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Ionic liquids catalyzed lignin liquefaction: Mechanistic studies using TPO-MS, FT-IR, RAMAN and 1D, 2D-HSQC/NOSEY NMR

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ABSTRACT. Valorization of profusely available alternate resource, biomass and in particular its 3-D intricate component lignin into low molecular weight aromatic products those are used as platform chemicals and fuel additives, by developing low temperature catalytic process is imperative to preserve atom efficiency. Ionic liquids due to their unique properties offer an advantage to develop such methods under milder conditions. Herein we show, use of $–SO_3H$ functionalized imidazolium based various recyclable Brønsted acidic ionic liquids (BAILs) in catalytic quantity under ambient pressure at 120 °C for depolymerization of lignin (60000 g/mol) into THF soluble products with high efficiency (78% yield, 95±5% mass balance). The decoding of this efficiency by 1D and 2D (HSQC/NOSEY) NMR, FT-IR and RAMAN studies exemplify that the –OH group(s) interact with electron deficient cation of BAIL. The mechanistic insights

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unraveled in this work open plethora of opportunities to design catalysts for developing efficient processes.

Introduction.

The non-edible lignocellulosic biomass (agriculture waste) made up of cellulose, hemicelluloses and lignin is the only alternate renewable resource of C, H and O elements available to us. Lignin (15-25 dry wt%), a cross-linked 3-D amorphous phenolic polymer accessible in plenty as a by-product from paper & pulp industry, is drawing lot of interest as an alternate resource for the synthesis of chemicals and fuels.[1-4] To attain the ambitious targets set for the synthesis of at least fraction of chemicals from biomass in near future and to augment the prospects of cellulose to ethanol process becoming lucrative, it becomes imperative to convert lignin into chemicals by developing competent methods.[3, 5, 6]

To invigorate the efforts in valorizing lignin, series of catalytic processes based on homogeneous base (>260 ^{o}C)[7, 8]; supported metal catalysts (200-450 ^{o}C; H_2, 40-180 atm)[2, 9, 10]; stand-alone homogeneous acids (H_3PO_4) or along with metal catalyst[11] etc. are developed to yield organic solvent soluble low molecular weight compounds. Moreover, exploitation of supercritical water (T_c=373.6 ^{o}C; P_c=246.7 atm)[12-14] as well is known to yield aromatic compounds along with char, tar and gas ($CO/CO_2/CH_4$/alkanes) formation. Solid acid based high temperature cracking (>300 ^{o}C)[15] and hydrolysis (<250 ^{o}C)[16, 17] is too known to yield aromatic monomers and gases. Of late, employment of ionic liquids (ILs) in the biomass conversions is intensifying since ILs are regarded as green solvents and have exploitable tunable properties.[18, 19] Use of ILs chiefly as a solvent is also identified in the depolymerization of lignin to facilitate the action of catalyst.[20-22] A recent study suggests that ionic liquid ([EMIM][CF_3SO_3]) and metal nitrate ($Mn(NO_3)_2$) can

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mediate depolymerization of lignin to yield aromatic products.[21] Few other reports as well scrutinize the role of different ionic liquids on the structures of pre-treated lignins.[23-30]

While in most of the works, ILs are used as solvents along with other catalysts[20, 21, 31-33], the methodical investigations on the correlation of lignin properties with products and mechanistic studies on the interaction between lignin and catalyst is poorly done. Moreover, use of ILs on larger scale as solvent would be costly and due to their viscous nature can become a hurdle in achieving higher yields. One acknowledged limitation in majority of the above studies is employment of model compounds (dimer/trimer) to demonstrate the competency of method.[34, 35] This is because lignins have very high molecular weights (>3000 Da) and those consists of difficult to cleave diversified linkages (β-O-4, α-O-4, β-5, β-1, β-β, 4-O-5 etc.; ESI, Section S1, Table S1, Fig. S1†), which all are not present in most of the model compounds.[36, 37] Additionally, in reality, impurities (Na, S, ignition residue) associated with lignin can pose a challenge in reuse of catalysts with the matching efficiency. Furthermore, use of high temperatures leads to formation of degradation products (char, tar) and thus it is necessary to achieve conversions at lower temperatures to accomplish higher atom efficiency by avoiding formation of char, tar and gases.

