expected dissolution, solvolytic degradation and undesired recondensation reactions take place simultaneously, and the process parameters for lignin purification from the biorefinery slurry have not yet been optimized.

Lignin consists of phenylpropane monomers connected primarily by C—O—C (β -O-4, α -O-4, 4-O-5) and C—C (β -1, β - β , 5-5) bonds.^[10] During depolymerization, the breaking of these bonds releases monomers and oligomers featuring reactive aromatic hydroxyl groups (Ar—OH).^[11] Interactions between the many Ar—OH groups led to repolymerization and condensation reactions, probably with formation of phenoxy radicals intermediates ArO \cdot .^[12] Stabilizing the phenoxy radical is key to avoid repolymerization reactions. One reported way for stabilizing these radicals is through alkylation of the ArO \cdot using ethanol to produce Ar—CH₂—CH₃^[10,13] or Ar—O—CH₂—CH₃^[14] species. In these reactions, known as transesterification or end-capping reactions, the alcohol acts as the solvent but also as a reactant.^[14a]

Both lignin depolymerization and transesterification are enhanced by the use of catalysts. In the case of homogenous catalysis, alkaline catalysts are generally preferred over acidic ones because they react

faster.^[15] However, acidic catalysts can offer advantages because the acid-catalyzed nucleophilic substitution mechanisms characteristic of these catalysts could enhance transesterification reactions.^[15,16] Understanding and maximizing the reactions of lignin with alcohols could help in lignin reactive fractionation and thus in the production of low-molecular-weight compounds with potential uses as surfactants or additives for liquid fuels, for example.

In this article, we analyze the reactive fractionation and mineral purification of wheat straw biorefinery lignin fractions that result after organosolv solubilization at temperatures lower than 200°C. Aliphatic and aromatic alcohols with different molecular weights and different reaction parameters were used. An acid catalyst (PTSA) was used to compare its performance. The final products were analyzed with FTIR, SEC, and ICP-OES elemental analysis.

MATERIALS AND METHODS

Organosolv Treatment

Biorefinery lignin from wheat straw was obtained from the Inbicon bioethanol production plant located in Kalundborg, Denmark. The process was described in Larsen et al.^[17] The dry matter content was determined before every experiment using a Sartorius MA 30 moisture analyzer at 105°C and the solid-to-liquid ratios as well as the yields of the experiments were calculated considering it. All other chemicals were lab grade from Sigma-Aldrich (nonyl phenol, oleyl alcohol, and p-toluene sulfonic acid, PTSA), or VWR International, LLC (95% ethanol) and were used without further purification.

As a standard procedure, the slurry was washed three times with demineralized water prior to the experiments to remove non-structural carbohydrates. Afterwards, 10–15 grams of the biorefinery lignin slurry (with a solid content of around 30%), together with 15–17 grams of an alcohol or a mixture of them, were weighted in a glass liner and then introduced into a 100 mL Parr reactor. The solid-to-liquid ratio was varied between 1:3 and 1:8 when

95% ethanol was used as solvent. 0.075 kmol of PTSA was added as catalyst in some trials. The reactions were carried out at 100, 150, and 200°C for 20 minutes. The pressure in the reactor achieved between 18 and 20 bars.

After cooling, the reaction products were diluted with 30 ml of ethanol. The mixture was heated to 70°C and hot filtered (fraction 1). The obtained liquid fraction was precipitated with cold water using three times the initial volume of the samples. The obtained solids or immiscible liquids (fraction 2) were washed out and separated by centrifugation. The solids were dried at 50°C for three days (Figure 1).

Compositional Analysis

The lignin and ash content, as well as residual carbohydrates of the samples, were determined following methods from the National Renewable Energy Laboratories.^[18] Briefly, acid-insoluble lignin content was determined as the residue after sulfuric acid hydrolysis. The ash content was determined by incineration of 0.5 g of dried sample at 550°C for 3 h. The hydrolysis of structural carbohydrates in sulfuric acid released monomeric forms that were measured by HPLC, using a Dionex ICS5000 HPAEC system (Dionex, Sunnyvale, CA, USA) equipped with a pulsed amperometric detector (PAD), a CarboPac-PA1 2 × 250 mm analytical column, and a CarboPac PA1 2 × 50 mm guard column.

Elemental Analysis

Multi-elemental analyses of the solid and liquid fractions were conducted using inductively coupled plasma-optical emission spectroscopy (ICP-OES). For the analysis, 10–50 mg of material was mixed with 500–2500 µL 70% HNO₃ (SCP science, Quebec, Canada), 250–1000 µL 15% H₂O₂ (Sigma-Aldrich) and 40–200 µL 49% HF (Sigma-Aldrich), and hereafter digested in a pressurized microwave oven (Ultrawave, Milestone Inc., Sorisole, Italy) for 10 minutes with a starting pressure of 40 bar and a temperature of 240°C. After digestion, samples were diluted to a final 3.5% acid concentration with Milli-Q water (Milli-Q Plus, Bedford, MA) before measurement on an ICP-OES (Model Optima 5300 DV,

PerkinElmer) equipped with a HF-resistant sample introduction kit. For quantification, an external 10-point calibration standard P/N 4400-132565 and P/N 4400-ICP-MSCS (CPI International, Amsterdam, The Netherlands) was used. A certified reference material (CRM) NCS 73013 Spinach leaf was analyzed together with the samples to evaluate the accuracy and precision of the analysis.

