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Lignin Depolymerisation and Lignocellulose Fractionation by Solvated Electrons in Liquid Ammonia

Pepijn Prinsen, Anand Narani, and Gadi Rothenberg*^[a]

We explored the depolymerisation of several lignins in liquid ammonia at relatively high temperatures and pressures (120 °C and 88 bar). Five different lignins were tested: Indulin AT kraft, Protobind 1000 soda, wheat straw organosolv, poplar organosolv and elephant grass-milled wood lignin (EG MWL). In pure liquid ammonia, all lignins underwent slow incorporation of nitrogen into their structure, resulting in higher molecular weight and polydispersity index. Subsequently, we show a reductive depolymerisation by solvated electrons at room tem-

perature by adding sodium metal to the liquid ammonia without any external hydrogen donor. The netto yields of bio-oil are low for technical lignins (10–23%), but with higher yields of alkylphenols. In the case of native EG MWL, netto yields of 40% bio-oil were achieved. Finally, when the room temperature method was applied to poplar wood fibre, we observe improved delignification upon the addition of sodium compared to poplar wood fractionation in pure liquid ammonia.

Introduction

Lignocellulosic biomass is available worldwide and is renewable on a human time scale.^[1] The main sources of commercial lignins are pulp and paper manufacturing, although they are mostly used in-house as boiler fuel.^[2] The fibre line capacity of current kraft paper pulp plants can be increased by extracting the lignin from the black liquors and thereby enhancing the turnover rate in the recovery boiler. Indeed, the Lignoboost^[2] process has applied this successfully by recovering high-purity lignin fractions through precipitation and filtration. In the future, lignins will also be produced in biorefinery processes from lignocellulosic feedstocks. Cellulosic ethanol production is already a commercial process,^[3] and gives a hydrolysis lignin as by-product that is burned to supply the energy needs of biorefineries. However, burning this lignin is a questionable practice. Lignin has tremendous value potential. It is the world's largest natural resource of aromatics,^[4] and its depolymerisation and subsequent conversion to high-value products may hold the key to biorefinery profitability.^[1]

That said, lignin depolymerisation has three inherent problems. The first comes from its heterogeneous structure that gives rise to a complex mixture of compounds. For each type of lignin, the botanic origin determines the ratio of *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, as well as the abundance of different inter-unit linkages that in turn influence the product yield and composition.

The second problem is that the isolation method itself can also affect the reactivity of lignins.^[5] Indeed, a core challenge in lignocellulosic biorefining is finding such isolation conditions that maintain their reactivity without hampering the main biorefinery products, such as pulp and bioethanol. Recently, Luterbacher and et al. addressed this problem for a corn stover fractionation process using γ -valerolactone as a carbohydrate-derived solvent.^[5] Elsewhere, Ferrini and Rinaldi^[6] succeeded in isolating a lignin derived non-pyrolytic bio-oil using a catalytic organosolv-pulping process followed by hydrotreating, without compromising the pulp hydrolysis yield. Thermolytic processes such as pyrolysis give typically a mixture of solid, liquid (bio-oil) and gaseous products. This method is very effective but energy-intensive.^[7] Other methods include enzymatic conversions^[8] and liquid-phase depolymerisation that can be combined with upgrading steps such as catalytic hydrodeoxygenation (HDO).^[9] Bio-oils contain oxygenated compounds, and therefore are less stable. Converting them into deoxygenated aromatics and cyclic aliphatics through HDO is an attractive solution, but gives even more complex product mixtures.^[9,10] Alternatively, oxidative upgrading of bio-oils can be used to isolate phenolic compounds.^[11] Moreover, an oxidative pretreatment prior to depolymerisation can improve the yield of low-molecular-weight (LMW) fragments.^[12]

The third problem is the harsh conditions needed for lignin depolymerisation.^[13] Selecting suitable solvents is an important technical and economic factor here. Methanol,^[14] ethanol^[10] or isopropanol,^[15] water/alcohol mixtures,^[16,17] or formic acid^[18] (which dissolves lignin at high temperatures) can also O-alkylate and C-alkylate the aromatic rings stabilizing the reacting lignin-derived fragments.^[5,10] Ethanol is also a formaldehyde scavenger, which may affect re-polymerisation. Moreover, ethanol can also react further under these harsh conditions,^[10,19] increasing solvent and separation costs.

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To address these problems, we approached the system from a different angle, using solvated electrons generated by sodium metal in liquid ammonia. This is not a radically new concept—the generation and application of solvated electrons were published in 1947 by Birch and MacDonald.^[20] Several studies followed in the next decades.^[21–23] Yet, all these studies were run at $-33\text{ }^{\circ}\text{C}$, in inert conditions, with excess sodium and long reaction times.

Aqueous ammonia is a well-known method for separating lignin from biomass, for example, by the Ammonia Fibre Explosion/Expansion (AFEX) process.^[24] Recently, Extractive Ammonia (EA) pretreatment of corn stover at $120\text{ }^{\circ}\text{C}$ was shown to be effective for both lignocellulose fractionation and lignin isolation.^[25] Anhydrous liquid ammonia, however, is not an innocent solvent. As we recently showed, liquid ammonia dissolves lignins, but some nitrogen is cross-linked into the structures, especially at $120\text{ }^{\circ}\text{C}$.^[26] Therefore, its reactivity in depolymerisation may be hampered. Indeed, this was experimentally observed for ethanol soluble EA lignin from corn stover.^[5]

Here, we combine the solubilisation power of liquid ammonia with the reduction power of solvated electrons, opening a route to non-pyrolytic bio-oils. We test five lignins and isolate bio-oils after treatment in liquid ammonia at $120\text{ }^{\circ}\text{C}$ and in the presence of metallic sodium at $20\text{ }^{\circ}\text{C}$. We also show that the latter treatment improves the EA lignocellulose-fractionation method.

Results and Discussion

High-temperature lignin depolymerisation in liquid ammonia

In a typical experiment, lignin was dissolved in liquid ammonia in an autoclave at $20\text{ }^{\circ}\text{C}$, and then heated for 3 h at $120\text{ }^{\circ}\text{C}/88\text{ bar}$ to study the extent of depolymerisation. After removing the ammonia, the solid residue was extracted with an organic solvent such as dichloromethane or acetone. The yields of bio-oil (organic solubles) and the residue (organic insolubles) are shown in Table 1. Except for Indulin AT (cf. Table 1, entries 1 and 2), all lignins gave less bio-oil after dissolution in liquid ammonia during 24 h at $20\text{ }^{\circ}\text{C}$ than organic solvent extraction alone (results not shown). We attribute this to covalent and/or non-covalent cross-linking induced by nitrogen incorporation

Entry	Dry lignin [mg]	Conditions	RL [wt%]	Bio-oil [wt%]	Mass balance [wt%] ^[b]
1	Indulin AT (236)	control	97.4	0.7	98.4
2	Indulin AT (236)	RT, 24 h	91.9	2.2	94.1
3	Indulin AT (236)	$120\text{ }^{\circ}\text{C}$, 3 h	92.1	10.1	102.2
4	EG MWL (49)	control	80.2	11.1	91.3
5	EG MWL (124)	$120\text{ }^{\circ}\text{C}$, 3 h	74.5	9.9	84.4

[a] Reaction conditions: 24 h treatment in 30 mL $\text{NH}_3(l)$ at $20\text{ }^{\circ}\text{C}/9\text{ bar}$ and after 3 h at $120\text{ }^{\circ}\text{C}/88\text{ bar}$. The control experiments refer to CH_2Cl_2 extraction only (without $\text{NH}_3(l)$). [b] Mass balance = RL + bio-oil.

into the lignin.^[5,26,27] This effect depends mainly on the lignin source and the temperature. Indulin AT, however, showed increased bio-oil yield after treatment at $120\text{ }^{\circ}\text{C}$ (Table 1, entry 3). Milled wood lignin isolated from elephant grass stems (EG MWL) was also tested under the same conditions (Table 1, entries 4 and 5).