Considering these shortcomings; it was contemplated to make use of ILs in catalytic amount for the depolymerization of (real) lignin without addition of supplementary catalyst in presence of water and alcohols. To accomplish this, exploitation of Brønsted acidic ionic liquids (BAILs) in depolymerization of lignin by virtue of cleavage of ether (β-O-4 etc.) bonds due to presence of $-SO_3H$ groups was contemplated. Given that both, BAIL and substrate are polar, those can form homogeneous phase in polar solvent (water/alcohols) and thus, diffusion limitations can be conquered to enhance the reaction rate. Besides, after reaction it was hypothesized that easy

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separation of BAILs from products (organic solvent extraction) will facilitate easy recycling of catalyst. Furthermore, despite its significance, current knowledge on the fundamental understanding on the depolymerization of lignin is limited[38], and hence robust evaluation of results to ascertain the reaction pathway is crucial. Subsequently in this work, reasonable deliberations on the mechanism through studies of ILs for their interaction with (real) lignin, structures & functional groups etc. were made by meticulous characterization of lignin and products.

In view of this, diverse imidazolium based BAILs and IL such as, 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogensulfate, [C_3SO_3HMIM][HSO_4]; 1-methyl-3-(3-sulfopropyl)-imidazolium *p*-toluenesulfonate, [C_3SO_3HMIM][PTS]; 1-methyl-3-(3-sulfopropyl)-imidazolium chloride, [C_3SO_3HMIM][Cl]; and 1-butyl-3-methylimidazolium chloride, [BMIM][Cl] were synthesized (ESI, Section S2, Scheme S1, Fig. S2†) and used for liquefaction of lignin. The analytical techniques (CHNS, NMR (^{1}H, ^{13}C), FT-IR, TGA and UV-Vis) (ESI, Section S2, Table S2, Figs. S3-S5†) disclosed that ILs are obtained in pure form, are stable until 250 ^{o}C and have different acid strength.

Experimental Section.

Synthesis procedure of BAILs and IL. Various imidazolium based BAILs such as, 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogensulfate, [C_3SO_3HMIM][HSO_4]; 1-methyl-3-(3-sulfopropyl)-imidazolium *p*-toluenesulfonate, [C_3SO_3HMIM][PTS]; and 1-methyl-3-(3-sulfopropyl)-imidazolium chloride, [C_3SO_3HMIM][Cl] were synthesized in a two-step method.[39-42] Along with BAILs, neutral IL, 1-butyl-3-methylimidazolium chloride [BMIM][Cl] was also synthesized (ESI, Section S2, Scheme S1, Fig. S2†).

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Liquefaction of lignin. Depolymerization reactions of lignin were conducted at desired temperature for required time in a batch mode reactor of 100 mL capacity (Parr Autoclave, USA). Unless specified, in all the reactions, lignin (2 wt.% solution H_2O:CH_3OH, 1:5 *v/v*, 30 mL) & catalyst (0.5g) were charged and the reactor was heated to desired temperature under slow stirring (100 rpm). After attaining the desired temperature, stirring was increased to 1000 rpm and this time was considered as starting time of reaction. At this temperature the pressure generated was 0.35 MPa due to presence of water and methanol. After completion of reaction, reactor was allowed to cool to room temperature under the flow of air and slow stirring (100 rpm) (ESI, Section S3†).

Analytical methods. The organic solvent (THF, EtOAc, DEE) soluble products were analysed using gas chromatography (GC), gas chromatography-mass spectroscopy (GC-MS), liquid chromatography-mass spectroscopy (LC-MS) and gel permeation chromatography (GPC) techniques (ESI, Section S3†).

Result and Discussion.

Depolymerization of lignin. When lignin depolymerization experiment was conducted in water:methanol (1:5 *v/v*) solvent system at lower temperature of 120 °C (than reported earlier)[2, 7-16] for 1 h, among all the BAILs evaluated, [C_3SO_3HMIM][HSO_4] achieved the best yield (78%, Fig. 1) for THF soluble products (ESI, Section S3, Fig. S6†) while complete conversion of lignin was seen. The insoluble fraction was composed of mainly larger molecules but undoubtedly with lower molecular weight than lignin. Although, other BAILs were too active, those presented lower yields (24-42%) compared to [C_3SO_3HMIM][HSO_4]. Interestingly, neutral IL, [BMIM][Cl] as expected showed inferior yield (18%) compared to BAILs because of absence of

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–SO_3H group, yet it offered improved yield than non-catalytic reaction (4%). This is owing to the fact that the hydrogen attached to the carbon linking two nitrogens (NCHN) is acidic. Since, in all the experiments same quantity of catalyst (0.5 g) was used, it was expected that due to disparity in H^+ concentration at 0.5 g loading of catalyst (H_2SO_4, 10.2 mmol; [C_3SO_3HMIM][HSO_4], 3.32 mmol; [C_3SO_3HMIM][PTS], 1.33 mmol) variation in activity was observed (98, 78 and 42% yield). To nullify this effect, reactions were performed using comparable H^+ concentration (2.78 mmol) in the reaction mixture by altering the catalyst quantities and the following order of activity was seen,

[H_2SO_4] (96%) > [C_3SO_3HMIM][HSO_4] (52%) > [C_3SO_3HMIM][PTS] (49%).

