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FULL PAPER

Imidazolium based Ionic liquids as efficient reagents for lignin C-O bond cleavage

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Abstract: Lignin chemical demethylation in ionic liquids was investigated using pure lignin-model monomers and dimer together with dioxan isolated lignins from poplar, miscanthus and maize. Different methylimidazolium ionic liquids (ILs) were compared, according to two different heating processes, microwave irradiation or conventional heating in sealed tube. The conversion yield and influence of the treatments on lignin structure were assessed by ^{31}P NMR, size exclusion chromatography and thioacidolysis. The acidic IL [HMIM][Br] was shown to be an effective combination solvent/reagent for the demethylation and even depolymerisation of lignin. The relatively mild reaction conditions, the clean work-up, and the ability to reuse the ionic liquid made the described procedure an attractive and new green method for the lignin conversion to produce phenol-rich lignin oligomers.

Introduction

Lignins are abundant cell wall biopolymers essentially made of monomethoxylated guaiacyl (G) and dimethoxylated syringyl (S) p-hydroxyphenylpropane (H) units (Fig. 1) in ratios depending on their botanical origin. Due to their aromatic structure, lignins are considered as the main natural source of phenolic molecules and could thereby be an alternative to fossil-oil based aromatics. G and S units are either linked by labile ϐ-*O*-4 aryl-alkyl ether bonds, that are the most frequent interunit bonds in native lignins and the main targets of lignin chemical depolymerisation processes,[1] or by resistant interunit bonds, such as 5-5, β-5 and β-β linkages (Fig. 1).[2] Many efforts have been dedicated to improve the usability of lignins for the production of value-added aromatic products by depolymerisation or structure modifications.[3] An important feature is also the relatively low amount of free phenol groups in lignins, as most of the phenol oxygen atoms are involved in interunit linkages.[4]

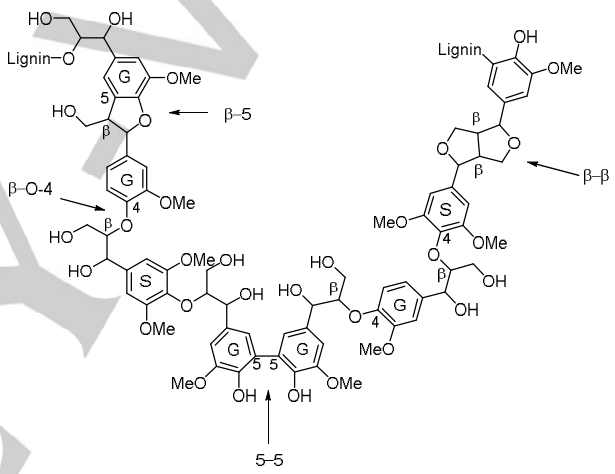

Figure 1. Schematic view of G and S phenylpropane units linked together with labile ϐ-*O*-4 and resistant bonds (5-5, ϐ-5 or ϐ-ϐ)

Therefore, a promising solution to enhance the chemical reactivity of lignins is based on aryl-alkyl ether cleavage in order to generate new reactive free phenol groups and/or induce depolymerisation.[5] The so formed oligomers, richer in free phenolic groups and also potentially exhibiting catechol moieties could thereby be used as biobased antioxidants for cosmetic and packaging applications or to substitute phenol in polymer chemistry.[6] A major drawback of usual dealkylation procedures however lies in the need of excess of reagents and/or high temperatures, favouring side reactions such as recondensation through intra- and intermolecular coupling reactions. These reactions are due to the reactivity of the substituted aromatic rings and induce reticulation of the polymer, and have been described in almost all processes dealing with lignin modification.[7] The poor solubility of most of the lignins in conventional organic solvents is also a feature to be taken in account for the design of new lignin modification processes.

A way for bypassing the solubility problem may lie in the use of ionic liquids (ILs).[8] Indeed, the potential of ILs in green chemistry processes has been proven and their good solvating properties, low vapor pressures, and high thermal stabilities make them good

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candidates to substitute a wide range of organic solvents. Moreover, they have been described as promising solvents to assist lignocellulosic biomass fractionation and/or lignins extraction.[9] On the other hand, the promising cleavage of methyl aryl ethers using ILs in the presence or not of acidic catalysts has already been described in the literature.[10] In addition, according to their structure, ILs may exhibit an acidic behaviour[11] that may enhance their efficiency for methyl-aryl ether cleavage; the mostly advocated chemical mechanism for this transformation being indeed a S_N2-like process of the phenol moiety by the IL's anion through electrophilic activation. However, to our knowledge, only one reported procedure has been conducted on ortho-substituted methyl ethers, a common structure found in lignins that may influence the course of the reaction.[12]

In this paper, we describe an efficient cleavage of alkyl-aryl ether bonds in lignins using ILs under microwave irradiation or with conventional heating in sealed tube. After optimization of the process on model compounds related to lignins, its implementation to isolated lignins will prove its ability to partially depolymerise lignins and to increase their free phenol content. As compared to published data about IL-induced demethylation of alkyl aryl ethers (Table 1), this is the first time to our knowledge that processes combining IL with MW irradiation or sealed tube heating (pressure tubes, PT) have been applied to isolated lignin.

Results and Discussion

1. Alkyl-aryl ether bond cleavage on model compounds

Our first goal was the cleavage of methyl-aryl ether bonds, and vanillin **1** was chosen as model compound exhibiting the same substitution pattern of the aromatic ring as the G units encountered in lignins. Methylimidazolium-based ionic liquids (MIM-ILs) were selected since they have been shown to be good solvents for lignocellulose dissolution,[13] used in a wide range of chemical processes. Moreover, the hydrogen in position 2 of the imidazolium ring was expected to play a role during the reaction as an acidic catalyst. From a practical point of view, they are easy to prepare and, for some of them, commercially available. Microwave irradiation (MW) was first tested as heating process, since ILs are suitable for the microwave assisted organic synthesis.[14] The reaction was also conducted in a sealed tubes under conventional heating in order to compare with microwave irradiation. The results obtained were presented in Table 2.