Figure 1 shows the monomer yields derived from different lignins (the corresponding chromatograms are shown in Figure S5 in the Supporting Information). Indulin AT in liquid ammonia alone gave few monomers (0.04 wt%) at $20\text{ }^{\circ}\text{C}$, but at high temperature, monomer yields increased (0.81 wt%, of

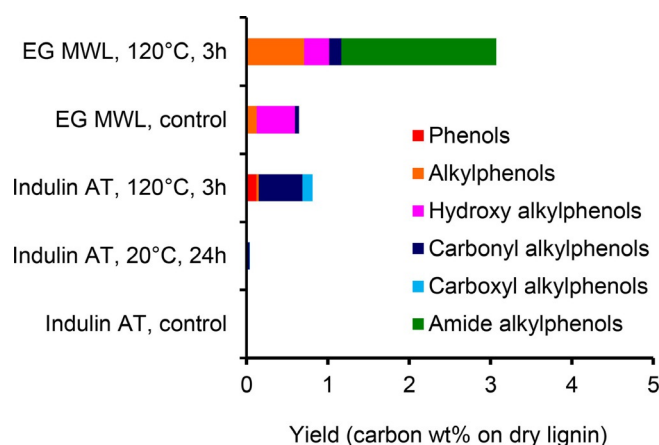


Figure 1. Monomer yield of the bio-oils obtained from Indulin AT and EG MWL by treatment in $\text{NH}_3(l)$ after 24 h at $20\text{ }^{\circ}\text{C}/9\text{ bar}$, after 3 h at $120\text{ }^{\circ}\text{C}/88\text{ bar}$ and in the control experiment.

which 33% were phenol and guaiacol). The remaining bio-oil consists of oligomers and contaminants. The EG MWL lignin yielded 3.7 wt% monomers after 3 h at $120\text{ }^{\circ}\text{C}$, compared to 1.1 wt% monomers in the control experiment. Interestingly, 59% of the monomers isolated from EG MWL consist of *p*-coumaramide and 3% of 4-hydroxy-3-methoxy-phenylpropenamide ("ferulamide"). Thus, liquid ammonia at $120\text{ }^{\circ}\text{C}$ cleaves ester-linked *p*-hydroxycinnamic acids, which are highly abundant in grasses.^[28] The effect on *p*-coumarates (PCA) and ferulates (FA) in the residual lignin (RL) of EG MWL is also seen in the HSQC 2D NMR spectra (Figure 2a and 2b). The corresponding structures from identified cross-signals are shown in Figure 3.

Table 2 shows the relative abundances of lignin inter-unit linkages, acylation degree and aromatic composition. The inter-unit linkage distribution was unchanged (except for substructures C'), retaining the $\beta\text{-O-4'}$ ether linkages. About 70% of the esterified groups in γ -position of EG MWL were removed. The signals of acetate methyl groups, which also acylate the $\gamma\text{-OH}$,^[28] disappeared in the RL. Only some residual PCA remained in the lignin structure. In agreement with the GC-MS analysis, we assigned the signals from *p*-coumaramide (PCAM, Figure 2b). The ammonolysis effect on PCA and FA was also observed during the in situ fractionation of wet corn stover in gaseous/liquid anhydrous ammonia,^[25,29] as well as after the AFEX treatment of dehydrodiferulates.^[30]

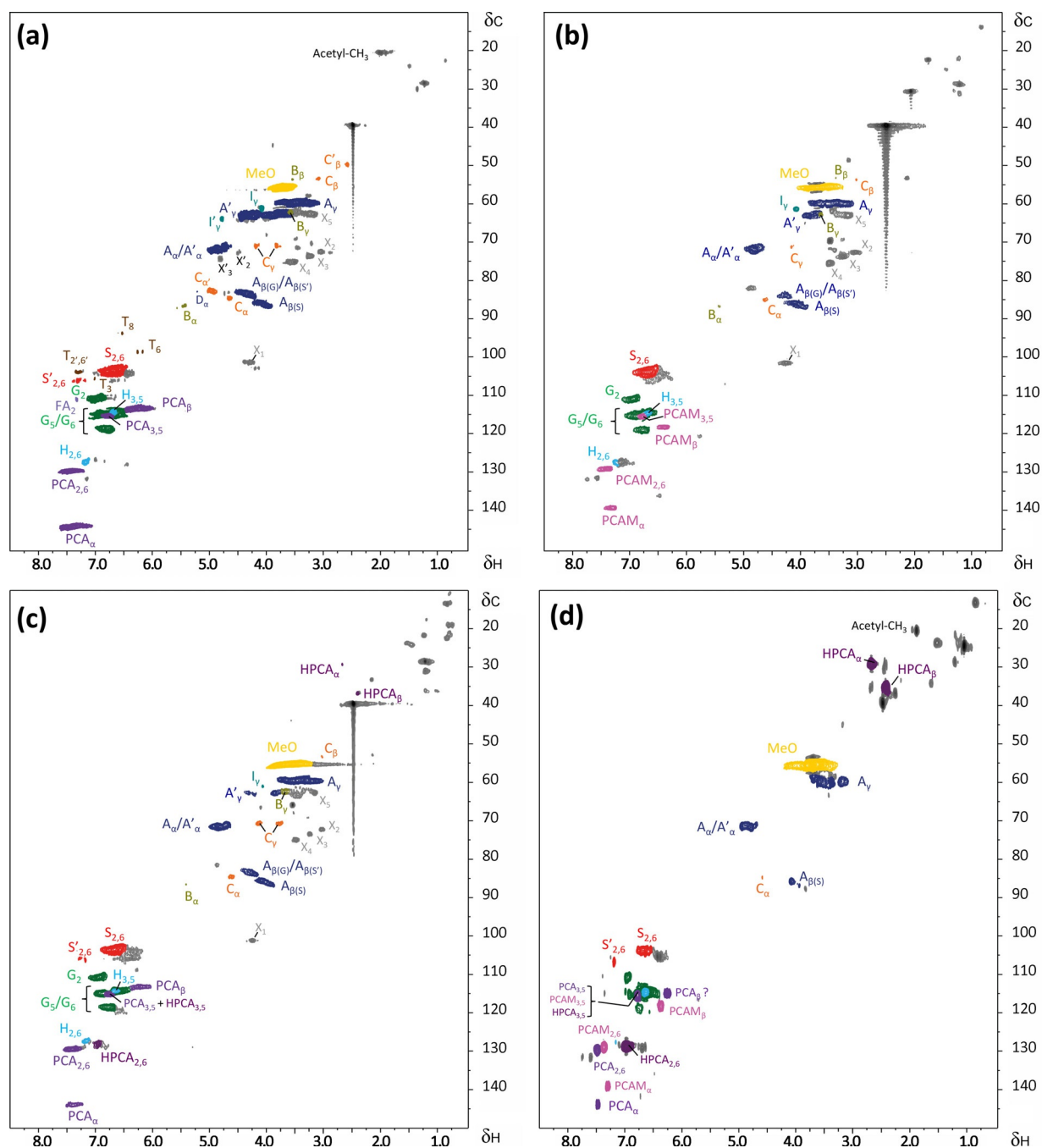


Figure 2. ^1H - ^{13}C HSQC spectra ($\delta_{\text{C}}/\delta_{\text{H}}$ 10–150/0.5–8.5 ppm) of (a) parent lignin (EG MWL), (b) RL after 3 h treatment in $\text{NH}_{3(0)}$ at 120 °C, (c) RL, (d) bio-oil, isolated after 6 h with 75 wt% $\text{Na}_{(s)}$ in $\text{NH}_{3(0)}$ at 20 °C.

Depolymerisation of isolated lignins by metallic sodium in liquid ammonia at room temperature

In the presence of metallic sodium ($\text{Na}_{(s)}$), nitrogen is not incorporated into the lignin structure, at least in the case of Indulin AT. The nitrogen content in the RL was half of that of the parent lignin (compared to a three-fold increase after treatment at 120 °C; see Table S1). We first studied the effect of the lignin type on the yields of bio-oil and monomers. Experiments were run at constant lignin loading with $\text{Na}_{(s)}$ (8.1 mmol, 75 wt% based on dry lignin) in liquid ammonia (20 mL) and

THF (10 mL) without any external hydrogen donor. The yields of RL, bio-oil and aqueous solubles (AS) are shown in Table 3. No drastic effect on the RL is observed (entries 1–8). The netto yields of bio-oil (corrected for the yield in the control experiments without using $\text{Na}_{(s)}$) range between 10–23%. Using EG MWL, 49% less RL and 40% more bio-oil was obtained compared to the control experiment (Table 3, entries 9 and 10). These results show the high reactivity of $\text{Na}_{(s)}$ in liquid ammonia towards the cleavage of aryl-alkyl ether linkages (more abundant in native lignins) and low reactivity to carbon-carbon linkages (more abundant in technical lignins).