This shows that if H^+ concentration is kept constant, analogous activity (52, 49%) can be observed with all the ILs with varying anions. This implies that the anion does not provide any contribution to the activity (ESI, Section S3†).

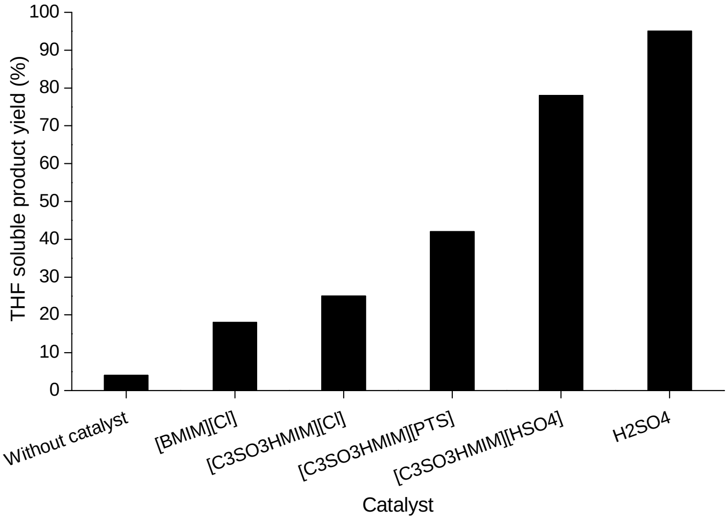

Fig. 1 Depolymerisation of lignin. Reaction condition: lignin (2 wt.% solution H_2O:CH_3OH, 1:5 *v/v*), 120 ˚C, 1 h, 1000 rpm. Values are average of three reactions with ±3% error observed.

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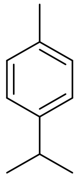
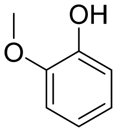
Effects of reaction temperature and time on activity are discussed in ESI, along with achievement of high mass balance of 95±5% in all the reactions (ESI, Section S3, Fig. S7†). The chromatographic technique coupled with mass spectroscopy (GC, GC-MS, LC-MS; ESI, Section S3, Figs. S8-S10†) confirmed the depolymerization of lignin and identified the low molecular weight aromatic products extracted in THF (102-220 gmol^{-1}, ESI, Fig. S11†). The finding was corroborated by injecting commercially procured chemicals (identified by above techniques). Besides formation of expected products, the appearance unexpected products such as *p*-cymene and butylated hydroxytoluene is possible because of acid catalyzed re-arrangement reactions of lignin fractions.[16, 43] The product distribution of the GC-FID identified low molecular weight products (m. wt. 124-196 g mol^{-1}) is given in Table 1. However, few of the GC-MS identified products are still not quantified since those are commercially not available and hence their calibration could not be carried out. Based on the results from GC analysis it is estimated that ca. 45% yield of the products extracted in THF is having molecular weight in the range of 124-196 g mol^{-1}. This suggests that out of 78% THF soluble products formed, 45% products are low molecular weight GC detected and quantified products.

Table 1. Summary on the quantification of GC and GC-MS identified low molecular weight products in the THF soluble product.

Sr. No.	**Aromatic monomers**	**Molecular weight (g mol^{-1})**	**Structure**	**Low molecular weight products distribution (wt %)**
1	*p*-cymene	134		4.8
2	2-methoxyphenol	124		22.3

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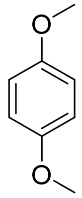
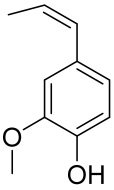
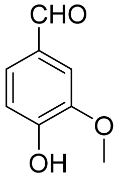
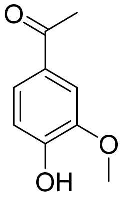
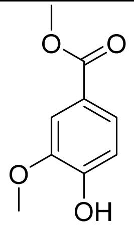
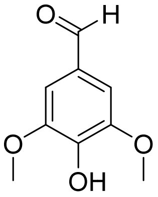
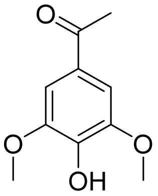
3	1,4-dimethoxy benzene	138		24.8
4	2-methoxy-4-(propenyl) phenol	164		23.0
5	4-hydroxy-3-methoxy benzaldehyde	152		8.1
6	1-(-hydroxy-3-methoxy phenyl) ethanone	166		8.0
7	methyl 4-hydroxy-3-methoxybenzoate	182		5.7
8	4-hydroxy-3,5-dimethoxy benzaldehyde	182		2.2
9	1-(4-hydroxy-3,5-dimethoxy phenyl) ethanone	196		1.2

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Reaction condition, lignin (2 wt.% solution $H_2O:CH_3OH$, 1:5 *v/v*), $[C_3SO_3HMIM][HSO_4]$ 0.5g catalysts, 120 ˚C, 1 h, 1000 rpm.