ATR-FTIR

ATR-FTIR spectra were obtained in triplicate using a ThermoFischer Scientific Nicolet 6700 FTIR spectrometer (Thermo Fischer Scientific, Waltham, MA, USA) equipped with a Goldengate ATR accessory (Specac Ltd, Orpington, Kent, UK). Spectra from 4000 to 600 cm⁻¹ were obtained with a 4 cm⁻¹ resolution, 200 background scans, and 100 scans for each sample spectrum. The average of the three spectra was calculated for each sample.

Size Exclusion Chromatography (SEC)

SEC was done by treating 100 mg of each sample, with a mixture of 9:1 DMSO in water and 0.05 M LiBr. The samples were left in the solution overnight at room temperature in an analog orbital shaker at 50 rpm. The next day, the samples were put in an ultrasound bath for 15 minutes. The portion of the samples that dissolved in this mixture was passed through a SEC column. This was a 300 mm, 5 µm particles, 100 Å porosity PolarSil column from Polymer Standard Service heated to 40°C. Flow was 1 ml/min and detection was done with a UV-Vis detector at 280 nm. The standards used to determine the molecular weight were phenol, guaiacylglycerol-β-guaicyl ether, and tannic acid.

RESULTS AND DISCUSSION

Compositional and Elemental Analysis

Compositional analysis of the lignin slurry prior to organosolv treatment showed the presence of 3.4% residual carbohydrates, 76% lignin content, and 14% ash content (Table 1). A complete chemical characterization of this residue was described previously.^[19]

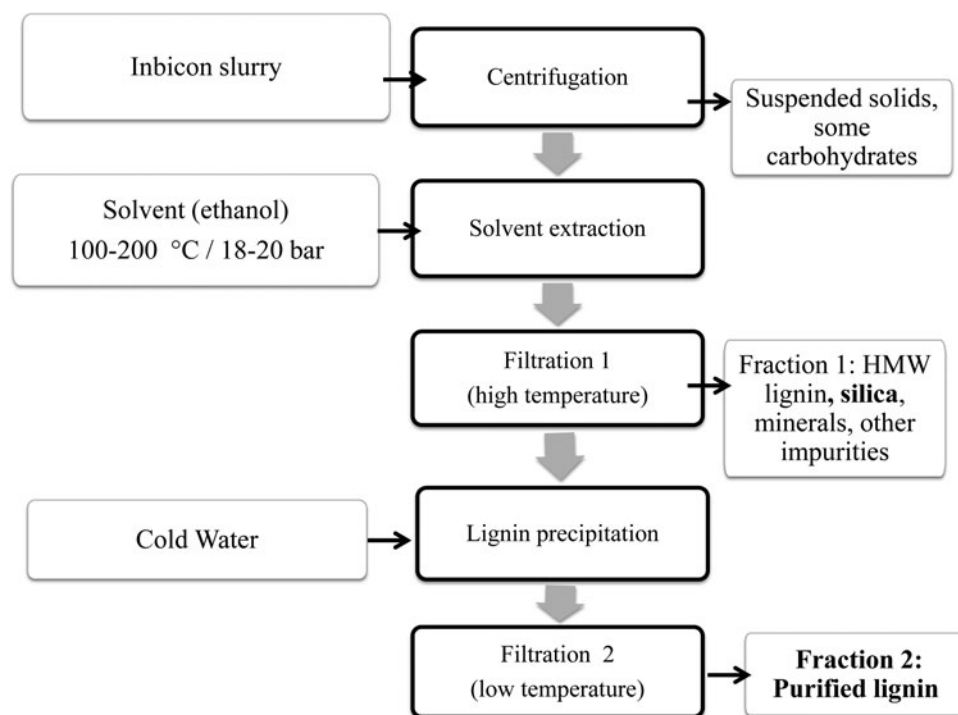


FIGURE 1. Organosolv treatment of lignin slurry from a cellulosic ethanol process (HMW high-molecular-weight, non-soluble fraction).

According to the procedure depicted in Figure 1, after organosolv treatment of biorefinery lignin, the reaction products are separated into two fractions; the first fraction is precipitated from hot ethanol, while the second fraction is the soluble correspondent filtrate that is precipitated from cold water. The chemical composition of selected samples is presented in Table 1. As expected, all of the ashes were concentrated in fraction 1, while fraction 2 contained a more purified lignin fraction. The mass balance of the fractions did not

come close to 100%. The solid fraction of the original slurry contains, in addition to lignin and structural carbohydrates, proteins, sucrose, and acids.^[17] For fraction 2, however, since neither significant quantities of carbohydrates nor ashes were detected, we assumed that the remaining 10 to 15% corresponded to acid-soluble lignin fractions and fractions that passed the filtration step used to calculate Klason-lignin. Nevertheless, for the yield calculations, it was assumed that fraction 2 was only 86.7% Klason lignin (Table 1).