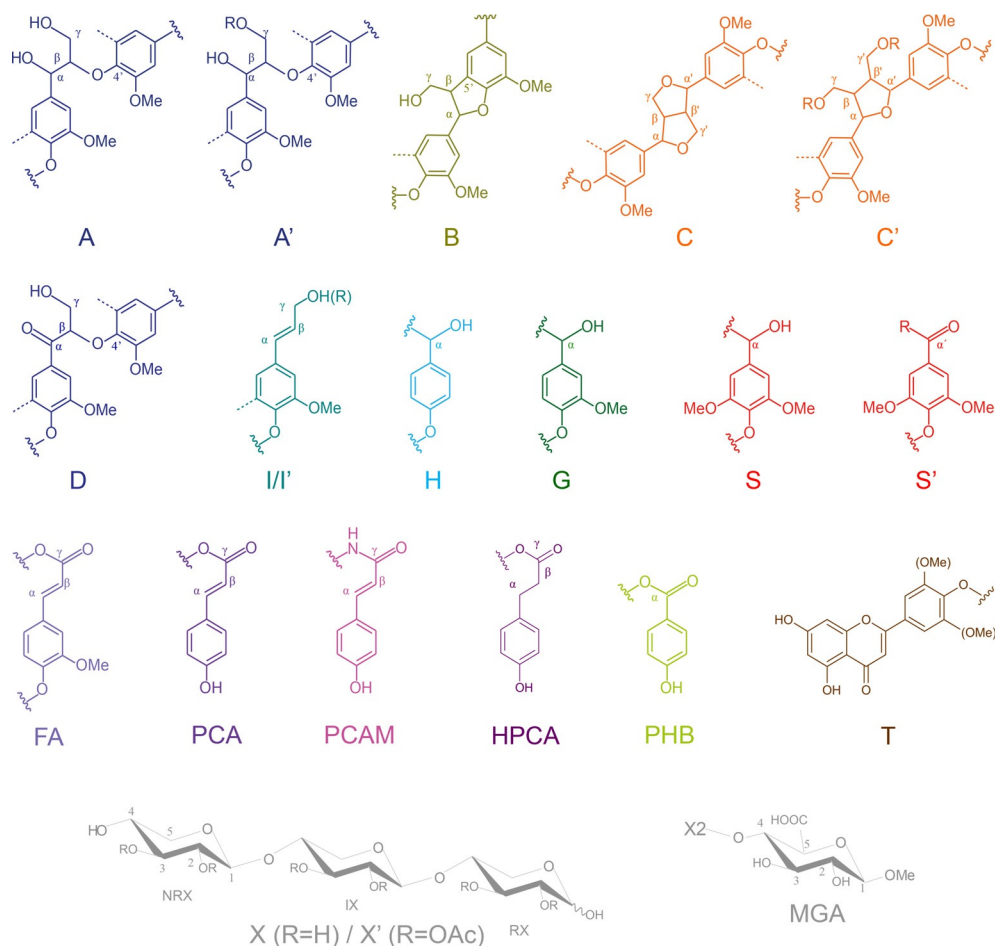


Figure 3. Structures identified in the parent lignin, residual lignin and bio-oil from EG MWL, and in the precipitated L fraction and bio-oil isolated from poplar wood fibre: **(A)** aryl-alkyl ether structures (β -O-4'), **(A')** β -O-4' structures with acylation in γ -OH, **(B)** phenylcoumaran structures (β -5'), **(C)** resinol structures (β - β'), **(C')** THF structures (β - β') with acylation in γ -OH, **(D)** C_{α} -oxidized β -O-4' structures, **(I)** *p*-hydroxycinnamyl alcohol end groups, **(I')** *p*-hydroxycinnamyl alcohol end groups with acylation in γ -OH, **(H)** *p*-hydroxy-phenyl units, **(G)** guaiacyl units, **(S)** syringyl units, **(S')** syringyl units bearing a carbonyl or carboxyl group at $C_{\alpha'}$, **(FA)** ferulate units, **(PCA)** *p*-coumarate units, **(PCAM)** *p*-coumaramide units, **(HPCA)** hydro-*p*-coumarate units, **(PHB)** *p*-hydroxybenzoate units, **(X)** β -D-xylopyranoside, **(X')** O-acetyl- β -D-xylopyranoside and **(MGA)** 4-O-methyl glucuronic xylopyranoside.

The total monomer yields obtained from the different lignins are shown in Figure 4. In the case of EG MWL, 3.1 wt% monomers were obtained. When $\text{Na}_{(s)}$ was used, all monomers were enriched with alkylphenolics such as methyl-, ethyl- and propyl-phenol/guaiacol/syringol. Remarkably, no hydrogen donor is needed for the hydrogenolysis of the aryl-alkyl linkages. The reductive cleavage may occur when the solvated electrons add to the carbon of the aryl group.^[31] Possibly, the ammonium ion (which complexes to the adjacent phenolic oxygen)^[27] acts as the hydrogen donor. Alternatively, Pernealm and Dence suggested that the hydrogen may be donated by lignin functional groups.^[32] No competing aromatic hydrogenation was observed in these conditions. The chemistry changes completely upon addition of an external hydrogen donor (loss of aromaticity). PCA-derived monomers are present in the bio-oils isolated from grass lignins. Hydro-*p*-coumaric acid (HPCA) accounts for 37% of the monomers isolated from EG MWL. In the case of poplar organosolv lignin, 35% of the isolated monomers are *p*-hydroxybenzoate (PHB)-derived, such as *p*-hydroxy-benzaldehyde and *p*-hydroxy-benzoic acid, but

surprisingly also small amounts of benzoic acid and benzamide. At first sight this is surprising as the phenol group is lacking in the latter compounds, but they are produced exclusively when poplar lignin, ammonia and sodium are used. This can be explained by the presence of PHB units in poplar lignin (see also 2D NMR results, Figure 6) and the chemistry changes when an external hydrogen donor is acting in the ammonia phase.^[32] The ratio of monomers derived from syringyl to guaiacyl is similar to the S/G ratio of the aromatic units present in the parent lignins. Thus, the composition of the monomers depends on the source and type of the lignins.

Dimers and oligomers account for the major part of the bio-oil. Size Exclusion Chromatography (SEC) analysis (Table 4, entries 1–9; for corresponding chromatograms see Figure S8) shows that all bio-oils have weight average molecular weights (M_w) ~40–60% lower than those of the parent lignins, with narrow distributions (polydispersity index, PDI, between 1.6–1.8). In contrast, the M_w and PDI of the RLs were higher than the corresponding parent lignins. When extracting the RL isolated from Indulin AT with 0 and 25 wt% $\text{Na}_{(s)}$, with CH_2Cl_2 , 4%

Table 2. Abundance of EG MWL lignin inter-unit linkages and aromatic groups at different treatment conditions.

Linkages/units	Parent lignin ^[a]	Abundance [%] ^[b]		
		120 °C, RL	75 wt% Na _(s) , 20 °C, RL	75 wt% Na _(s) , 20 °C, bio-oil
<i>lignin inter-unit linkages abundance</i> ^[c]				
β-O-4' aryl-alkyl ether (A)	54 (9.6)	49 (9.5)	55 (11.1)	70 (3.4)
β-5' phenylcoumaran (B)	2 (0.4)	2 (0.3)	1 (0.2)	0 (0.0)
β-β' resinol (C)	1 (0.2)	1 (0.2)	3 (0.5)	2 (0.1)
β-β' tetrahydrofuran (C')	3 (0.5)	0 (0.0)	0 (0.0)	0 (0.0)
α-oxidized β-O-4' substructures (D)	1 (0.1)	0 (0.0)	0 (0.0)	0 (0.0)
<i>lignin end-groups</i> ^[d]				
cinnamyl alcohol end-groups (I)	7	9	2	0
γ-cinnamyl alcohol end groups (I')	4	0	0	0
side-chain γ-acylation	40	12	13	1
<i>lignin aromatic units</i>				
H	3	3	2	2
G	40	33	36	42
S	57	64	62	56
S/G ratio ^[e]	1.4	1.9	1.7	1.4
tricin ^[d]	1.3	0.2	0.2	0.0
PCA/p-coumaric acid ^[f]	39	0	19	33
p-coumaramides ^[f]	0	24	3	50
FA ^[f]	2	0	1	0

[a] Trace correlation signals from spirodienone substructures. [b] Abundance per 100 lignin aromatic units. [c] The values between brackets compares the ratio of the inter-unit linkage correlation integral to the sum of integrals of all aromatic correlation signals. [d] Expressed as a fraction of the total lignin inter-unit linkage types A–D. [e] Expressed as ratio, instead of %. [f] Expressed as a fraction of lignin content (sum of H, G and S unit integrals).