While with all BAILs similar peak patterns (GC-MS, ESI, Fig. S8†) were observed yet, differences in peak intensities due to disparity in yields (Fig. 1) are apparent. Contrary to this, GC-MS profile (ESI, Fig. S8f†) of H_2SO_4 catalyzed reaction showed only few peaks compared with $[C_3SO_3HMIM][HSO_4]$ signifying that BAIL has superior capability to yield low molecular weight aromatic products even if H_2SO_4 exhibits higher yield (98%) than BAILs (Fig. 1). Owing to insolubility of few THF soluble products in other extracting solvents such as EtOAc and DEE because of dissimilarity in Hansen solubility parameter (HSP, ESI, Section S3, Table S3†) lower yields of 36% and 14%, respectively were observed (ESI, Fig. S6†). This finding can be substantiated by evaluating the GC-MS profiles of the products extracted in these solvents with THF (ESI, Figs. S8d-e†). Incidentally, this divergence in solubility facilitates the separation of products from each other.

The comparable performance in minimum five recycles runs Fig. 2 (ESI, Section S3†) of $[C_3SO_3HMIM][HSO_4]$ and detailed characterization of recovered BAILs by CHNS, NMR (^1H, ^{13}C), FT-IR and TGA studies (ESI, Table S4, Figs. S12-S13†) divulge that the catalysts were stable under reaction conditions.

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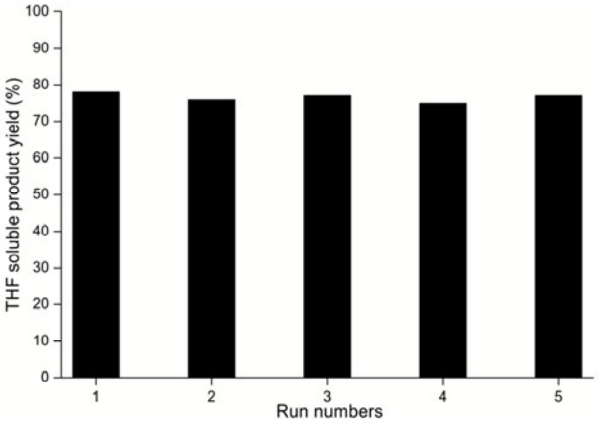

Fig. 2 Results for the recycle study using [C_3SO_3HMIM][HSO_4] catalyst. Reaction condition: lignin (2 wt.% solution H_2O:CH_3OH, 1:5 *v/v*) and catalyst [C_3SO_3HMIM][HSO_4] (0.5 g), 120 ˚C, 1 h, 1000 rpm.

Mechanistic studies.

Albeit the importance of depolymerization, investigations on the mechanistic insights on the roles of interaction between lignin and catalyst, linkages in lignin, cation/anion, concentration of H^+, etc. are largely not performed and hence deserves attention.

Lignin characterization. In this work depolymerization studies were performed with real lignin and since it is recognized that the properties of lignins are dependent on the type/age of plant and isolations procedures, it was obligatory to investigate those and therefore, lignin[44] was systematically characterized by assorted thermal/spectroscopic techniques (ESI, Sections S3-S4, Tables S3, S5, Figs. S14-S16†). To understand the TGA results, TPO-MS studies were undertaken and it was observed (Fig. 3) that lignin decomposes in a wide range of temperature, probably because it contains various linkages, functional groups and bond dissociation enthalpies etc. (ESI, Section S1, Table S1, Fig. S1†).[45, 46] It is worth noting that when experiment was performed with 5% oxygen (*v/v*), intense peaks for gaseous products ($CO/CO_2/CH_4/H_2$ etc. ESI, Section S4, Table S6, Equations S1-S16†) were observed at lower temperatures (<550 °C), but formation of these products was less under helium atmosphere even until 800 °C. This is usual

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since oxygen helps degradation. Importantly, observance of ozone under both the conditions is possibly due to radical mechanism under thermal conditions. However, for the explanations on the formation of ozone,[47] typically radical mechanism is discussed.