Table 1. Previous studies relative to demethylation of alkyl aryl ethers in ionic liquids

Entry	Substrate	IL	Temp (°C)	Time	yield (%)	Ref N°	
1	anisole	[HMIM][Br]-HBr	RT	9h	62	15c	Conventional heating
2	2-methoxynaphtalene	[BMIM][BF_4]	115	9h	97	15a	
3	Alkyl aryl ethers	[BMIM][BF_4]/MgI_2	50	4h	85 to 92	15d	
4	1-methoxynaphtalene	[BMIM][Br]	210	40min	92	16	MW
5	4-methoxyphenol	[BPy][Br]	100	4*30s	77	15b	
6	Alkyl aryl ethers	[BPy][Br]	110	30s, cycles	71 to 95	12	

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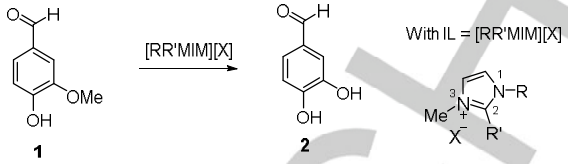
Table 2. Demethylation of vanillin in various MIM-Ils



1 **2**

Entry	R	Rô	X	IL (equiv)	Heating process	Temp (°C)	Time	Product 2 yield[a] (%)	Residual vanillin[a] (%)
1	C_4H_9	H	Br	6	MW	110	1min	24	3
2	C_4H_9	H	Br	6	MW	110	10s	47	14
3	C_4H_9	H	Br	6	MW	150	10s	12	8
4	C_4H_9	H	I	6	MW	110	10s	24	37
5	C_4H_9	H	Cl	6	MW	110	10s	29	37
6	C_4H_9	H	F	6	MW	110	10s	3	17
7	C_4H_9	H	OTf	6	MW	110	10s	0	100
8	C_4H_9	H	HSO_4	6	MW	110	10s	0	100
9	C_4H_9	H	NTf_2	6	MW	110	10s	0	100
10	C_4H_9	CH_3	Br	6	MW	110	10s	22	27
11	C_8H_{17}	H	Br	6	MW	110	10s	7	65
12	H	H	Br	6	MW	110	10s	56	11
13	H	H	Br	12	MW	110	10s	61	0
14[c]	H	H	Br	12	PT	110	5h	83	0

[a] Calculated percentages after compounds isolation by flash chromatography.

Firstly, the reactions were conducted under microwave irradiation using 6 equivalents of [BMIM][Br] for one minute at 110°C.[15] Despite an almost quantitative conversion, the desired catechol **2** was isolated in only 24% yield (entry 1). Decreasing reaction time to only 10s allowed a better yield (47%, entry 2). When using [BMIM][Br], 4-hydroxy-3-butoxybenzaldehyde was also identified as an abundant reaction product. Migration of the butyl group from the IL to the demethylated intermediates has already been described in the literature in closely related cases.[16] Higher temperature led to undesired reactions with a more important insoluble fraction (entry 3). Counter anion effect was then evaluated, and the best result was obtained with the bromide anion confirming the necessity of using a good nucleophile as imidazolium counter anion (entries 2, 4-9). The substitution at position 2 (entry 10) as well as the increase of the alkyl chain length at position 1 (entry 11) was deleterious to the yield. On the other hand, when acidic [HMIM][Br] was used, the yield raised up to 56% (entry 12). Using 12 equiv. of IL, demethylation took place in 61% yield with total conversion of the starting vanillin (entry 13). Finally the reaction was conducted in a sealed tube under conventional heating leading to the formation of the desired product in 83% yield (entry 14). However, a longer reaction time was needed (5 h) to reach a complete conversion, but the reaction was cleaner with no formation of insoluble fraction. The use of hydrobromic acid for the demethylation process was already described but it gave only poor yield. [17] This result points out the crucial role of imidazolium in the mechanism of the reaction.[18] According to these preliminary results, the following studies were carried out in [HMIM][Br] under MW irradiation for 10s at 110°C or in PT at 110°C.[19]

The same reaction was thereafter performed on commercially available guaiacylglycerol-ß-guaiacyl ether **3** (Figure 2) as a model of β-*O*-4 bonds, that are the most encountered alkyl-aryl ether groups found in lignins after methyl ethers. This compound has indeed already been used in previous works to study the acidolysis of β-*O*-4 bonds.[20] The reaction in sealed tube was first tested with a short reaction time to avoid as far as possible recondensation reactions. The substrate **3** totally disappeared in only 5 minutes. The PT treatment with this acidic IL induced the cleavage of the β-*O*-4 bond, yielding to 84% of the acidolysis ketone **4** and guaiacol **5**. With a longer PT treatment (20 minutes) the demethylation reaction occurred in addition to β-*O*-4 cleavage yielding in 78% yield the reduced and demethylated compound **6** and catechol. The low yields obtained for molecules **5** and **8** can

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be explained by the reaction work-up, the ionic liquid taking them away in the aqueous phase. On the other hand, using microwave irradiation, the reaction afforded directly ketone **6** in 95% yield. GC-MS analyses were performed to confirm the formation of ketone **6** in both cases and spectroscopic data were similar to those previously described in the literature.[21] Presence of over oxidized compounds such as α,β-diketone **7** (Figure 3) was also detected through GC-MS experiments and may explain the formation of the reduced compound **6**. The presence of such compounds was already reported in Lundquistõs work on lignin acidolysis.[22]