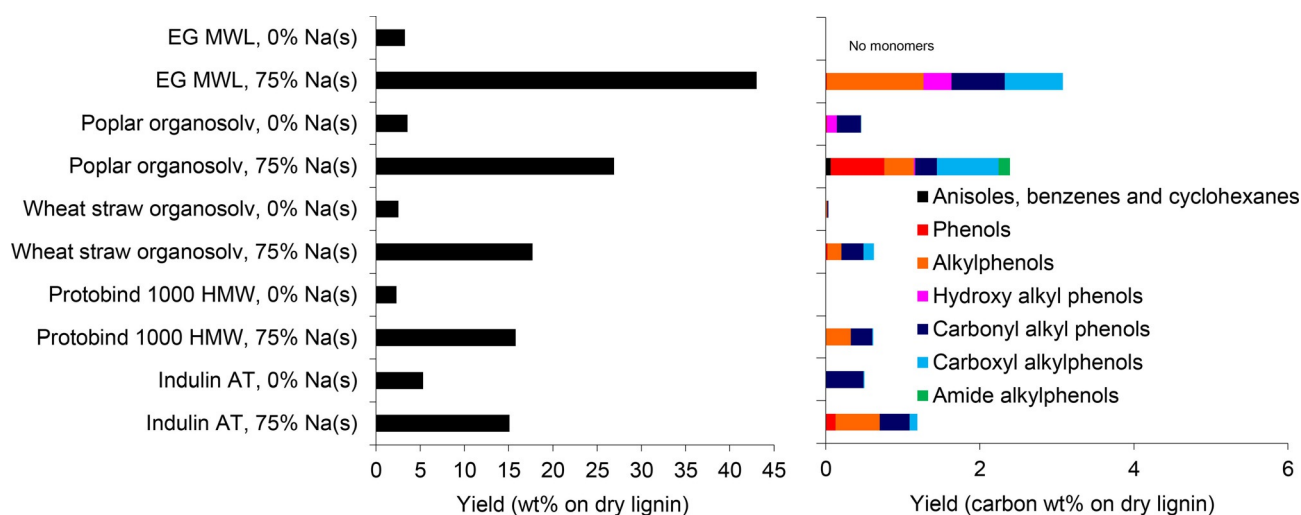


Figure 4. Bio-oil yield (left) and monomer yield (right) obtained with 75 wt% Na_(s) and 0 wt% Na_(s) in 20 mL NH₃₍₀₎ + 10 mL THF at 20 °C, from Indulin AT, Protobind 1000 LMW, Protobind 1000 HMW, wheat straw organosolv, poplar organosolv and EG MWL lignins.

and 40% CH₂Cl₂ solubles were isolated, respectively. Some of them (0.3 wt% on dry lignin) consisted of monomers that were entrapped during the precipitation of RL.

The same set of samples were also analysed by Direct Insertion Probe Electron Impact (DIP–MS, see Figure S9). The bio-oils show well-defined volatile fractions that elute earlier than the volatile fractions from the parent lignins. Interestingly, the fragments present in the first part of the chromatograms of the bio-oils are almost exclusively phenolics, whereas associated fatty-acid-derived fragments dominate in the parent lignins. The rest of the chromatograms from both parent lignin and bio-oil show mainly phenolic oligomer fractions.

We analysed the parent lignin (EG MWL), RL and bio-oil obtained after treatment with 75 wt% Na_(s) (Table 3, entries 9 and 10) by HSQC 2D NMR. Figure 2 shows their corresponding HSQC spectra and Table 2 shows the relative abundances of inter-unit linkages. At first sight, both RL and bio-oil are enriched in β-O-4 ether and β-β' resinol linkages. However, comparing the integral volume ratio of the linkage correlation signal with the sum of all aromatic signals, we see that only the RL is enriched with these linkages, whereas the bio-oil is depleted. Similar de-acylation levels are achieved compared to the high-temperature treatment mentioned before. No γ-OH-acylation is seen in all bio-oils where PCA and acetate are

Table 3. Residual lignin, bio-oil and aqueous solubles yields.

Entry	Dry lignin [mg]	Na _(s) [wt%]	RL [wt%]	Bio-oil [wt%]	AS [wt%] ^[a]	Mass balance [wt%] ^[b]
1	Indulin AT (248)	75	79.6	15.1	41.9	136.6
2	Indulin AT (248)	0	77.5	3.9	17.5	98.9
3	Protobind 1000 HMW (244)	75	78.2	15.8	-14.8	79.2
4	Protobind 1000 HMW (244)	0	84.8	2.3	15.4	102.5
5	wheat straw organosolv (247)	75	78.4	17.1	34.2	129.7
6	wheat straw organosolv (247)	0	76.1	2.5	14.3	92.9
7	poplar organosolv (248)	75	74.9	26.8	7.9	109.6
8	poplar organosolv (248)	0	80.9	3.6	8.5	93.0
9	EG MWL (99)	75	31.8	43.0	-1.2	73.6
10	EG MWL (94)	0	80.8	3.3	7.9	92.0

[a] The netto yield of AS was determined as the difference between the theoretical NaCl yield (formed upon acidification with HCl of the aqueous phase obtained after separation of RL and extraction of bio-oil) and the experimentally determined dry residual aqueous extract. Negative AS yield are caused by entrapping of Na⁺/Cl⁻ salts in the RL owing to insufficient washing. [b] In some cases the mass balance varied from 100% (see Supporting Information).

Table 4. SEC analysis of parent lignins and the corresponding residual lignin and bio-oil fractions.^[a]

Entry	Lignin	M _n ^[b]	M _w	PDI
1	wheat straw organosolv	540	2260	4.2
2	wheat straw organosolv, RL	690	2980	4.3
3	wheat straw organosolv, bio-oil	560	1000	1.8
4	poplar organosolv	570	2180	3.8
5	poplar organosolv, RL	810	3190	3.9
6	poplar organosolv, bio-oil	620	1000	1.6
7	EG MWL	460	1930	4.2
8	EG MWL, RL	760	5530	7.3
9	EG MWL, bio-oil	640	1140	1.8

[a] RL and bio-oil obtained with 75 wt% Na_(s) in 20 mL NH_{3(l)} and 10 mL THF at 20 °C. [b] Average number molecular weight.

present in free form. The HSQC spectrum of the bio-oil (Figure 2d) shows more correlation signals in the aliphatic region. In this region, signals from HPCA are assigned, together with the corresponding aromatic signals.^[33] This matches with the GC-MS results, confirming the reduction by solvated electrons.

In situ lignin depolymerisation by Na_(s) in liquid ammonia at room temperature

Here we tried to both depolymerise and remove lignin from a woody fibre (poplar). We studied the effect on the poplar lignin by adding Na_(s) in liquid ammonia for 3 h at 20 °C. After removing the ammonia and adding water, most of the Na⁺ salts were converted to NaOH_(aq) resulting in a pH of 12.5 (Na_(s)/NH_{3(l)} treatment). We compare this to the treatment in pure liquid ammonia followed by addition of water and an equimolar amount of NaOH_(s) (denoted as NH_{3(l)} + NaOH_(s), control experiment).

Adding Na_(s) leads to the isolation of non-pyrolytic bio-oil. The yield is approximately 24 wt% of the lignin content in the parent fibre whereas only 2 wt% was obtained in the control

experiment (Figure 5). After the alkali extraction, the lignin-rich fraction was isolated by acid precipitation (L fraction, ~20 wt% of the lignin content in the fibre, 19 wt% in the control, Table 5). About 58% of residual fibre was recovered, compared to 76% in the control experiment. The total lignin content was ~30% in the parent fibre (Table 6). Based on the total lignin content in the residual fibre, 60–70% of the lignin was removed from the parent fibre (cf. only 35–45% in the control). This indicates the positive effect on the lignin removal by adding Na_(s) in the liquid ammonia.