TABLE 1. Compositional analysis of samples prior and after ethanol organosolv treatment at 200°C

Sample	Klason lignin (%)	Ash (%)	Galactan (%)	Glucan (%)	Xylan (%)	Mannan (%)	Mass balance (%)
Solid fraction of the slurry	76	14	n.d.	1.6	1.1	0.7	93
Fraction 1	1:8	67	24	0.4	1.4	n.d.	92
	1:5	66	24	0.4	1.4	n.d.	92
	1:3	69	25	0.4	1.4	n.d.	97
	1:8	87	0	n.d.	n.d.	n.d.	85
Fraction 2	1:5	90	0	n.d.	n.d.	n.d.	89
	1:3	87	0	n.d.	n.d.	n.d.	86

1:8, 1:5, and 1:3 are the solid-to-liquid ratios used for the organosolv treatment. Each data represent the average of two samples analyzed in triplicate. Standard deviations varied between 0.00 and 0.5.

TABLE 2. ICP-OES elemental analysis data of lignin fractions treated in modified organosolv experiments

Sample	Temp °C	Al μg/g		Ca μg/g		Fe μg/g		K μg/g		Na μg/g		P μg/g		S μg/g		Si μg/g	
		1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd
Slurry		336 (7)		4711 (70)		1627 (41)		340 (26)		815 (39)		687 (11)		1307 (33)		44287 (1326)	
S/L ratio: 1:8	100	541 (35)	nd	6182 (719)	Nd	2137 (39)	917 (55)	568 (45)	120 (47)	390 (37)	40 (20)	642 (191)	nd	1001 (218)	961 (211)	48154 (5083)	233 (83)
	150	550 (39)	nd	6618 (719)	Nd	2084 (202)	1162 (85)	485 (33)	109 (6)	308 (24)	18 (8)	788 (108)	nd	901 (120)	1061 (62)	43276 (3629)	713 (97)
S/L ratio: 1:5	200	574 (38)	nd	7272 (569)	Nd	2410 (72)	592 (27)	539 (60)	153 (49)	278 (27)	60 (45)	858 (150)	nd	825 (190)	641 (149)	54923 (8901)	194 (66)
	100	611 (12)	nd	6902 (777)	Nd	2291 (164)	804 (109)	633 (44)	122 (34)	386 (59)	16 (9)	772 (112)	nd	1224 (142)	668 (225)	48707 (8174)	162 (39)
S/L ratio: 1:3	150	556 (18)	nd	6677 (433)	Nd	2178 (16)	941 (164)	673 (21)	146 (59)	401 (84)	55 (35)	622 (39)	nd	774 (67)	1019 (85)	50719 (3151)	589 (822)
	200	622 (74)	nd	7607 (771)	Nd	2449 (193)	532 (51)	559 (58)	108 (63)	296 (40)	316 (551)	934 (146)	nd	990 (165)	965 (197)	55570 (11328)	90 (70)
S/L ratio: 1:3	100	638 (38)	nd	6844 (389)	Nd	2238 (30)	775 (94)	748 (39)	196 (132)	579 (42)	179 (250)	697 (68)	nd	1171 (90)	750 (173)	57091 (2978)	111 (85)
	150	599 (23)	5	7186 (477)	Nd	2256 (61)	867 (42)	668 (26)	171 (63)	477 (34)	163 (58)	816 (84)	nd	1067 (110)	1105 (154)	54474 (4199)	151 (40)
S/L ratio: 1:3	200	604 (48)	nd	7612 (341)	Nd	2381 (55)	489 (18)	671 (35)	111 (70)	429 (63)	67 (57)	825 (72)	nd	966 (52)	957 (210)	59887 (4014)	110 (62)

S/L stands for solid-to-liquid ratio. 1st and 2nd represent the two fractions left after organosolv treatment. Each number represents the average of four samples; the value in parenthesis is the standard deviation. Note that the silica content of the second fraction in all treatments was reduced in comparison with the parent material.

TABLE 3. Yields of un-catalyzed organosolv reactions at different solid/liquid ratios and different temperatures

Solid-to-liquid ratio	Temperature (°C)	Yield (%)
1:8	100	6(0.4)
	150	7(0.2)
	200	23(5.3)
1:5	100	6(0.6)
	150	9(0.5)
	200	30(0.2)
1:3	100	8(0.5)
	150	9(0.6)
	200	26(1.1)

Each number represents the average of four samples; the value in parenthesis is the standard deviation.