Product(s) stability. The foremost cause to obtain poor yields of low molecular weight products in lignin depolymerization reactions is the likelihood of repolymerization of products at high temperatures.[2, 3, 32, 48, 49] To comprehend this, commercially available chemicals (identified by GC/GC-MS/LC-MS) were acquired, mixed along with [C_3SO_3HMIM][HSO_4] in water:methanol (1:5 *v/v*) and scrutinized for their stability (ESI, Section S4, Fig. S17†). The change in the concentrations of these chemicals was monitored by GC and LC analysis. Whilst the study was performed at 120 °C for 1 h, slight change (±3%) in the peak areas was seen however, large decline (10-30%) in the peak areas for few chemicals due to char formation was noticed when the study was performed at 170 °C. These results explicate the decline in yields for THF soluble products when reactions were done at higher temperatures.

Correlation between lignin structure and products.

As disclosed earlier, substantiation for formation of depolymerized products was done by spectroscopic techniques (ESI, Figs. S8-S10†). Nonetheless, to perceive the changes transpiring in lignin structure and existence of several functional groups in both, lignin and product on bulk and molecular level was done using several techniques (GPC, DSC, UV-Vis, FT-IR, 1D and 2D (HSQC) NMR).

Though, irrefutable estimation of molecular weight of lignin and products from GPC analysis is not feasible owing to multifarious structure of lignin and non-availability of standards for calibration, it is noticeable from the GPC profiles (ESI, Fig. S18†) that lignin undergoes depolymerisation as emergence of new major peak with solvent is detected in products.

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In the thermogram obtained from DSC analysis of lignin (Fig. 4a), peaks were recorded at 230 and 245 ^{o}C, due to melting (endothermic) and crystallization/char (exothermic), respectively. Nonetheless, nonappearance of these peaks in the products and observance of multiple new peaks (Fig. 4b) denote that lignin was depolymerised into products having diverse transition temperatures. Additionally, it is advocated that the products are low boilers (<300 ^{o}C) as no peak for crystallization was spotted and subsequent to analysis, sample pan was empty. This finding is in line with the products ascertained from spectroscopic analysis.

Efforts were undertaken to identify functionalities (conjugation, function groups) by UV-Vis (ESI, Fig. S19†) absorption measurement study and as seen, in both the samples, existence of three peaks (280, 230, 206 nm) due to occurrence of various types of chromophores/substituent in aromatic compounds proved that almost all the functionalities are preserved in products, as such present in lignin. Nevertheless, to delve more into this, FT-IR study for lignin and products was carried out (ESI, Section S4, Fig. S20†). The emergence of two new peaks for phenolic C-O stretch in phenol (1180 cm^{-1}) and enhancement in intensity for few peaks along with decrease in peak intensity for ether linkages (1040 and 1125 cm^{-1}) in the FT-IR spectrum of products exhibits depolymerization of lignin.

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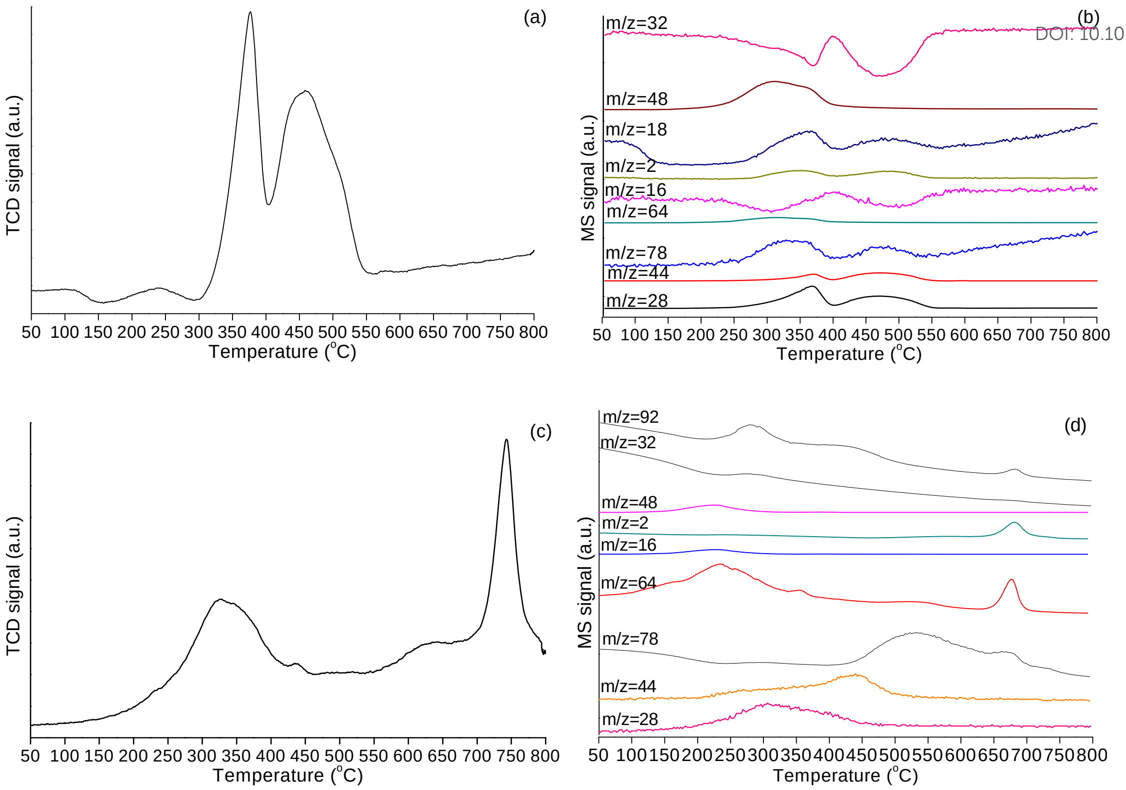