The bio-oil yield from poplar wood fibre is similar to the yield obtained from isolated organosolv poplar lignin (Table 3, entry 7). However, monomer yields are lower. Interestingly, this bio-oil is enriched with propylphenols, and particularly propylsyringol, the yield of which was 4 times higher than that of the organosolv lignin. This shows the high abundance of

syringyl units associated with β-O-4' ether linkages in native poplar lignin. In contrast, organosolv lignin yields more phenols.

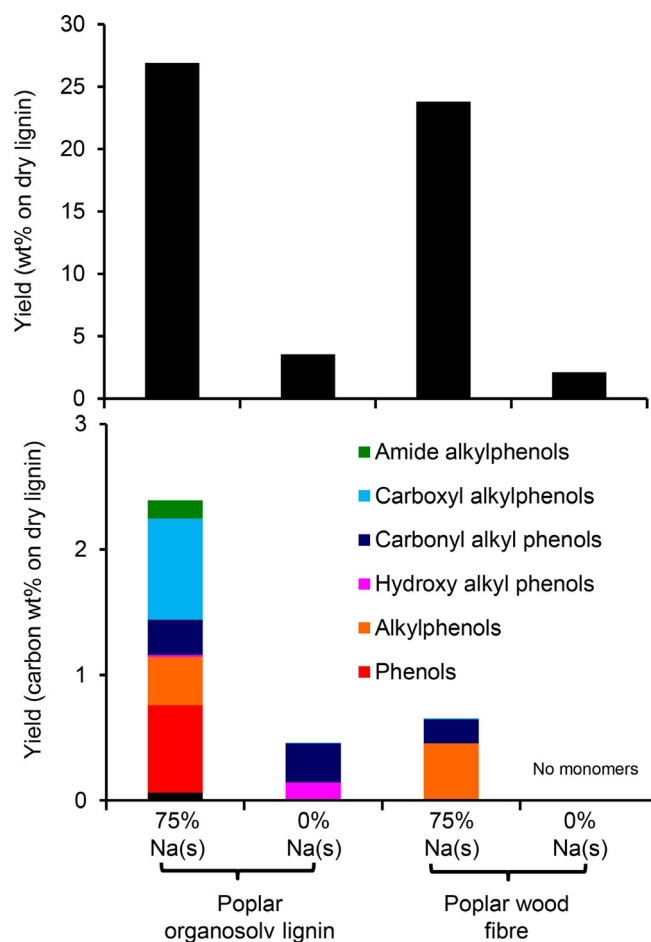


Figure 5. Bio-oil yield (up) and monomer yield (bottom) obtained at 20 °C with 75 wt% Na_(s) and 0 wt% Na_(s) from poplar organosolv and poplar lignins in situ.

Table 5. Yields of residual fibre, precipitated ligning-rich fraction, bio-oil and aqueous solubles.^[a]

Treatment	Na _(s) [mmol]	NaOH _(s) [mmol]	Residual fibre [wt %]	L fraction [wt %]	Bio-oil [wt %]	AS [wt %]	Mass balance [wt %]
Na _(s) /NH _{3(l)} ^[b]	8.1	0.0	57.8	6.0	7.0	13.1	83.9
control ^[c]	0.0	8.1	75.5	5.6	0.6	2.2	84.0

[a] All yields are in wt % on dry initial fibre. [b] Poplar wood fibre treated with 75 wt % Na_(s) in NH_{3(l)} for 3 h at 20 °C followed by alkaline extraction for 1 h/80 °C. [c] Treated with NH_{3(l)} and an equimolar amount of NaOH_(s) was added after removing ammonia to the fibre suspension for alkaline extraction.

Table 6. Total lignin content of the parent poplar wood fibre and of the residual fibre after treatment with and without Na_(s) in NH_{3(l)} at room temperature.

Sample	AIL [%] ^[a]	AL [%] ^[b]	Total lignin content [%]	Delignification [%] ^[c]
parent fibre	(27.7 ± 2.6)	(1.8 ± 0.1)	(29.5 ± 2.5)	
(Na _(s) /NH _{3(l)}), residual fibre	(13.7 ± 0.5)	(1.9 ± 0.1)	(15.5 ± 0.6)	61–70
control (NH _{3(l)} + NaOH _(s)), residual fibre ^[d]	(18.3 ± 1.1)	(2.4 ± 0.1)	(20.7 ± 1.0)	36–47

[a] Acid-insoluble lignin (wt % on dry fibre). [b] Acid-soluble lignin (wt % on dry fibre). [c] The exact value depends on how much residual fibre loss accounts for the incomplete mass balance. [d] An equimolar amount of NaOH_(s) was added to the fibre suspension for alkaline extraction.

The bio-oil and L fractions were then analysed by SEC. The bio-oil shows a low PDI (1.5). The molecular weight of the bio-oil obtained in situ from poplar lignin was low ($M_w = 650$) compared to the bio-oil obtained from organosolv poplar lignin (Table 4, $M_w = 1000$). In contrast, the L fractions have a high molecular weight and PDI ($M_w = 11\,670$, PDI ≈ 18). Furthermore, we analysed these fractions by HSQC (Figure 6; the corresponding quantification is included in Table 7). Although the bio-oil has a relatively low molecular weight, it still contains some residual β -O-4' ether linkages. Most of the acylation groups are present in the free form (*p*-hydroxybenzoic acid). The recovered L fractions contain more inter-unit linkages, and the abundances in the lignin isolated with Na_(s)/NH_{3(l)} is slightly lower compared to the control experiment. This contrasts with the SEC results, where the chromatogram of the Na_(s)/NH_{3(l)} treatment is broader in the high-molecular-weight (HMW) region. But, when looking closer to the SEC chromatograms (for details see Figure S9), the L fractions show a narrow peak in the LMW region and a broad peak in the HMW, unlike the bio-oil. Next to lignin correlation signals, the HSQC spectra of the L fractions (Figure 6a and c) also show signals from xylans and 4-O-methylglucuronoxylans, whereas the bio-oil spectrum (Figure 6b) does not contain any carbohydrate signals. From these results, we conclude that hemicelluloses or lignin-carbohydrate-complexes, as suggested by Yoo and et al.,^[29] represent the main fraction eluting in the HMW region of

the SEC chromatograms. The L fraction from the Na_(s)/NH_{3(l)} treatment contains more hemicelluloses, as seen from the higher HSQC integral ratio of the anomeric xylan correlation signal (IX₁) to the lignin methoxyl (MeO) signal (MeO) (the same can be concluded when considering the sum of lignin aromatic signals instead of the MeO signal). Moreover, the hemicelluloses present in the L fraction in the control experiment are more degraded, as seen from the higher abundance of reducing end xylopyranosyl units and 4-O-methyl- α -D-glucuronic acid residues (higher (RX₁/X₁ and MGU₁/X₁ ratios, respectively, Table 7). Adding Na_(s) improves the extraction of lignin, hemicelluloses and/or lignin-hemicellulose complexes and preserves better the extracted hemicelluloses. However, no direct conclusion can be drawn on the glucan fraction, as it is not observable in the HSQC spectra when present as crystalline cellulose.

Liquid ammonia preserves most of the carbohydrates, reduces the cellulose crystallinity and is highly selective to lignin.^[29,34–36] Therefore, EA-lignocellulose fractionation is a promising pretreatment in view of conversion to bioethanol, especially considering the much lower energy needed to recover and recycle the ammonia compared to extraction with aqueous ammonia.^[25] Our results show that the

present method is not suitable for the production of renewable aromatics as the monomer yields are too low. But, our results do show that adding Na_(s) enables the EA fractionation of lignocellulosic biomass (at least for poplar wood) under

Table 7. Abundance of lignin inter-unit linkages, aromatics and carbohydrates in the precipitated fractions and in the bio-oil.