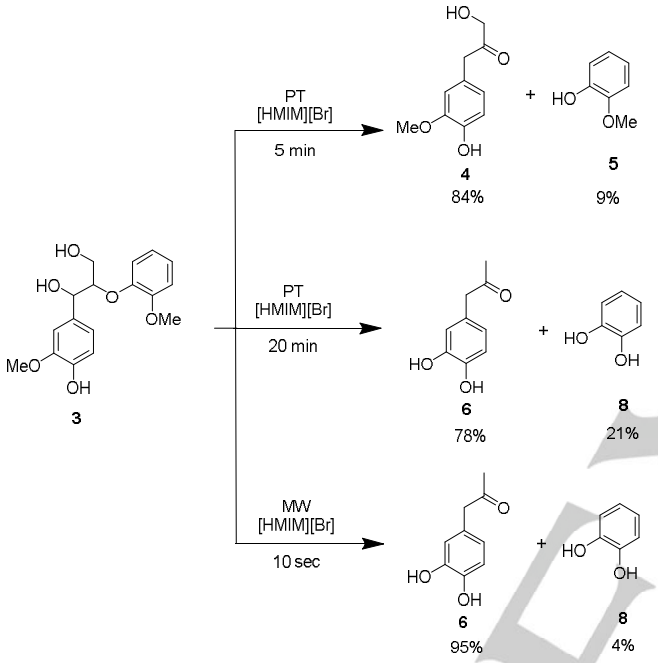

Figure 2. Reaction of the ß-*O*-4 dimer **3** in [HMIM][Br] IL (12 eq) in sealed tube (PT, 5 or 20 minutes) or in microwave (MW).

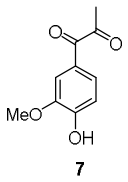

Figure 3. Schematic view of α,β-diketone **7**.

Noteworthy, no brominated phenylpropane molecules were detected in these reactions, demonstrating that the chemical mechanism leading to the cleavage of the β-*O*-4 bond is different to that of the methyl-aryl ether cleavage. β-*O*-4 bond acidolysis may result from a dehydration process, due to the presence of the hydroxyl group in benzylic position and the acidity of the reaction medium, affording the corresponding enol ether which is thereafter hydrolysed to the final ketone, as postulated in previous works.[22] Similarly, MW-assisted IL treatment gave rise in only 10s to the same catechol derivative **6** and catechol **8** with even higher reaction yield. The differences observed between the two processes can be explained by the specificities of the heating modes and devices. With MW, the absorption of the electromagnetic wave energy by IL allows a rapid rise of temperature in the medium. Stabilization of polar molecules or the transition state by magnetic field also has a direct effect on the reaction kinetics. Moreover, the employed IL may be present in two forms, ionic and methylimidazole/HBr. In the PT, the equilibrium is displaced, more HBr is released leading to a lowering of the bromide anionõs reactivity, thus increasing the reaction time in PT.

2.Application to dioxan-isolated lignin samples

2.1. Experimental strategy and lignin characteristics

The preliminary studies carried out with vanillin and with the β-*O*-4 dimer allowed us to establish that the treatment with [HMIM][Br] IL efficiently induced the demethylation of aryl methyl ether groups and the cleavage of ether bonds representative of the lignin β-*O*-4 interunit linkage. The next and most important step regarding the targeted application was to evaluate its impact on lignins. Upon lignin treatment, both bond cleavage and condensation reactions were likely to occur, leading to the formation of low-molar-mass compounds (monomers and oligomers) and polymers, respectively. In order to assess the efficiency of the treatment to depolymerize lignin and to identify markers of the depolymerisation mechanisms, ethyl acetate extractable compounds (ñsoluble fractionò) were analyzed by GC-MS, SEC and ^{31}P NMR. Ethyl acetate was selected as extraction solvent due to its non-miscibility with aqueous IL and to the good solubility of lignin low-molar-mass oligomers expected to be released by the treatment. This analysis was completed by the analysis of the residual lignin fraction (ñinsoluble fractionò) by thioacidolysis, in order to assess the proportion of residual β-*O*-4 ether bonds with respect to carbon-carbon bonds, and to bring evidences for demethylation in the polymer. The mass balance between the soluble and insoluble fraction was used as marker of the ratio between depolymerisation and condensation reactions. In view of this analytical strategy, dioxan-isolation was selected to obtain the starting lignin material from plants. Indeed, dioxan-isolated lignins combined several advantages compared to other types of isolated lignins: they keep most structural features of the native lignins, in particular a high proportion of β-*O*-4 bonds, they show low contamination degree by carbohydrates likely to interfere with lignin analysis and they contain an abundant ethyl acetate extractable fraction (about half of the lignin mass, Table 3) useful for the investigation of depolymerisation mechanisms. Three different plants representative of lignocellulosic biomass of agronomical and industrial interest for biorefinery (poplar wood, maize and miscanthus stems) were selected as starting materials for lignin isolation (Populus trichocarpa, cv. Fritzi Pauley; Zea mays, F2 line; Miscanthus giganteus). Though obtained in the

same isolation conditions, the corresponding dioxan-isolated lignins (initial samples) exhibited differences in thioacidolysis yields (2 and 3 times lower proportion of β-*O*-4 linked units in maize than in miscanthus and poplar respectively; Table 4), reflecting lignin structural variations according to botanical origin.[23] Their respective ethyl acetate-soluble fractions showed similar molar mass distributions (Figure 5) but a lower content in phenolic OH for the poplar lignin (Table 5). In order to assess the influence of botanical origin on lignin reactivity towards the treatment, the three lignins were subjected to the [HMIM][Br] treatment, either in microwave-assisted conditions or in sealed tube under inert atmosphere with a short reaction time (20 or 40 min) to limit recondensation reactions.

2.2. Mass balance of the soluble and insoluble fractions

Comparison of the amounts of soluble and insoluble fractions recovered from the initial and treated samples (Table 3) showed that PT treatment lead to an increase of the insoluble amount, whatever the lignin and the reaction time.