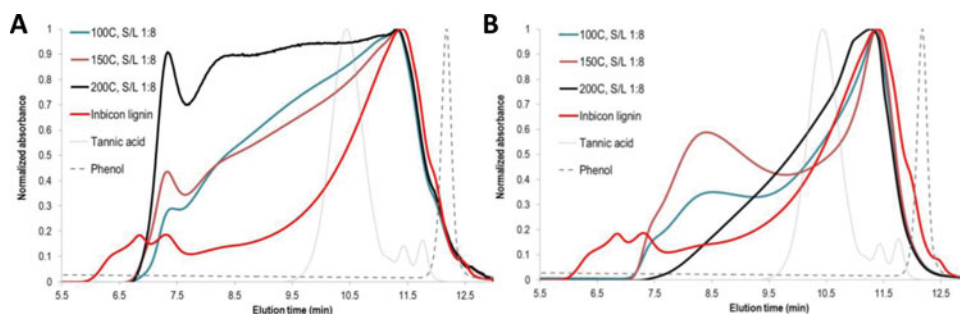
Elemental analysis of the fractions showed that some elements were washed out while others remained in either fraction 1 or 2 (Table 2). Elements that were concentrated and retained in fraction 1 (Si, P, Ca, Al) are insoluble and might be tightly attached to the organic fraction. Elements that remained in fractions 2 are Fe, K, Na, and S. Some of these elements are passed to fraction 2 because they are soluble in ethanol, while other elements are attached to the lignin. Sulfur is probably attached to every lignin fraction, because it is present in both fractions at almost the same quantities. Conversely, in comparison with fraction 1, smaller concentrations of Fe, K, and Na were present in fraction 2, possibly because of the partial solubility of their corresponding salts in ethanol/water mixtures.

Uncatalyzed Conditions

Organosolv Treatment. Trials with 50:50% water/ethanol as solvent and at different temperatures and solid/liquid ratios were performed without any catalyst (Table 3). The yields of the procedure were calculated comparing the weight of the purified lignin fraction with the amount of lignin on a dry basis in the slurry, namely 76% as calculated in the compositional analysis (Table 1). Consequently, a yield of 100% would mean that the whole of the lignin in the slurry was extracted in fraction 2, and the weight of this was multiplied by a factor of 86.7% to account for the fact that the mass balances did not close. The yields varied from 6% to 30%, with the highest always at 200°C (Table 3).

Molecular Weight Distribution (MWD).

The SEC chromatograms of both fractions at different temperatures and solid-to-liquid ratios are shown in Figure 2; the starting material of biorefinery lignin is shown for comparison. Biorefinery lignin featured a polymodal distribution with a high-molecular-weight band between 5.5 and 8 minutes and a low-molecular-weight band between 8 and 15 minutes (red line in Figures 2A and 2B). The high-molecular-weight band possibly corresponded to condensation products of the same monomers and oligomers that occur in the low-molecular-weight fractions. Phenol (FW: 94) and tannic acid (FW: 1701) were used for reference (grey lines in Figures 2A and 2B).

**FIGURE 2.** Normalized SEC chromatograms of different lignin fractions from biorefinery lignin: (A) Fraction rich in minerals; (B) fraction free of minerals. Each line represents the molecular weight distribution of four samples treated with ethanol and cooked at different temperatures (100, 150, or 200°C). Each temperature/fraction treatment has a different color. Phenol and tannic acid were used as references for the molecular weight. Inbicon slurry is the parental material containing lignin.

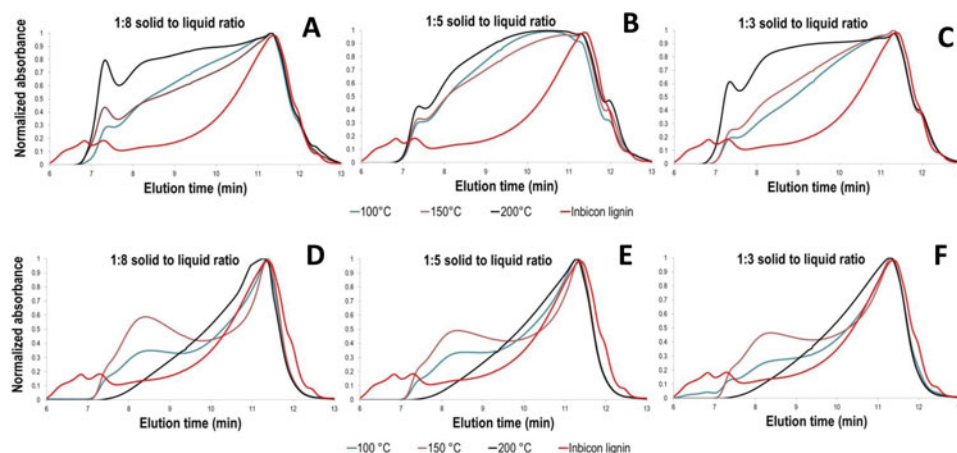


FIGURE 3. Normalized SEC chromatograms of different lignin fractions from bioethanol lignin. Each line represents the molecular weight distribution of four samples treated with ethanol and processed at different temperatures (100, 150, or 200°C). (A), (B), and (C) Fractions rich in minerals. (D), (E), and (F) Fractions free of minerals.

The MWD of the biorefinery lignin changed as a result of organosolv treatment. As expected, the molecular weight in fraction 2 (Figure 2B) is low enough to be soluble in ethanol. However, the same low-molecular-weight chemical species are found in fraction 1 and even in the biorefinery lignin. This suggests that solubility of lignin in ethanol water mixtures depends not only on a reduction of the molecular weight of the polymer, but also on other characteristics of the lignin, like the disaggregation of lignin macromolecules.