Linkages/units	Abundance [%] ^[b]		
	(Na _(s) /NH _{3(l)}), L	(Na _(s) /NH _{3(l)}), bio-oil	control, L ^[a]
<i>lignin inter-unit linkages abundance^[c]</i>			
β -O-4' aryl-alkyl ePDIther (A)	48 (10.9)	35 (3.9)	48 (12.9)
β -5' phenylcoumaran (B)	0 (0.1)	0 (0.0)	1 (0.2)
β - β' resinol (C)	2 (0.5)	1 (0.1)	4 (1.0)
<i>side-chain γ-acylation</i>	23	4	23
<i>lignin aromatic units</i>			
H	0	0	1
G	38	39	20
S	62	61	79
S/G ratio ^[d]	1.6	1.6	3.9
PHB ^[e]	10	44	21
<i>carbohydrates</i>			
internal xylan unit/lignin methoxyl (IX ₁ /MeO)	10	0	7
reducing end xylan unit/internal xylan unit (α RX ₁ /IX ₁)	2	0	11
4-O-methyl- α -D-glucuronic acid/ β -D-xylopyranoside (MGU ₁ /IX ₁)	5	0	8

[a] Treated with NH_{3(l)} and without Na_(s), instead an equimolar amount of NaOH_(s) was added to the fibre suspension for alkaline extraction. [b] Abundance per 100 lignin aromatic units. [c] The value between brackets compares the ratio of the inter-unit linkage correlation integral to the sum of integrals of all aromatic signals. [d] Expressed as ratio, instead of %. [e] Expressed as a fraction of lignin aromatic content (H + G + S).

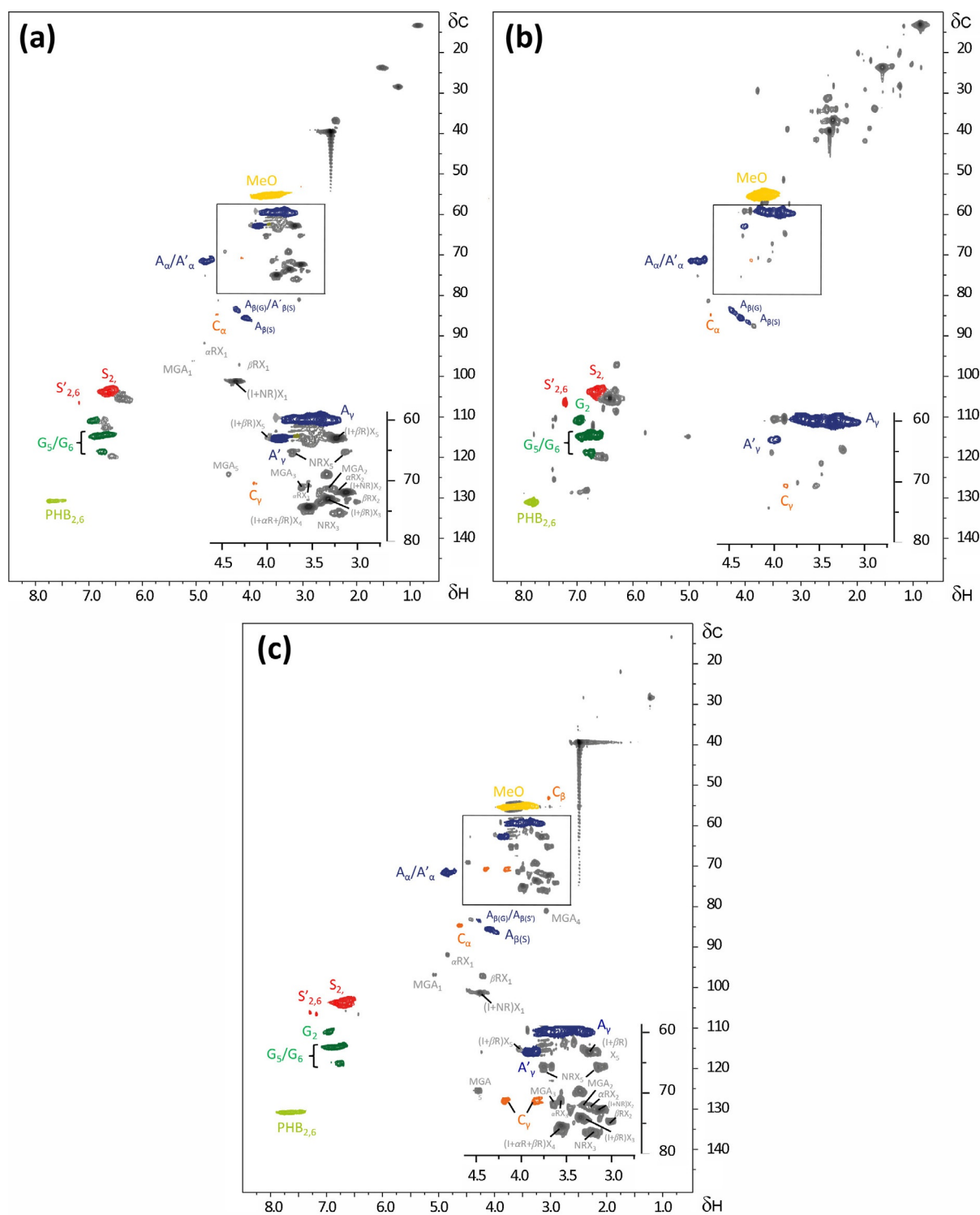


Figure 6. ^1H - ^{13}C HSQC spectra ($\delta_{\text{C}}/\delta_{\text{H}}$ 10–150/0.5–8.5 ppm) of (a) precipitated L fraction, (b) bio-oil obtained from poplar wood fibre with 75 wt% $\text{Na}_{(\text{s})}$ after 3 h/20 °C in 30 mL $\text{NH}_{3(\text{l})}$ followed by alkaline extraction for 1 h/80 °C ($\text{Na}_{(\text{s})}/\text{NH}_{3(\text{l})}$ treatment), and (c) L fraction obtained with 0 wt% $\text{Na}_{(\text{s})}$, 3 h/20 °C in 30 mL $\text{NH}_{3(\text{l})}$ followed by alkaline extraction for 1 h/80 °C, after adding an equimolar amount of $\text{NaOH}_{(\text{s})}$ ($\text{NH}_{3(\text{l})} + \text{NaOH}_{(\text{s})}$ control).

moderate conditions (20 °C/9 bar), thus avoiding the elevated pressures of ammonia at high temperature.^[25,26] Reductive depolymerisation of the lignin facilitates its extraction from the lignocellulose thereby shortening the extraction time. At first glance, the amount of $\text{Na}_{(\text{s})}$ needed for lignocellulose fractiona-

tion may seem unsustainable regarding its safety and cost (23 wt% on dry lignocellulose). However, the solvated electron method is actually applied at industrial scale to remove polychlorinated biphenyl (PCB) contaminants from (wet) soils, mainly in the USA.^[37] Moreover, in view of the application in

lignocellulose fractionation, the cost is reasonable compared to the load applied when using ionic liquids (typically around 10 wt %).^[38] In practice, the major part of the $\text{Na}_{(s)}$ cost is owed to transport-safety requirements. As $\text{Na}_{(s)}$ is produced by electrolysis of molten NaCl at high temperature, on-site production could lower the cost substantially. Alternatively, one could generate the solvated electrons by electrolysis of NaCl in liquid ammonia, as described elsewhere.^[39–41]

Conclusions

Liquid anhydrous ammonia preserves carbohydrates very well and dissolves lignins effectively while retaining their ether linkages. However, it is not an innocent solvent as after removing the ammonia some nitrogen remains incorporated in the solid residue. Adding $\text{Na}_{(s)}$ to liquid ammonia at room temperature avoids this (at least with kraft lignin) and cleaves the ether linkages, allowing depolymerisation of the lignin at ambient conditions. The bio-oil can also be produced from technical lignins, but it is enriched in oligomers and contains low amounts of phenolic monomers. The use of native lignins enriched in ether linkages leads to significantly higher bio-oil yields. Non-pyrolytic bio-oil can be isolated directly from biomass, as shown by the treatment of poplar wood fibre with $\text{Na}_{(s)}$ in liquid ammonia at room temperature with short residence times. This lignin-depolymerisation method opens opportunities for lignocellulose fractionation.

Experimental Section

Materials and instrumentation: A detailed description of the equipment used for GC–MS, DIP–MS analysis, SEC, 2D NMR and ICP–MS analysis, including calibration graphs and analysis procedures, is included in the Supporting Information.