Table 3. Mass balance (mg) of soluble and insoluble fractions in ethyl acetate before and after treatment of DL lignins in [HMIM][Br]

DL sample	Initial mass	soluble EtOAc fraction	insoluble EtOAc fraction
Poplar DL samples			
Initial	200	98	102
MW	200	60	70
PT (20 min)	200	61	132
PT (40 min)	200	65	125
Miscanthus DL samples			
Initial	200	120	80
MW	200	71	70
PT (20 min)	200	55	135
PT (40 min)	200	57	125
Maize DL samples			
Initial	200	106	94
MW	200	75	73
PT (20 min)	200	56	142
PT (40 min)	200	57	140

Concomitant to a decrease of the soluble fraction amount, this evolution was diagnostic of condensation reactions. It was found more pronounced for the miscanthus and maize samples than for the poplar one (69% and 51% insoluble fraction increase for miscanthus and maize, respectively, against 22% for poplar). Interestingly, the MW treatment did not lead to apparent recondensation, the proportion between soluble and insoluble fractions remaining close to 50/50 after treatment. However, this treatment led to a global material loss of 26-35%, which could be explained by the generation of volatile substances and their loss in non-sealed tubes. Beside the formation of insoluble compounds with PT and material loss with MW, interesting qualitative changes in the composition of the soluble fraction were likely to occur. Therefore the ethyl acetate-extracts were analyzed by size-exclusion and gas chromatography.

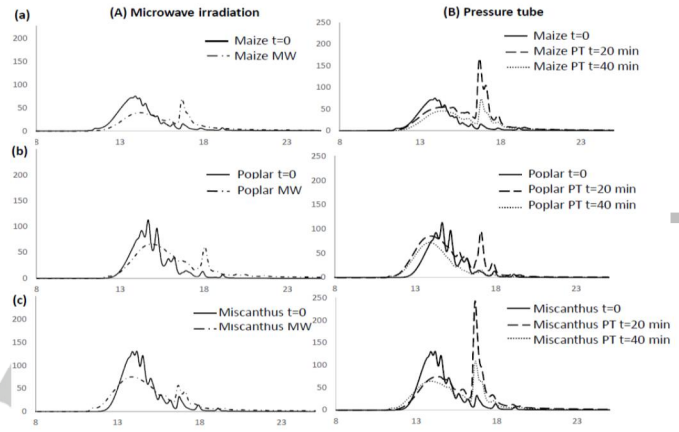

Figure 4. HPSEC-PDA profiles of the demethylation reactions using (A) microwave irradiation or (B) pressure tube on (a) maize (b) poplar or (c) miscanthus. The axes represent the elution time (min) horizontally and the absorbance at 280 nm (a.u.) vertically.

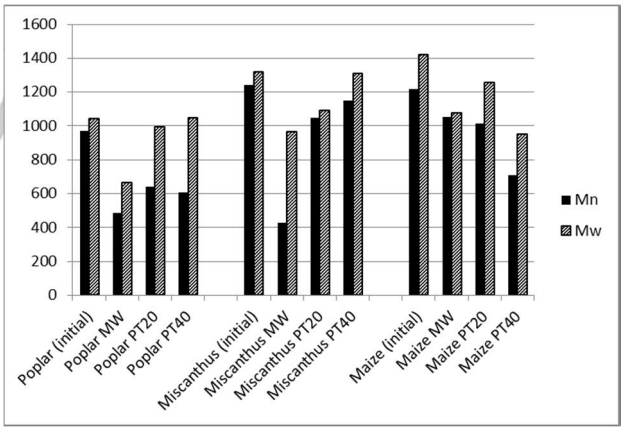

Figure 5. Estimated Mass- and Number-Average Molar Mass (Mw and Mn, g.mol^{-1}) by size-exclusion chromatography

2.4. Evidence of demethylation brought by thioacidolysis of the soluble and insoluble fractions

Thioacidolysis specifically cleaves lignin β-*O*-4 interunit bonds, releasing H, G and S thioethylated species from H, G and S lignin units only involved in labile β-*O*-4 interunit bonds.[24] Thus, the thioacidolysis yield (µmol of thioethylated monomers recovered from 1 g lignin) is indicative of the proportion of β-*O*-4 in the

sample, relative to the other types of bonds, resistant to thioacidolysis. Whatever the lignin soluble or insoluble fractions, this yield was found dramatically reduced by all the treatments (Table 4), compared to the initial lignins. The lowest final yields were obtained for the soluble fractions and with the MW treatment (4-5 µmol.g^{-1} against 7-19 µmol.g^{-1} for the PT treatments). This result was found consistent with the cleavage of β-*O*-4 bonds but could also be explained by the formation of new bonds resistant to thioacidolysis. One main advantage of thioacidolysis is to avoid side reactions and to preserve the structure of the aromatic phenyl rings of lignins. Thus, the structure of the thioethylated released products can be used to assess the structure of the initial lignin unit, in particular their methoxylation degree. Since H species (released from non methoxylated units) were recovered in very low amounts or even as trace components (<1%), only G and S species (carrying one and two methoxy groups, respectively) were taken into account for lignin structural investigation. An increase of the S/G unit ratio in all soluble and insoluble lignin fractions upon treatment was observed. This indicated that the lignin structural alterations induced by the treatments more specifically involved G units. In addition to the conventional G and S thioacidolysis monomers, the GC-MS analyses of thioacidolysis mixtures revealed the occurrence of catechol (C), of 5-hydroxyguaiacyl (5-OH G) and of 3,5-dihydroxyphenyl (3,5-OH-P) monomers released from the [HMIM][Br] IL treated samples. The recovery yields of these catechol derivatives often exceed those of the conventional monomers, as revealed by the relative importance of the corresponding peaks on the GC-MS traces (Fig. 6). This result definitely established that demethylation reactions occurred in lignins during the IL treatment, whether depolymerisation took place or not. Indeed, the demethylated units were detected after all treatments, even when no significant change in Mn and Mw were observed. Thus, whatever the treatment, ether bond cleavages were shown to take place, within methyl-aryl-ether and β-*O*-4 structures. An expected consequence of these cleavages was the release of phenolic hydroxyls, which was further investigated by ^{31}P NMR.