According to the SEC chromatograms, fraction 1 (insoluble in hot ethanol) has bimodal or polymodal distribution (Figure 3A, B, and C). The high-molecular-weight fraction of the original lignin is partially absent. Between different solid/liquid ratios (S:L) and different temperatures, there are consistent changes. The chromatograms for reactions at 200°C always show a sharp band at a high molecular weight (7.5 min); at 150°C, this band decreases, and at 100°C it almost disappears and the distribution is close to monomodal. There is also an intermediate-molecular-weight fraction band at about 8.5 min that increases with increasing reaction temperature and is only slightly present in the parent material. This band may be due to disaggregation of supramacromolecular lignin structures or depolymerization reactions. However, increased recondensation processes of the

lower-molecular-weight species with increased reaction temperature could also explain this sharp band.^[12,20]

As mentioned, most of the species in fraction 1 and the parent material are of low molecular weight (11.5 min retention). It is possible that these lignin monomers and oligomers are aggregated with the inorganic portion of the slurry, in its majority silica, which is strongly concentrated in this fraction, affecting its solubility. The presence of salts has been shown to increase aggregation of Kraft lignin^[21]; however, further research has to be done to confirm this hypothesis.

The MWD for fraction 2 is opposite to fraction 1. The high-molecular-weight fraction of the parent material is almost absent in fraction 2. At 100 and 150°C, there is a bimodal distribution with two peaks at 8.5 and 12 min. At 200°C, there is a monomodal distribution. It is likely that, at 200°C, the disaggregation of supramacromolecular lignin structures is completed, while below this temperature it is only partial.

Apparently, there was no effect of the S:L ratio on the final MWD. At 1:3 S:L ratio, the behavior of the middle-molecular-weight fraction can be observed clearly (Figure 3F). It increases from 100 to 150°C but disappears at 200°C. Again, this behavior suggests that, from 100 to 150°C, there is solubilization, but only a

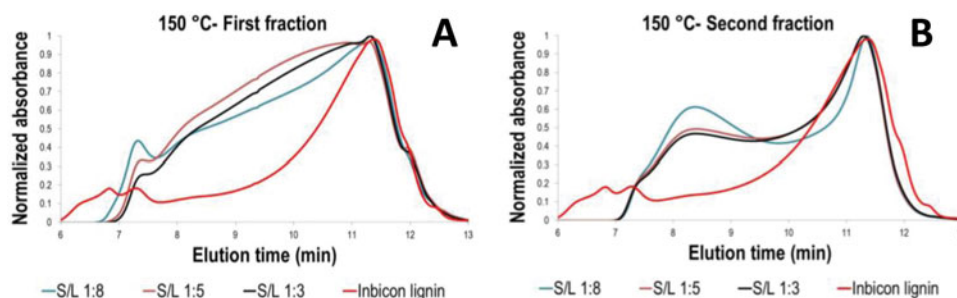


FIGURE 4. Normalized SEC chromatograms of the two different organosolv lignin fractions obtained at 150°C. Each line represents the molecular weight distribution of four samples. (A) Fraction rich in minerals; (B) fraction free of minerals.

partial disaggregation of lignin aggregates, while at 200°C there is complete disaggregation. The effect of the variation of the S:L ratio is best observed at 150°C (Figure 4). In both fractions 1 and 2, the higher the S:L ratio the higher the solubilization and/or disaggregation of supra-macromolecular structures. At 100 and 200°C, no observable effect of this parameter can be observed.

Experiments with LiBr

Lithium bromide was added to some solutions to test the hypothesis that lignin was aggregated by supramolecular forces that could not be broken by the solvent systems used in the previous experiments. LiBr has been used to decrease the forces of cohesion between lignin molecules during SEC.^[22] The yields at 150°C increased from 6–9% to a range between 24–31% by the addition of salt (Figure 5). Contrary to this, at 200°C, there were no significant yield increments, meaning that at this temperature the disaggregation is completed due to the thermal energy input alone.

Catalyzed Conditions

Transesterification reactions in which ethanol reacts by alkylation with lignin fragments have been reported.^[10,13a,14a,23] PTSA is a well-known catalyst for transesterification and for depolymerization of polyethers.^[16b] Esterification reactions of organosolv wheat straw lignin with PTSA using ethanol as solvent were recently reported, and the $-\text{COO}-\text{CH}_2-\text{CH}_2-\text{OH}$ methylenes of non-lignin aliphatic esters and ferulates were

identified using 2D $^{13}\text{C}-^1\text{H}$ HSQC NMR.^[23] Therefore, PTSA was tested for its ability to catalyze the possible reactive fractionation or depolymerization of biorefinery lignin. Several trials were performed at 100, 150, and 200°C, with 2 mol% (0.075 kmol) concentration relative to the amount of ethanol in the reaction mixture. In contrast to uncatalyzed conditions, the reaction yields increased considerably, with the highest for 200°C (Table 4).