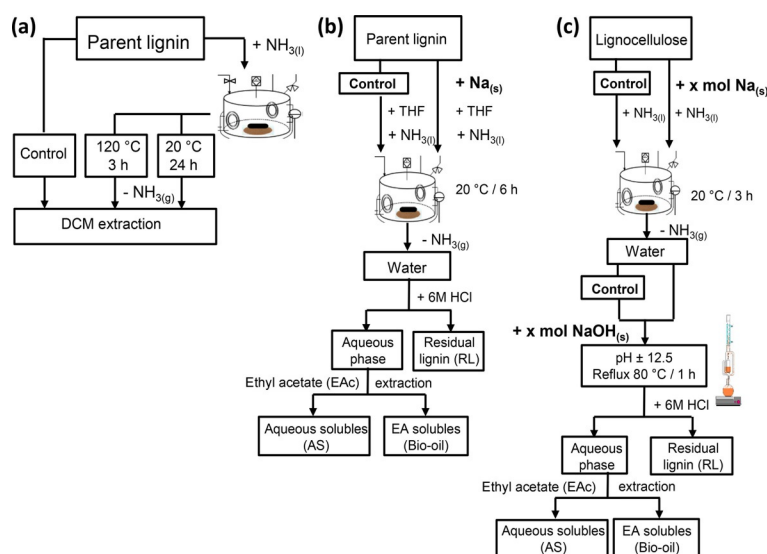
Lignin samples: Indulin AT (kraft pine wood lignin) was purchased from Sigma–Aldrich. Mixed wheat straw/Sarkanda grass soda lignin (Protobind 1000) was purchased from GreenValue S.A., Granit (Switzerland). In the case of Protobind 1000, the HMW fraction was used for the experiments. The fractionation was done by consecutive extraction steps with CH_2Cl_2 (details in the Supporting Information). Organosolv lignins were isolated from poplar wood and wheat straw at the Energy Research Centre of the Netherlands (ECN). The wheat straw fibre was cut to < 10 mm and pulped at 140 °C for 120 min using 50% w/w aqueous acetone ($L/S = 10 \text{ L kg}^{-1}$ dry weight) and H_2SO_4 (60 mM) in a 20 L batch autoclave reactor according to a patented procedure.^[42] The poplar fibre was cut to < 10 mm and pulped at 190 °C for 60 min using 50% w/w aqueous ethanol ($L/S = 10 \text{ L kg}^{-1}$ dw) and H_2SO_4 (20 mM).^[43] Both wheat straw and poplar lignins were precipitated from the organosolv liquors by adding the liquor to a three-fold excess of cold water following the work of de Wild and et al.^[44] The humidity of the different lignins was determined and the dry lignin content was used for further calculations. For the depolymerisation experiments with $\text{Na}_{(s)}$ in liquid ammonia, lignins were dried for 48 h with 40 °C / < 100 mbar (humidity 1–2%). Milled wood lignin isolated from the cortex of elephant grass

stems (EG MWL)^[28] was provided by Dr. J.C. del Río and Dr. A. Gutiérrez (IRNAS, Seville, Spain).

Biomass samples: Poplar hardwood fibre was used as whole biomass. The composition of the hardwood fibre is described elsewhere.^[45] The fibre (5.0 g, < 1 mm) was extracted twice with water (0.5 L) at 100 °C, dried at 70 °C and then extracted with acetone in a Soxhlet extractor for 8 h to remove lipophilic extractives. The extracted fibre was dried until reaching a low humidity (1–2%).

Procedure for determining lignin content: The lignin content was determined as the sum of acid-insoluble lignin (AIL) and acid-soluble lignin (ASL). The AIL content was determined as the dry residue from of extracted fibre after hydrolysis (0.300 g) with sulfuric acid according to the TAPPI method T222 om-88.^[46] The ASL was determined after the insoluble lignin was filtered off, by UV spectroscopy at 205 nm using $110 \text{ L cm}^{-1} \text{ g}^{-1}$ as the extinction coefficient.

Procedure for high-temperature lignin depolymerisation in liquid ammonia: Scheme 1a summarizes the high-temperature experiments. First, the lignin was charged in a specially built autoclave described in detail elsewhere^[26] (see also diagram and photo in the Supporting Information). For Indulin AT, 250 mg were used; for EG MWL ~100 mg were used. Then, liquid ammonia (30 mL)



Scheme 1. (a) High-temperature experiments with isolated lignins, (b) room-temperature experiments with isolated lignins and $\text{Na}_{(s)}$, (c) room-temperature experiments with lignin in situ and $\text{Na}_{(s)}$.

was charged into the autoclave. The autoclave was heated to 120 °C / 88 bar (~20 min.) and stirred for 3 h at 750 rpm (additional technical details on the working with liquid ammonia are included in the Supporting Information). Before removing the ammonia the autoclave was cooled to < 30 °C with ice. The remaining dry residue was extracted with CH_2Cl_2 (40 mL) for 3 h and filtered. The solvent was evaporated at 40 °C / 400 mbar and the extract was further dried under a nitrogen flow until reaching constant weight (in the control experiment, the lignin was directly extracted with CH_2Cl_2 at the same solid–liquid ratio for 3 h). The dry extract was then re-dissolved in CH_2Cl_2 (acetone in the case of EG MWL) for GC–MS analysis (anisole internal standard). The experiments at 20 °C / 9 bar were done identically but for 24 h instead of 3 h.

Procedure for room-temperature depolymerisation of isolated lignins by metallic sodium in liquid ammonia: Scheme 1b summarizes the experiments with isolated lignins. Example: lignin (250 mg) was added to dry THF (10 mL) in an autoclave together with Na_(s) (186 mg, 8.1 mmol). No Na_(s) was added in the control experiments. The use of THF assured the complete submersion of the Na_(s) pieces, avoiding any contact with the atmosphere inside the reactor. The autoclave was purged with air, followed by adding liquid ammonia (20 mL). In the case of EG MWL THF (4 mL) and liquid ammonia (12 mL) were used. The reaction mixture was stirred at 500 rpm for 6 h at 20 °C. The ammonia was removed as a gas, isopropanol (0.5 mL) was added followed by adding water (60 mL) to solubilise the dry residue. The lignin was precipitated by adding HCl (6 M) at pH 2.0, stored at 4 °C and separated by centrifuging (9500 rpm, 40 min, 4 °C). The lignin was recovered and dried at 70 °C until reaching constant weight. After separating the residual lignin solids, the remaining supernatant was extracted with 3 × 30 mL ethyl acetate (EAc). The organic phase was dried over MgSO₄ and the solvent was evaporated (EAc1). The residual aqueous phase was evaporated to ~20 mL and extracted with 2 × 15 mL ethyl acetate (EAc2), dried over MgSO₄ and evaporated. The bio-oil yield was determined gravimetrically from the dry combined extracts EAc1 + EAc2. The dry bio-oils were then re-dissolved in EAc (4 mL), from which an aliquot (250 µL) was taken for GC–MS analysis (anisole internal standard). The residual aqueous phase was dried at 70 °C and the AS solids were weighed. Further experimental details including photos of the various stages are included in the Supporting Information (Figure S4).

Procedure for in situ lignin depolymerisation by metallic sodium in liquid ammonia: Scheme 1c shows the experiments with in situ lignins. Extracted poplar wood fibre (852 mg dry fibre) was charged in an autoclave together with Na_(s) (8.1 mmol). Then, liquid ammonia (30 mL) was added. The mixture was stirred for 3 h at 20 °C. After removing the ammonia as a gas, water (100 mL) was added to recover all solubilised and suspended solid matter. The mixture was transferred to a round bottom flask. The pH of the aqueous fibre suspension was 12.5. This suspension was refluxed at 80 °C during 1 h under air atmosphere. Then, the suspension was cooled to 40 °C, filtered and washed with water (200 mL). The residual fibre on the filter was dried at 70 °C and weighed. The filtrate was concentrated to 100 mL by evaporation at 50 °C/90 mbar and then acidified with HCl (6 M) to pH 2.4. The precipitated L fraction was separated and the supernatant was treated further to isolate the bio-oil and the AS identically as in the isolated lignin procedure described above. Control experiments were done identically, except that no Na_(s) was added. Instead, aq. NaOH_(s) (100 mL, 8.1 mmol) was added to the solid residue in the autoclave after removing the ammonia. The pH of this aqueous phase was 12.5.