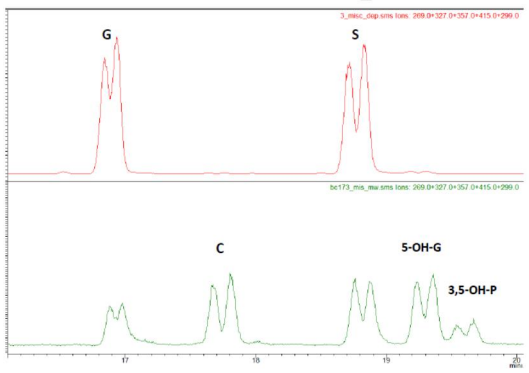

Figure 6. Lignin demethylation proofs on GC-chromatograms after thioacidolysis, example of miscanthus samples (red) before and (green) after microwave treatment.

Table 4. Amount of guaiacyl G and syringyl S monomers released by thioacidolysis of DL fractions before (initial DL) and after microwave (MW)- or pressure tube (PT)-assisted treatments in [HMIM][Br] IL.

DL sample	Soluble fraction		Insoluble fraction	
	yield (G+S) µmol/g	S/G molar ratio	yield (G+S) µmol/g	S/G molar ratio
Poplar DL samples				
Initial	1171	2.33	-	-
MW	4	3.10	-	-
PT (20 min)	19	3.03	37	3.82
PT (40 min)	16	2.92	21	3.59
Miscanthus DL samples				
Initial	807	0.91	-	-
MW	4	1.54	-	-
PT (20 min)	9	2.79	13	3.64
PT (40 min)	10	1.49	18	2.04
Maize DL samples				
Initial	411	1.28	-	-
MW	5	1.72	-	-
PT (20 min)	10	1.52	18	2.40
PT (40 min)	7	1.83	9	2.86

- Not measured

2.5. Increase in the phenolic/aliphatic OH ratio in the soluble fraction shown by ^{31}P NMR

^{31}P NMR after phosphitylation provides a way to determine the amount of functional groups in lignin, in particular hydroxyl groups accessible to the derivatisation reagent. Comparison of the functional OH group distributions of the soluble fractions before and after IL-treatments (Table 5) showed a systematic increase in the phenolic / aliphatic OH proportion, which reached for all lignin a maximum with the MW treatment. Though an increase in phenolic OH amount was expected from ether bond cleavages, the increase in the phenolic/aliphatic OH ratio mainly resulted from the severe decrease in the aliphatic OH amount. This decrease could be due to dehydration phenomenon but was also fully consistent with the depolymerisation mechanism observed for β-*O*-4 structures with formation of the acidolysis ketones and loss of one or two OH groups adjacent to the β-*O*-4 linkage (Figure 2). Accordingly, the lowest aliphatic OH amounts were obtained for the MW treatment, which was shown to induce more extensive depolymerisation. Thus, ^{31}P NMR analysis confirmed that structural changes took place within all the lignins upon treatments, whatever their botanical origin, and that MW treatment induced lignin depolymerisation through β-*O*-4 cleavage.

Table 5. ^{31}P NMR analysis[a] of the lignin samples before and after demethylation

DL sample	Aliphatic OH	Phenolic OH	Phenolic/ Aliphatic ratio
Poplar DL samples			
Initial	6.22	1.75	0.3
MW	0.01	2.52	252
PT (20 min)	0.43	3.52	8
PT (40 min)	0.24	2.61	11
Miscanthus DL samples			
Initial	5.21	2.53	0.5
MW	0.01	2.63	263
PT (20 min)	0.24	2.34	9
PT (40 min)	0.48	3.29	7
Maize DL samples			
Initial	4.23	2.55	0.6
MW	0.01	4.22	422
PT (20 min)	0.31	2.57	9
PT (40 min)	0.10	1.81	18

[a]Amount (mmol.g^{-1}) of aliphatic and phenolic (syringyl, guaiacyl and phenol) OH groups in lignin samples by quantitative ^{31}P NMR analysis.

Conclusions

In this paper, we addressed the possibility to use new processes based on ionic liquids to obtain phenols enriched oligomers from lignin in an environmentally friendly manner. We have shown that acidic IL [HMIM][Br] is an effective combination solvent/reagent for the demethylation and even depolymerisation of lignin. Among the different conditions tested, the treatment under microwave showed several advantages: the short reaction time, the limited formation of insoluble material and the final highest phenolic/aliphatic OH ratio. The relatively mild reaction conditions (low temperature compared to other lignin catalytic conversion processes[3c]), the clean work-up, the stability of the products and the ability to reuse the ionic liquid made the procedure described an attractive method for the lignin conversion. Applying different conditions in terms of time and processes allowed recovering phenolic oligomers with higher proportion of free phenolic groups. Such bio-based extracts could be advantageously used for their tunable functional properties, in particular as antioxidants in cosmetics and packaging applications.

Experimental Section

General Materials and methods

Guaiacylglycerol-β-guaiacyl ether (GG 99 %) was purchased from Tokyo Chemical Industry (Belgium). Ionic liquids [BMIM][OTf], [BMIM][HSO_4], [BMIM][NTf_2], [BDMIM][Br], [OMIM][Br] were purchased from Solvionic (France). [BMIM][I], [BMIM][Br], [BMIM][Cl], [BMIM][F], [HMIM][Br] were synthesized in the lab following previously reported procedures (supporting information S1 and S2).[25] Ethyl acetate, cyclohexane, diethyl ether were purchased from Carlo Erba Reagents (France) and were used as received. All other reagents were purchased from Sigma-Aldrich Chemical Co. (USA) and were used as received.