Fig. 3 Temperature programme oxidation-mass spectroscopy (TPO-MS) of lignin. (a) TCD-(95%He+5%O_2 *v/v*), (b) MS profile-(95%He+5%O_2 *v/v*) (c) TCD-100%He (d) MS profile-100% He. The different m/z denotes following: 2:H_2, 16:CH_4, 18:H_2O, 28:CO, 32:O_2, 44:CO_2 etc.

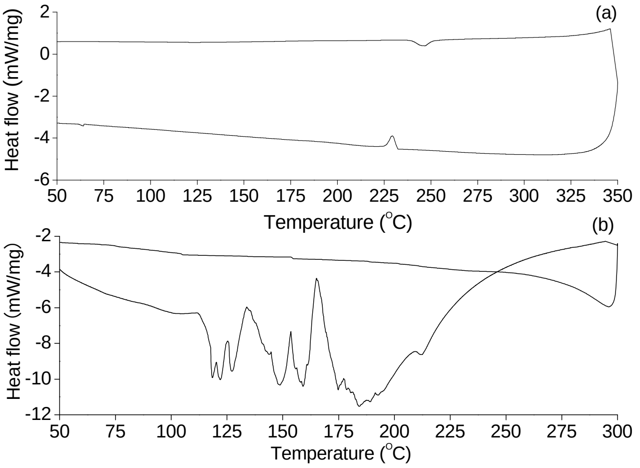

Fig. 4 DSC analysis. (a) lignin (b) THF soluble products obtained in [C_3SO_3HMIM][HSO_4] catalyzed reaction.

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To ascertain the linkages and functional groups present in lignin and products, advance analytical tool, 2D (HSQC) NMR was employed (Fig. 5, ESI, Section S4, Tables S7a-b, Fig. S11†). The HSQC spectrum shows signals for oxygenated aliphatic and aromatic lignin structures in the characteristic regions of δ_C/δ_H 50-90/2-6 and 100-140/6-8 ppm, respectively.[50-55] In lignin sample, strong signal for –OR groups (etherified) was observed at δ_C/δ_H 56/3.2-4.0 ppm (Fig. 5a). Nonetheless, in products, the intensity of this signal was decreased (Fig. 5d) manifesting that during depolymerisation, most of the ether linkages were cleaved. However, presence of few –OR groups in products is in line with the products identified (ESI, Figs. S8 and S11†) with $–OCH_3$ groups. Likewise, in products (Fig. 5d), low intensity signals (δ_C/δ_H 62-64/3.2-3.65 ppm) for C_γ-H_γ was observed compared with lignin sample (Fig. 5a) hinting decrease in concentration of these species. On the contrary increase in intensity for signal (δ_C/δ_H 60-62/3.2-3.5 ppm) assigned to C_γ-H_γ specifies emergence of new moieties in products. The nonappearance of signals for A_β (δ_C/δ_H 84.2/4.3 ppm) for Guaiacol moiety (G) and Bα (δ_C/δ_H 85.5/4.6 ppm) in products (Fig. 5e) again accentuate that lignin (Fig. 5b) undergoes depolymerisation. Generally, the cross-signals observed at δ_C/δ_H 100-140/6-8 ppm corresponds to aromatic moieties such as, *p*-hydroxyphenol (H), guaiacyl (G) and syringyl alcohol (S) (Fig. 5). While in lignin sample (Fig. 5c), prominent signals for 'G' units are observed (δ_C/δ_H 111/7.4, 115.4-115.7/6.7-7.0 ppm for C_2-H_2, C_5-H_5 and C_6-H_6 in 'G' units), those were decreased in products (Fig. 5f) due to cleavage of –OR bonds. The observance of new signals for 'H' units (δ_C/δ_H 125.4-127.1/6.0-7.1 ppm) in products (Fig. 5f) again emphasize that lignin is depolymerised. The same observation is made for A_β (δ_C/δ_H 84.2/4.3 ppm) as reviewed above. Since similar 2D NMR results were also observed when other BAILs were used in these reactions, as is also found from GC-MS analysis (ESI, Fig. S8†) it is advocated that anions do not influence the course of reaction. Moreover, H^+ concentration study (ESI, Section S3†) also exhibit that anions do not impact activity. In view of this, it is compelling to study the interaction of cation, imidazolium with lignin.