The MWD of the catalyzed reactions are different than the MWD of the uncatalyzed reactions. In fraction 1 of the catalyzed reactions, the polymodal pattern of the chromatograms is more pronounced with species of several molecular weights. The molecular weight fraction around 11.5 min is lower, indicating that the aggregation observed in the uncatalyzed tri-

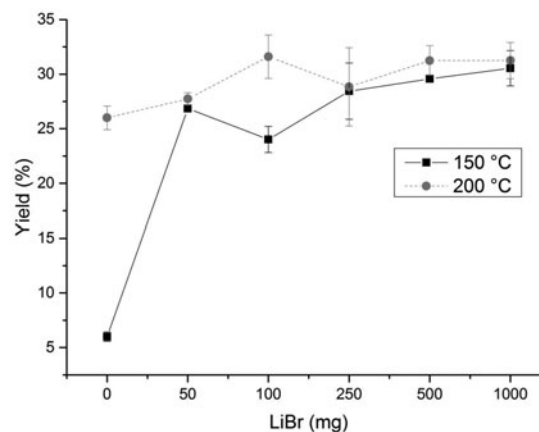


FIGURE 5. Yields of organosolv reactions at different solid/liquid ratios and different temperatures and supplemented with different doses of LiBr.

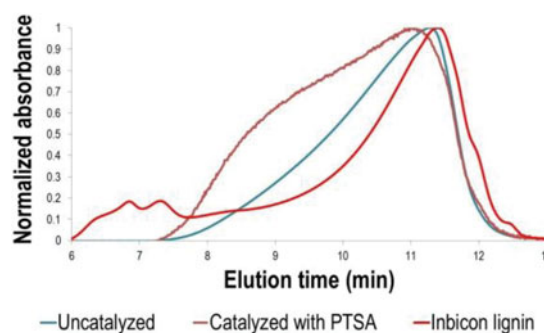
TABLE 4. Yields of PTSA-catalyzed ethanol organosolv reactions of biorefinery lignin

Temperature (°C)	Yield in % (SD)	Mass balance in % (SD)
100	28 (2.2)	95 (0.1)
150	33 (4.3)	84 (0.1)
200	35 (2.0)	89 (0.2)

Each number represents the average of four samples; the value in parenthesis is the standard deviation.

als is absent (Figure 6A). At 100°C, the reaction products are mainly in the middle-molecular-weight range, while at 150°C the bands at high molecular weight (around 7 min) are higher. This suggests that again repolymerization reactions are favored at 150°C. At 200°C, the samples followed the same trend.

In fraction 2 (Figure 6B), the patterns are monomodal for the 150°C and 200°C products and almost monomodal for the 100°C that shows a small amount of high-molecular-weight species. There is a shift of the peak maximum towards longer retention times when the temperature is increased, which indicates that the disaggregation process is favored with increased temperature. This clear shift is not seen in uncatalyzed reaction. Also, in the catalyzed reactions, the low- and middle-molecular-weight fractions are bigger (Figure 7). These MWDs, together with the increased yields, suggest that the presence of the acid catalyst promotes either lignin disaggregation or increased depolymerization with inhibition of repolymerization reac-

**FIGURE 7.** Normalized SEC chromatogram of two fractions free of minerals, PTSA catalyzed and uncatalyzed, organosolv-type reactions of biorefinery lignin at 200°C, compared to the parental material called Inbicon lignin.

tions, or perhaps any combination of these two contributing processes, with the net effect of a higher proportion of middle-molecular-weight species in the soluble fraction.

Use of High-Molecular-Weight Alcohols

Ethanol is able to dissolve and possibly also react with lignin partially due to its hydroxyl group. Alcohols with larger hydrophobic regions, in addition to their hydrophilic hydroxyl, may also react in different manners. To test this effect, long-chain alcohols, namely nonylphenol and oleyl alcohol, were tested as reactive solvents using a 1:8 solid/liquid ratio. It must be considered, however, that as the lignin source is a slurry containing approx. 30% solids, then the presence of some ethanol and water was unavoidable. When water/ethanol mixtures were used as solvent, the second fraction (i.e., the

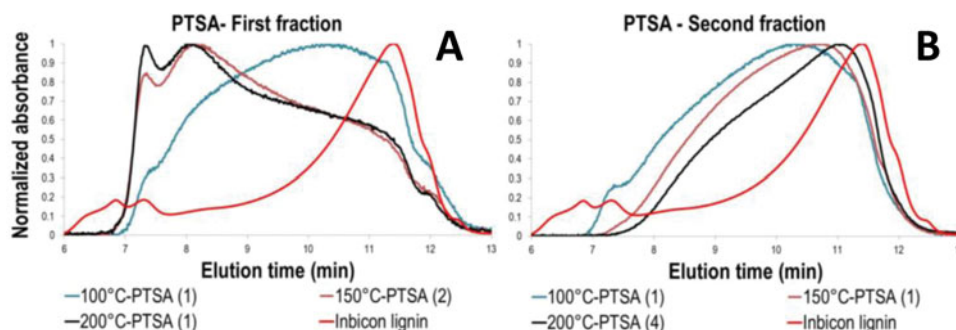
**FIGURE 6.** Normalized SEC chromatograms of PTSA catalyzed organosolv-type reactions of biorefinery lignin at different temperatures (100, 150, or 200°C). Each line represents the molecular weight distribution of four samples. (A) Fraction rich in minerals; (B) fraction free of minerals.