Microwave experiments were conducted in an Anton Paar Monowave 300 instrument using the following method: P=300W, Tmax= 110°C, Ramp 30s, Hold 10s, Full air cooling ON, Stirring ON. TLC experiments were performed on an aluminium strip coated with Silica Gel 60 F_{254} from Macherey-Nagel, revealed under UV-light (254 nm), then in the presence of a 5% w/w ethanolic solution of phosphomolybdic acid. Evaporations were conducted under reduced pressure at temperatures below 35°C unless otherwise stated. Column chromatography (CC) was carried out with an automated flash chromatography PuriFlash system and pre-packed INTERCHIM PF-30SI-HP (30 εm silica gel) columns. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ or CD_3OD at 400, 100 and 162 MHz respectively on a Bruker Ascend instrument. Chemical shifts are reported in parts per million relative to internal references (solvent signal or phosphorylated cyclohexanol). High-resolution mass spectra (HRMS) were recorded on a Bruker Impact II instrument, the accurate masses are reported for the molecular ion $[M-H]^-$ and are reported with an error <2 ppm.

Plant material. Isolation of DL fractions. Dioxan lignin fractions were isolated from three different plants representative of lignocellulosic biomass, prepared from poplar wood (Populus trichocarpa, cv. Fritzi Pauley), mature maize (Zea mays, F2 line) or miscanthus (Miscanthus giganteus) stems according to a published procedure.[26] About 30g of sample was suspended in 50mL of a dioxan: 0.2 M HCl aqueous solution (9:1, v/v) mixture. The suspension was heated at 100°C. After 30 minutes, the cooled reaction mixture was filtered over a Büchner funnel, and the residue was washed three times with 10 mL of a dioxan:HCl mixture (9:1, v/v). All the filtrates containing the dissolved lignins were pooled, and the pH of the resulting solution was adjusted to pH 3-4 (saturated $NaHCO_3$ aqueous solution). The solution was concentrated under reduced pressure at 45°C to about 10 mL. The concentrated DL solution was then injected into about 100 mL of cold water under magnetic stirring. The lignin precipitate was recovered by centrifugation (30 min at 2,000*g* and 10°C), washed with pure water, centrifuged again, and freeze-dried to recover a purified DL fraction (supporting information S5).

GC-MS analysis. In a 200 µl GC-MS vial fitted with a Teflon-lined screwcap, 20 µl of ethyl acetate solutions (1mg/ml previously dried on sodium sulfate) were silylated with 100 µl of bistrimethylsilyl-trifluoroacetamide (BSTFA) and 10 µl of GC-grade pyridine. The silylation was completed within few minutes at room temperature. The GC-MS analyses were performed on an Agilent Instrument, with a poly(dimethylsiloxane) column (30 m × 0.25 mm; Rxi-5Sil, RESTEK), working in the temperature program mode from 70 to 330 °C at +30°C min^{-1}, during 20 minutes, with helium as carrier gas, a moving needle type injector and a flame ionization detector. The chromatographic system was combined to a quadrupole spectrometer operating in the electron impact mode (70 eV), with a source at 230°C and an interface at 300°C, and with a 50 to 800 m/z scanning range (supporting information S6).

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Quantitative ^{31}P NMR and samples preparation. Derivatization of the lignin samples with 2-chloro-4,4ǫ5,5ôtetramethyl-1,3,2-dioxaphospholane (TMDP, Sigma-Aldrich, France) was performed according to Granata *et al*. (1995). Lignin samples (20 mg) were dissolved in 400 µL of a mixture of anhydrous pyridine and deuterated chloroform (1.6:1 v/v). Then was added 150 µl of a solution containing cyclohexanol (6 mg/mL) and chromium(III)acetylacetonate (3.6 mg/mL), which served as internal standard and relaxation reagent respectively. NMR spectra were acquired on a Bruker Biospin Avance III 400 MHz spectrometer. A total of 128 scans were acquired with a delay time of 6 s between successive pulses. The spectra were processed using Topspin 3.1. All chemical shifts are reported relative to the product of TMDP with cyclohexanol, which has been observed to give a doublet at 145.1 ppm referenced from the water-TMDP signal (132.2 ppm). The content of hydroxyl groups (in mmol.g^{-1}) was calculated on the basis of hydroxyl groups contained in the internal reference cyclohexanol and by integration of the following spectral regions: aliphatic hydroxyls (150.8ï 146.4 ppm), condensed phenolic units (145.8-143.8 ppm; 142.2-140.2 ppm), syringyl phenolic hydroxyls (143.8-142.2 ppm), guaiacyl phenolic hydroxyls (140.2ï 138.2), *p*-hydroxyphenyl phenolic hydroxyls (138.2ï 137.0 ppm), and carboxylic acids (136.6-133.6 ppm) (supporting information S7).