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Interaction studies.

Since, BAILs displayed better performance than other catalysts (Fig. 1, ESI, Section S3†), it is anticipated that because of their ionic nature BAILs can interact with lignin moieties which would facilitate cleavage of C-O-C (ether/ester) bonds. Moreover, catalytic results point out that lignin may interact more with cation than anion. To unravel this phenomenon, ^{1}H NMR studies were performed with monomers (cumene, vanillin), dimer (guaiacol glyceryl ether) and polymer (lignin) (Fig. 6, ESI, Section S4, Tables S7a-b†). In the spectra recorded for mixture of IL and vanillin (Fig. 6b), chemical shifts of proton in IL (δ, ppm:9.43→9.36 (NCHN, 'h'), shielding) and vanillin (δ, ppm:10.27→10.60 (-OH, 'o'), 6.98→7.10 and 6.94→7.06 (doublet, Ar-H, 'k'), deshielding] compared to neat spectra (of IL and vanillin) were observed. Additionally, broadening of –OH peak is indisputably visible in the mixture compared with neat sample. This effect is best explained on the basis of transfer of electron density (through 'O' of –OH) of vanillin to electron deficient imidazolium ring (cation of IL). To eliminate the possibility of involvement of pi electrons, NMR spectra were recorded with cumene (without –OH group) and as anticipated no shift in proton peaks was observed (Fig. 6a) which reaffirmed that IL interacts with substrates having –OH groups via 'O'.

In a vanillin concentration study (ESI, Section S4.4.b, Figs. S21a, b), maximum (^{1}H) chemical shift was observed at 0.5 and 1 molar ratio (vanillin/IL) for vanillin and later at higher molar ratios (1.5, 3 and 5) it declined. Nevertheless, at the same time continuous increase in chemical shift in IL was seen (Fig. 6f). These contrasting results were exhibited due to change of concentration of both vanillin and IL in DMSO-d_6. Until reaching stoichiometric amount of vanillin to IL, increase in chemical shift was observed but when surplus (above stoichiometric >1 molar ratio) vanillin ^{1}H 1D NMR studies (Fig. 6b). The 2D (HSQC) NMR study performed for neat lignin and mixture of lignin with IL also demonstrate similar observations. For e.g. signal for NCHN in IL was shifted to upfield (δ_C/δ_H 136.55/9.72→136.57/9.47 ppm for 'h') after addition of lignin (Fig. 7b). Thus, it can be affirmatively inferred from NMR studies that lignin interacts with cation of IL via 'O' of –OH groups was present it had limitations to interact with IL and thus chemical shifts were averaged out towards neat. But as these

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interactions are rapid, IL was competent of interacting with numerous vanillin molecules and thus displayed uninterrupted increase in chemical shift. Next, interaction study was performed with dimer, guaiacol glyceryl ether (Fig. 6c) and analogous trend in chemical shift was observed for IL (δ, ppm:9.42→9.35 (NC**H**N, 'h'), shielding) and ether (δ, ppm:4.94→5.06 (-OH, 'o'), 4.65→4.80 (-OH, 'n'), deshielding) as found with vanillin. In case of lignin, low intensity peaks for –OH and Ar-H were visible (Fig. 6d) owing to its polymeric nature. Yet, an apparent shift in NCHN peak was visible. This is because lignin is comprised of higher concentration of –OH and other functional groups (than other studied molecules here) which can interact with IL. The similar observation was made during vanillin study.

To underpin the explanations derived from 1D (^{1}H) NMR, interactions were studied with the help of 2D (HSQC) NMR. As seen from Fig. 7, the signal for NCHN in IL was shifted to upfield (δ_C/δ_H 136.55/9.75→136.74/9.37 ppm for 'h') after addition of vanillin. Similarly, signal for Ar-H in vanillin (Fig. 7a) was shifted to downfield (δ_C/δ_H 115.4/6.97→115.63/7.11 ppm for 'k'). These results reinforce the observations made from in the RAMAN studies (ESI, Fig. S22†), characteristic peaks for stretching mode of C=O were visible at 1661, 1667 and 1692 cm^{-1} for neat vanillin, but those were shifted to positive wavenumber (1667, 1699, 1758, 1770 cm^{-1}) after addition of IL.