CAUTION! Working with liquid anhydrous ammonia requires special attention. We ran all our reactions in a built-to-purpose stainless steel autoclave installed in suitable premises. Metallic sodium can be handled safely under atmospheric conditions provided that a thin oxide layer is already present on the surface of the sodium pieces, but caution is required at all times.

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Keywords: biomass · bio-oils · depolymerization · lignin · liquid ammonia

- [1] Z. Strassberger, S. Tanase, G. Rothenberg, *RSC Adv.* **2014**, *4*, 25310–25318.
- [2] P. Tomani, *Cell. Chem. Technol.* **2010**, *44*, 53–58.
- [3] T. Brown, R. Brown, *Biofuels Bioprod. Biorefin.* **2013**, *7*, 235–245.
- [4] J. Zakzeski, A. L. Jongerius, P. C. A. Bruijninx, B. M. Weckhuysen, *ChemSusChem* **2012**, *5*, 1602–1609.
- [5] J. S. Luterbacher, A. Azarpira, A. H. Motagamwala, F. Lu, J. Ralph, J. A. Dumesic, *Energy Environ. Sci.* **2015**, *8*, 2657–2663.
- [6] P. Ferrini, R. Rinaldi, *Angew. Chem. Int. Ed.* **2014**, *53*, 8634–8639; *Angew. Chem.* **2014**, *126*, 8778–8783.
- [7] M. I. Jahiril, M. G. Rasul, A. A. Chowdhury, N. Ashwath, *Energies* **2012**, *5*, 4952–5001.
- [8] V. Sáez-Jiménez, M. C. Baratto, R. Pogni, J. Rencoret, A. Gutierrez, J. I. Santos, A. T. Martínez, F. J. Ruiz-Duenas, *J. Biol. Chem.* **2015**, *290*, 23201–23213.
- [9] M. Saidi, F. Samimi, D. Karimipourfard, T. Nimmanwudipong, B. C. Gates, M. R. Rahimpour, *Energy Environ. Sci.* **2014**, *7*, 103–129.
- [10] X. Huang, T. I. Korányi, M. D. Boot, E. J. M. Hensen, *Green Chem.* **2015**, *17*, 4941–4950.
- [11] H. Lange, S. Decina, C. Crestini, *Eur. Polym. J.* **2013**, *49*, 1151–1173.
- [12] A. Rahimi, A. Ulbrich, J. J. Coon, S. S. Stahl, *Nature* **2014**, *515*, 249–252.
- [13] C. Xu, R. A. D. Arancon, J. Labidi, R. Luque, *Chem. Soc. Rev.* **2014**, *43*, 7485–7500.
- [14] A. Narani, R. K. Chowdari, C. Cannilla, G. Bonura, F. Frusteri, H. J. Heeres, K. Barta, *Green Chem.* **2015**, *17*, 5046–5057.
- [15] X. Wang, R. Rinaldi, *Angew. Chem. Int. Ed.* **2013**, *52*, 11499–11503; *Angew. Chem.* **2013**, *125*, 11713–11717.
- [16] F. P. Bouxin, A. McVeigh, F. Tran, N. J. Westwood, M. C. Jarvis, S. D. Jackson, *Green Chem.* **2015**, *17*, 1235–1242.
- [17] A. McVeigh, F. P. Bouxin, M. C. Jarvis, S. D. Jackson, *Catal. Sci. Technol.* **2016**, *6*, 4142–4150.
- [18] W. Xu, S. J. Miller, P. K. Agrawal, C. W. Jones, *ChemSusChem* **2012**, *5*, 667–675.
- [19] B. Güvenatam, E. H. J. Heeres, E. A. Pidko, E. J. M. Hensen, *Catal. Today* **2016**, *259*, 460–466.
- [20] A. J. Birch, D. K. C. MacDonald, *Nature* **1947**, *159*, 811–812.
- [21] N. N. Shorygina, T. Y. Kefeli, A. F. Semchikina, *J. Gen. Chem. USSR* **1949**, *19*, 1558–1566.
- [22] A. Yamaguchi, M. Miyazaki, A. Sakakibara, *Mokuzai Gakkaishi* **1973**, *19*, 23–28.
- [23] N. Morohoshi, W. G. Glasser, *Wood Sci. Technol.* **1979**, *13*, 165–178.
- [24] J. S. Kim, Y. Y. Lee, T. H. Kim, *Bioresour. Technol.* **2016**, *199*, 42–48.
- [25] L. Da Costa Sousa, M. Foston, V. Bokade, A. Azarpira, F. Lu, A. J. Ragauskas, J. Ralph, B. Dale, V. Balan, *Green Chem.* **2016**, *18*, 4205–4215.
- [26] Z. Strassberger, P. Prinsen, F. Van Der Klis, D. S. Van Es, S. Tanase, G. Rothenberg, *Green Chem.* **2015**, *17*, 325–334.
- [27] P. Ji, J. Atherton, M. I. Page, *J. Org. Chem.* **2011**, *76*, 1425–1435.
- [28] J. C. del Río, P. Prinsen, J. Rencoret, L. Nieto, J. Jiménez-Barbero, J. Ralph, A. T. Martínez, A. Gutiérrez, *J. Agric. Food Chem.* **2012**, *60*, 3619–3634.
- [29] C. G. Yoo, H. Kim, F. Lu, A. Azarpira, X. Pan, K. K. Oh, J. S. Kim, J. Ralph, T. H. Kim, *Bioenergy Res.* **2016**, *9*, 67–76.
- [30] A. Azarpira, F. Lu, J. Ralph, *Org. Biomol. Chem.* **2011**, *9*, 6779–6787.

- [31] N. F. Éfendieva, N. N. Shorygina, N. P. Krasovskaya, *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1973**, *22*, 2748–2751.
- [32] P. A. Pernemalm, C. W. Dence, *Acta Chem. Scand.* **1974**, *28B*, 453–464.
- [33] S. Ralph, L. Landucci, J. Ralph, NMR database of lignin and cell wall model compounds, US Forest Prod. Lab.: One Gifford Pinchot Dr., Madison, WI 53705 (<http://ars.usda.gov/Services/docs.htm?docid=10491>) (accessed: January 2009), **2004**.
- [34] T. H. Kim, J. S. Kim, C. Sunwoo, Y. Y. Lee, *Bioresour. Technol.* **2003**, *90*, 39–47.
- [35] T. H. Kim, Y. Y. Lee, *Appl. Biochem. Biotechnol.* **2005**, *124*, 1119–1132.
- [36] N. Mosier, C. Wyman, B. Dale, R. Elander, Y. Y. Lee, M. Holtzapple, M. Ladisch, *Bioresour. Technol.* **2005**, *96*, 673–686.
- [37] W. L. Foutz, J. E. Rogers, J. D. Mather, *Solvated Electron Technology TM Non-Thermal Alternative to Waste Incineration-8461, WM2008 Conference, Phoenix, AZ*, **2008**.
- [38] A. Brandt, J. Gräsvik, J. P. Hallett, T. Welton, *Green Chem.* **2013**, *15*, 550–583.
- [39] C. Combellas, H. Marzouk, A. Thiebault, *J. Appl. Electrochem.* **1991**, *21*, 267–275.
- [40] L. I. Krishtalik, N. M. Alpatova, *J. Electroanal. Chem.* **1975**, *65*, 219–229.
- [41] A. G. Krivenko, N. S. Komarova, N. P. Piven, *Electrochem. Commun.* **2007**, *9*, 2364–2369.
- [42] A. T. Smit, W. J. J. Huijgen, R. J. H. Grisel, Google Patents, Improved process for the organosolv treatment of lignocellulosic biomass, WO 2015/009145, **2015**.
- [43] J. Wildschut, A. T. Smit, J. H. Reith, W. J. J. Huijgen, *Bioresour. Technol.* **2013**, *135*, 58–66.
- [44] P. J. de Wild, W. J. J. Huijgen, H. J. Heeres, *J. Anal. Appl. Pyrolysis* **2012**, *93*, 95–103.
- [45] S. Constant, H. L. J. Wienk, A. E. Frissen, P. De Peinder, R. Boelens, D. S. van Es, R. J. H. Grisel, B. M. Weckhuysen, W. J. J. Huijgen, R. J. A. Gosse-link, P. C. A. Bruijninx, *Green Chem.* **2016**, *18*, 2651–2665.
- [46] Tappi Test Methods 2004–2005, 2004, Tappi Press, Norcross, GA 30092, USA.

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