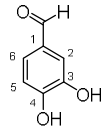
Thioacidolysis. Thioacidolysis of lignins (5 mg) was carried out according to the literature,[27] using heneicosane ($C_{21}H_{44}$, Fluka) as internal standard (IS). Lignin-derived p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) thioacidolysis monomers were analyzed as their trimethylsilyl derivatives by a gas chromatographyī mass spectrometry (GC-MS) instrument (Saturn 2100, Varian) equipped with a poly(dimethylsiloxane) column (30 m × 0.25 mm; SPB-1, Supelco) and using the following heating program: 40 to 180 °C at 30 °C minï 1, then 180 to 260 °C at 2 °C minï 1. The mass spectrometer was an ion trap with a ionization energy of 70 eV and positive mode detection. Quantitative determination of H, G, and S monomers was performed from ion chromatograms reconstructed at m/z 239, 269, and 299, respectively, as compared to the IS signal measured from the ion chromatogram reconstructed at m/z (57 + 71 + 85). The molar yield of the detected thioethylated monomers was calculated on the basis of the Klason lignin content of the sample, determined according to a published procedure.[28]

Molar Mass (MM) Distribution. The mass-average MM of each lignin sample was estimated via high-performance size-exclusion chromatography (HPSEC) using a styrene - divinylbenzene PL-gel column (Polymer Laboratories, 5 µm, 100 Å, 600 mm x 7.5 mm I.D.) with photodiode array detector (Dionex Ultimate 3000 UV/vis detector) set at 280 nm UV and THF (1 mL.minī 1) as eluent. Samples were solubilized in THF, filtered on PTFE membrane 0.45 ε m before analysis by HPSEC. Polymerisation degrees were assessed from the apparent molar masses determined by a calibration curve based on polyethylene oxide standards (Igepal, Aldrich) and injection of pure coniferyl alcohol monomers and dimers.

Synthetic procedures

Procedure for vanillin under microwave irradiation, data reported in Table 1.

The ionic liquid was vacuum dried at room temperature before use. Vanillin (100 mg, 0.66 mmol) and the appropriate quantity of ionic liquid (6 or 12 equivalents, see Table 1) were placed in an Anton Paar 30 mL reaction tube with a magnetic stirrer. The mixture was irradiated with P=300 W, Tmax=110°C, Ramp 30 sec, Hold 10 sec, with full air cooling and stirring. At the end of the reaction, water (10 mL) and ethyl acetate (10 mL) were added. The biphasic solution was filtered to remove solid residues, if any. The layers were separated, the aqueous layer was extracted with ethyl acetate (2* 10 mL). The combined ethyl acetate extracts were dried on $MgSO_4$ and concentrated under reduced pressure. The resulting 3,4-dihydroxybenzaldehyde **2** and the residual vanillin were purified by flash column chromatography (elution with 50 to 100% ethyl acetate in cyclohexane).



2

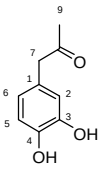
R_f =0.32 (cyclohexane/ethyl acetate 1:1); brown spot; ^{1}H NMR (400 MHz, CD_3OD, 25°C): δ_H 6.91 (d, ^3J(H/H)=8.0 Hz, 1H, H_5), 7.31 (s+d, ^3J(H/H)=8.0 Hz, 2H, H_2 and H_6), 9.69 (s, 1H, CHO); ^{13}C NMR (100 MHz, CD_3OD, 25°C): δ_C 117.21, 125.03, 117.43 (C_2, C_5 and C_6), 130.45, 146.62, 153.14 (C_1, C_3 C_4), 191.85 (CO); HRMS: m/z [M-H]$^-$ calcd for $C_7H_5O_3$: 137.0239, found: 137.0243.

Procedure for vanillin in sealed tube, data reported in Table 1.

The ionic liquid was vacuum dried at room temperature before use. Vanillin (100 mg, 0.66 mmol) and [HMIM][Br] (1.27 g, 12 equivalents relatively to vanillin) were added into an Ace pressure tube (Ace glass Inc., Sigma Aldrich) with a magnetic stirrer under inert atmosphere. The tube was sealed and the mixture was stirred in an oil bath at 110 °C. After 5 hours, water (10 mL) and ethyl acetate (10 mL) were added. The layers were separated, the aqueous layer was extracted with ethyl acetate (2* 10 mL). The combined ethyl acetate extracts were dried on $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (elution with 50 to 100% ethyl acetate in cyclohexane) to yield 83% of 3,4-dihydroxybenzaldehyde **2**.

Procedure for Guaiacylglycerol-β-guaiacyl ether 3 under microwave irradiation, data reported in Figure 2.

The ionic liquid was vacuum dried at room temperature before use. Guaiacylglycerol-β-guaiacyl ether **3** (100 mg, 0.31 mmol) and [HMIM][Br] (610 mg, 12 equivalents relatively to **3**) were placed in an Anton Paar 30 mL reaction tube with a magnetic stirrer. The mixture was irradiated with P=300 W, Tmax=110°C, Ramp 30 sec, Hold 10 sec, with full air cooling and stirring. At the end of the reaction, water (10 mL) and ethyl acetate (10 mL) were added. The layers were separated, the aqueous layer was extracted with ethyl acetate (2* 10 mL). The combined ethyl acetate extracts were dried on $MgSO_4$ and concentrated under reduced pressure. The resulting mixture was purified by flash column chromatography (elution with 50 to 100% ethyl acetate in cyclohexane) to yield 95% of product **6**. The product was characterized by NMR and mass spectrometry.



6

R_f =0.33 (cyclohexane/ethyl acetate 1:1); ^{1}H NMR (400 MHz, CD_3OD, 25°C): δ_H 2.10 (s, 3H, $CH_{3\text{-}9}$), 3.55 (s, 2H, $CH_{2\text{-}7}$), 6.52 (dd, ^3J(H/H)=8.0 Hz and ^4J(H/H)=2.0 Hz, 1H, H_6), 6.63 (dd, ^4J(H/H)= 2.0 Hz, 1H, H_2), 6.71 (d,

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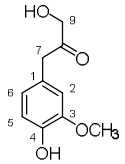
^3J(H/H)=8.0 Hz, 1H, H_5); ^{13}C NMR (100 MHz, CD_3OD, 25°C): δ_C 27.44 (C_9), 49.59 (C_7), 115.12, 116.06, 120.43 (C_2, C_5 and C_6), 125.87, 145.14, 145.65 (C_1, C_3 C_4), 208.85 (CO); HRMS: m/z [M-H]$^-$ calcd for $C_9H_9O_3$: 165.0552, found: 165.0560.