TABLE 5. Weight and yield of uncatalyzed organosolv reactions of biorefinery lignin with nonylphenol and oleyl alcohol

Alcohol	Initial weight (g)	Dry weight (g)	Weight of fraction 1 (g) + residual alcohol	Approx. % of lignin dissolved
Oleyl alcohol	12.8	2.9	4.2	0%
Nonylphenol	12.8	3.0	2.5	17%

purified lignin) was isolated as a solid. Contrary to this, when oleyl alcohol and nonylphenol were used, the second filtrate was an oily substance composed of a mixture of the unreacted alcohol, a low-molecular-weight lignin fraction, and the reaction products. This effect made it impossible to calculate the yield of the extraction in the same way as with ethanol as solvent. To circumvent this problem, yields were indirectly calculated from the weight of fraction 1 compared with the original amount of lignin in the slurry. It has to be emphasized that this is an approximated yield, since fraction 1 also contained the remaining alcohol absorbed by the solid.

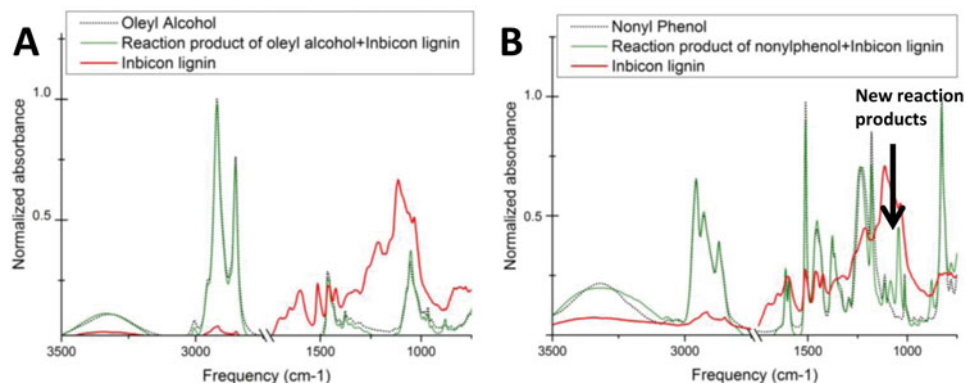
In the case of oleyl alcohol, minor weight differences were observed in fraction 1, and the weight of fraction 2 was negligible, suggesting that oleyl alcohol has a very poor dissolution capacity towards lignin (Table 5). Additionally, the FTIR spectrum of the liquid fraction 2 shows that it is composed almost of pure oleyl alcohol (Figure 8A).

Contrary to this, when nonylphenol was used, 17% lignin was dissolved under uncatalyzed conditions (Table 5) and the presence of new bands at 1040 cm^{-1} in the FTIR spectra suggested that a chemical reaction occurred

(Figure 8B) and that the alcohol certainly acted as a reactive solvent. Here, the polar phenol group accounts for a better dissolution and diffusion in the slurry. However, considering the new bands found in the FTIR spectra of the products, it is possible that the much higher yield compared with oleyl alcohol can be attributed to the higher reactivity of phenolic alcohols. The pK_a of a primary aliphatic alcohol is around 16, whereas phenolic alcohols is around 10, so the reactivity is magnitudes higher for phenol compared with the aliphatic analogues.

When the nonyl phenol reactions were catalyzed with PTSA, the yield increased proportionally to the temperature (Table 5). From the indirect yield calculation, it was possible to deduce that, at 200°C , almost all lignin (above 72%) was solubilized, which is a much higher yield compared with ethanol.

The SEC analysis of the reaction products with nonylphenol shows, firstly, that all samples contain high quantities of unreacted nonylphenol that appears between 11.5 and 12.0 min. This was expected from the mass balance of the different fractions. However, a closer look at the chromatograms shows that the patterns are similar to the ethanol-PTSA catalyzed trials. Fraction 1 (Figure 9A) shows a high-molecular-

**FIGURE 8.** FTIR spectra of a pure alcohol—(A) oleyl alcohol; (B) nonyl phenol—biorefinery lignin, and the reaction product of the two compounds.