Procedure for Guaiacylglycerol-β-guaiacyl ether 3 in sealed tube 5 minutes, data reported in Figure 2.

The ionic liquid was vacuum dried at room temperature before use. Guaiacylglycerol-β-guaiacyl ether **3** (100 mg, 0.31 mmol) and [HMIM][Br] (610 mg, 12 equivalents) were placed into the Ace pressure tube with a magnetic stirrer under inert atmosphere. The tube was sealed and the mixture was stirred in an oil bath at 110 °C. After 5 minutes, water (10 mL) and ethyl acetate (10 mL) were added. The layers were separated, the aqueous layer was extracted with ethyl acetate (2* 10 mL). The combined ethyl acetate extracts were dried on $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (elution with 50 to 100% ethyl acetate in cyclohexane) to yield 84% of product **4**. The product was characterized by NMR and mass spectrometry.



4

R_f =0.43 (cyclohexane/ethyl acetate 1:1); ^{1}H NMR (400 MHz, CD_3OD, 25°C): δ_H 3.82 (s, 3H, OCH_3), 3.62 (s, 2H, $CH_{2\text{-}7}$), 4.26 (s, 2H, $CH_{2\text{-}9}$), 6.66 (d, ^3J(H/H)=8.2 Hz, 1H, H_6), 6.73 (d, ^3J(H/H)=8.2 Hz, 1H, H_5), 6.80 (s, 1H, H_2); ^{13}C NMR (100 MHz, CD_3OD, 25°C): δ_C 45.64 ($CH_{2\text{-}7}$), 56.46 (CH_3), 67.59 ($CH_{2\text{-}9}$), 114.23, 115.06, 122.83 (C_2, C_5 and C_6), 125.97, 147.18, 147.65 (C_1, C_3 C_4), 208.95 (CO); HRMS: m/z [M-H]$^-$ calcd for $C_{10}H_{11}O_4$: 195.0657, found: 195.0656.

Procedure for Guaiacylglycerol-β-guaiacyl ether 3 in sealed tube 20 minutes, data reported in Figure 2.

The ionic liquid was vacuum dried at room temperature before use. Guaiacylglycerol-β-guaiacyl ether **3** (100 mg, 0.31 mmol) and [HMIM][Br] (610 mg, 12 equivalents) were placed into the Ace presssure tube with a magnetic stirrer under inert atmosphere. The tube was sealed and the mixture was stirred in an oil bath at 110 °C. After 20 minutes, water (10 mL) and ethyl acetate (10 mL) were added. The layers were separated, the aqueous layer was extracted with ethyl acetate (2* 10 mL). The combined ethyl acetate extracts were dried on $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (elution with 50 to 100% ethyl acetate in cyclohexane) to yield 78% of product **6**.

Procedure for Dioxan extracted Lignin samples under microwave irradiation, data reported in Tables 2, 3, 4.

The ionic liquid was vacuum dried at room temperature before use. DL samples (200 mg) and [HMIM][Br] (1g, excess to dissolve DL) were placed in an Anton Paar 30 mL reaction tube with a magnetic stirrer. The mixture was irradiated with P=300 W, Tmax=110°C, Ramp 30 sec, Hold 10 sec, with full air cooling and stirring. At the end of the reaction, water (10 mL) and ethyl acetate (10 mL) were added. The layers were separated, the aqueous layer was extracted with ethyl acetate (2* 10 mL). The combined ethyl acetate extracts were dried on $MgSO_4$ and concentrated under reduced pressure. The crude mixture was analysed by ^{31}P NMR, HPSEC and thioacidolysis.

Procedure for Dioxan extracted Lignin samples in sealed tube, data reported in Tables 2, 3, 4.

The ionic liquid was vacuum dried at room temperature before use. DL samples (200 mg) and [HMIM][Br] (1g, excess to dissolve DL) were placed into the Ace presssure tube with a magnetic stirrer under inert atmosphere. The tube was sealed and the mixture was stirred in an oil bath at 110 °C. After 20 or 40 minutes, water (10 mL) and ethyl acetate (10 mL) were added. The layers were separated, the aqueous layer was extracted with ethyl acetate (2* 10 mL). The combined ethyl acetate extracts were dried on $MgSO_4$ and concentrated under reduced pressure. The crude mixture was analysed by ^{31}P NMR, HPSEC and thioacidolysis.

Recycling of the ionic liquid.

The aqueous layer, containing the unreacted ionic liquid [HMIM][Br], was kept and concentrated under vacuum. The resulting ionic liquid was washed with ether. An NMR spectrum was realized showing the recovery of a very clean ionic liquid. 75% of the starting [HMIM][Br] was recovered and usable for further similar reactions.

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Keywords: biomass Å dealkylation Å green chemistry Å ionic liquids Ålignin

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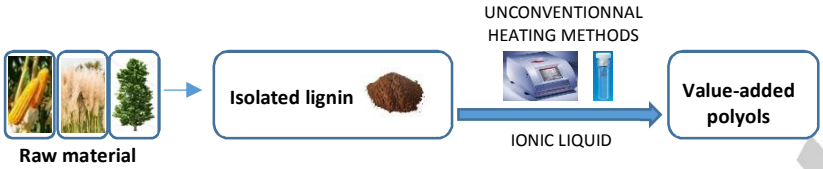

Lignin chemical demethylation in ionic liquids was investigated using pure lignin-model monomers and dimer together with dioxan isolated lignins from poplar, miscanthus and maize. Different methylimidazolium ionic liquids were compared, according to two different heating processes, microwave irradiation and conventional heating in sealed tube.

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Ionic liquids as efficient reagents for lignin C-O bond cleavage

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