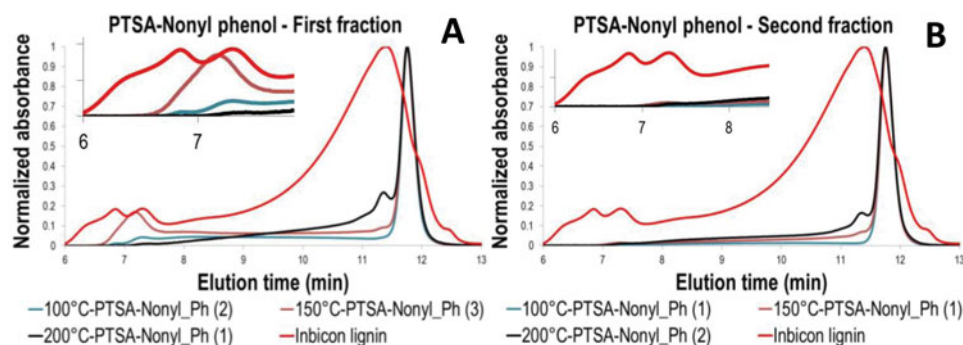


FIGURE 9. Normalized SEC chromatograms of PTSA-catalyzed organosolv-type reactions of biorefinery lignin in ethanol-nonylphenol mixtures at different temperatures (100, 150, or 200°C). (A) Fraction rich in minerals; (B) fraction free of minerals.

weight band at 7 min, a continuous middle-molecular-band between 7.5 and 11 min, and a low-molecular-weight band that appears as a shoulder of the nonylphenol band at 11.4 min. Fraction 2 (Figure 9B) shows a small high-molecular-weight fraction at 7.5 min and a continuous increasing middle- and low-molecular-weight band that ends at 11.4 min with a much higher low-molecular-weight fraction.

The differences in the chromatograms, depending on the reaction temperature, are as expected from the yields obtained. The reactions at 100°C show a pronounced high-molecular-weight band in fraction 1 and almost only nonyl phenol in fraction 2, indicating that almost no disaggregation or depolymerization took place. Contrary to this pattern, the reactions at 200°C show a much pronounced low-molecular-weight band and almost negligible high-molecular-weight band.

Elemental Analyses of Catalyzed Fractions

As expected from the high content of unreacted alcohol, fractions 2 of the reactions with nonyl phenol have very low concentrations of

inorganic elements (Table 6). For example, in the case of silicon, fractions 2 of the uncatalyzed reactions in ethanol contain between 850 and 7,172 ppm of silicon, but fractions 2 of reactions with nonylphenol have between 198 and 443 ppm. The same applies to all other elements. However, observing the concentration of the same element in fraction 1, it goes from 55,472 to 71,193 ppm in the reactions with ethanol, while it achieves values between 25,853 and 110,101 ppm (which means approx. 20% content of silica!). It means that, especially at 200°C, the inorganic fraction of the slurry is concentrated in fraction 1 when nonyl phenol is used.

Other elements like sodium are also concentrating in fraction 1. Interestingly, there is a good relationship between temperatures and Na content as follows:

The experiments at 100°C have between 473 and 544 ppm of Na;
 The experiments at 150°C have between 960 and 1,824 ppm Na;
 The experiments at 200°C have between 2,222 and 3,450 ppm of Na.

TABLE 6. Weight of the filtrated fraction of PTSA catalyzed nonylphenol organosolv reactions of biorefinery lignin

Temperature (°C)	Initial lignin weight (g)	Weight of fraction 1+ residual nonylphenol	Approx. % of lignin dissolved
100	3.3	3.7	−12.2 (8.2)
150	3.3	3.0	10.3 (8.3)
200	3.3	0.9	72.1 (5.9)

Each number represents the average of four samples; the value in parenthesis is the standard deviation.

TABLE 7. ICP-OES elemental analysis data of lignin fractions treated in modified organosolv experiments

Reaction	T (°C)	Al μg/g		Ca μg/g		Fe μg/g		K μg/g		Na μg/g		P μg/g		S μg/g		Si μg/g	
		1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd
In nonylphenol catalyzed with PTSA	100	939	12	647	9	385	11	596	nd	3441	5	80	nd	9686	651	25833	443
	150	2097	15	1332	10	484	9	1357	nd	2222	4	59	nd	9530	1178	65323	224
	200	3566	13	3834	11	2766	73	1933	nd	2399	5	639	nd	10880	1602	110101	198
In ethanol catalyzed with PTSA	100	2156	262	1340	359	782	547	1267	134	831	172	137	52	12607	9598	64602	7172
	150	1918	99	916	205	617	417	1050	27	675	137	73	33	13629	10638	55472	796
	200	2307	210	1704	480	603	363	1202	32	711	150	85	43	16764	12277	71193	853
In ethanol uncatalyzed	100	541	nd	6182	nd	2137	917	568	120	390	40	642	nd	1001	961	48154	233
	150	550	nd	6618	nd	2084	1162	485	109	308	18	788	nd	901	1061	43276	713
	200	574	nd	7272	nd	2410	592	539	153	278	60	858	nd	825	641	54923	194

1st and 2nd correspond to first and second fractions. Each number represents the average of four samples; the value in parenthesis is the standard deviation.

These results suggest that using nonylphenol in the solution mixture not only solubilize lignin but also further reduce the silica content of the samples.

CONCLUSIONS

During ethanol organosolv fractionation of biorefinery lignin, both aggregation/disaggregation of lignin macromolecules and depolymerization reactions occur. At temperatures below 200°C and with the use of PTSA, an efficient disaggregation/depolymerization of lignin is possible. With the use of an aromatic alcohol like nonylphenol, a high-yield reactive purification of biorefinery lignin is possible. This may open new possibilities for processing of lignin to higher-added-value products.

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