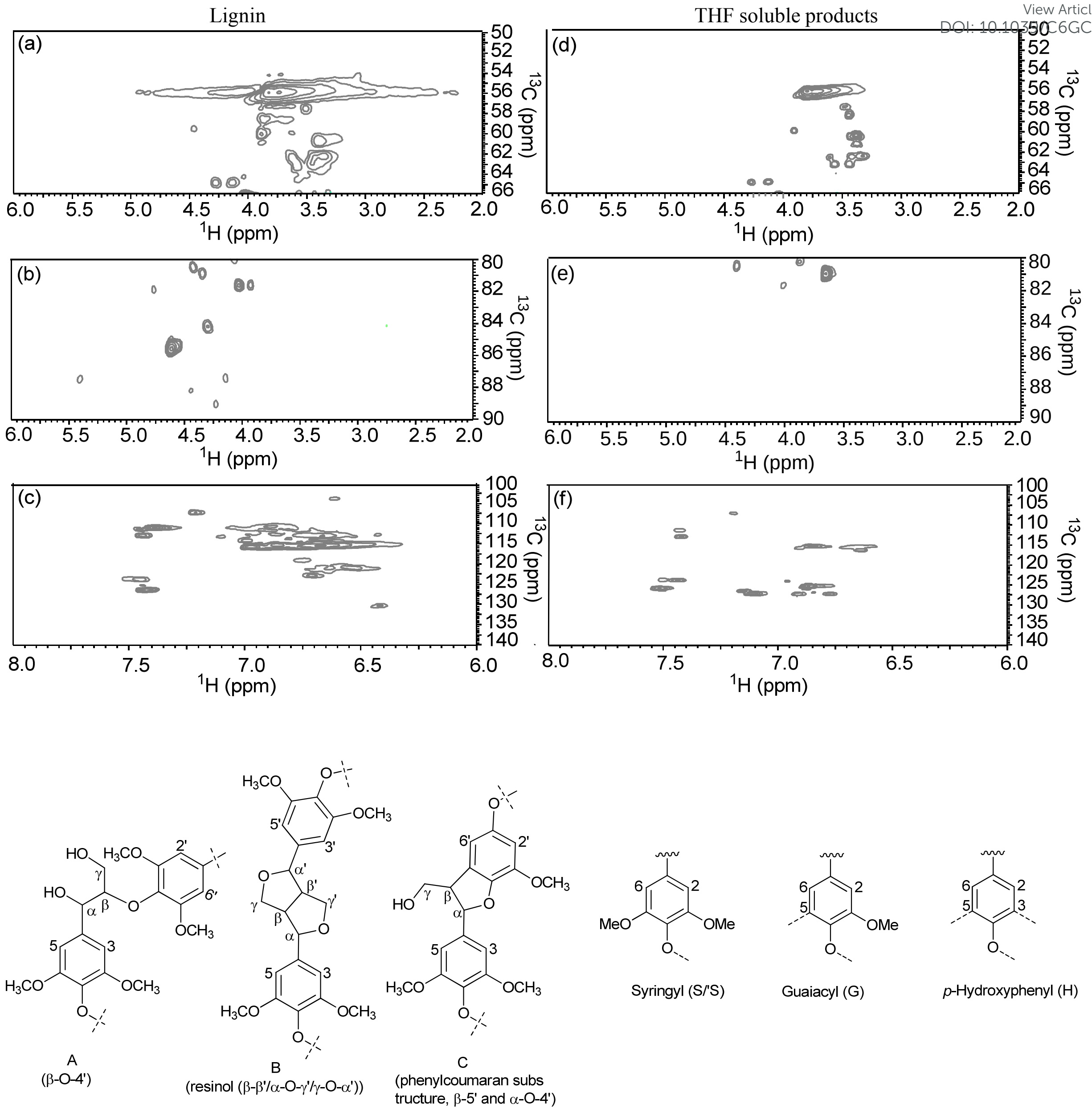

Fig. 5 2D (HSQC) NMR spectra of lignin (a, b, c) and of THF soluble products (d, e, f) obtained in [C_3SO_3HMIM][HSO_4] catalyzed reaction. All the spectra were measured after dissolving samples in DMSO-d_6.

Simultaneously, in the mixture, negative shift in wavenumber (3090 to 3068 cm^{-1}) for C-H (NCHN) of imidazolium ring (cation of IL) was noticed. The observed positive shift was because of transfer of electron density from vanillin to imidazolium via aromatic ring and ‘O’ of -OH, which enhances the double bond character of C=O as it is located to para position to –OH. Similarly, with increase in

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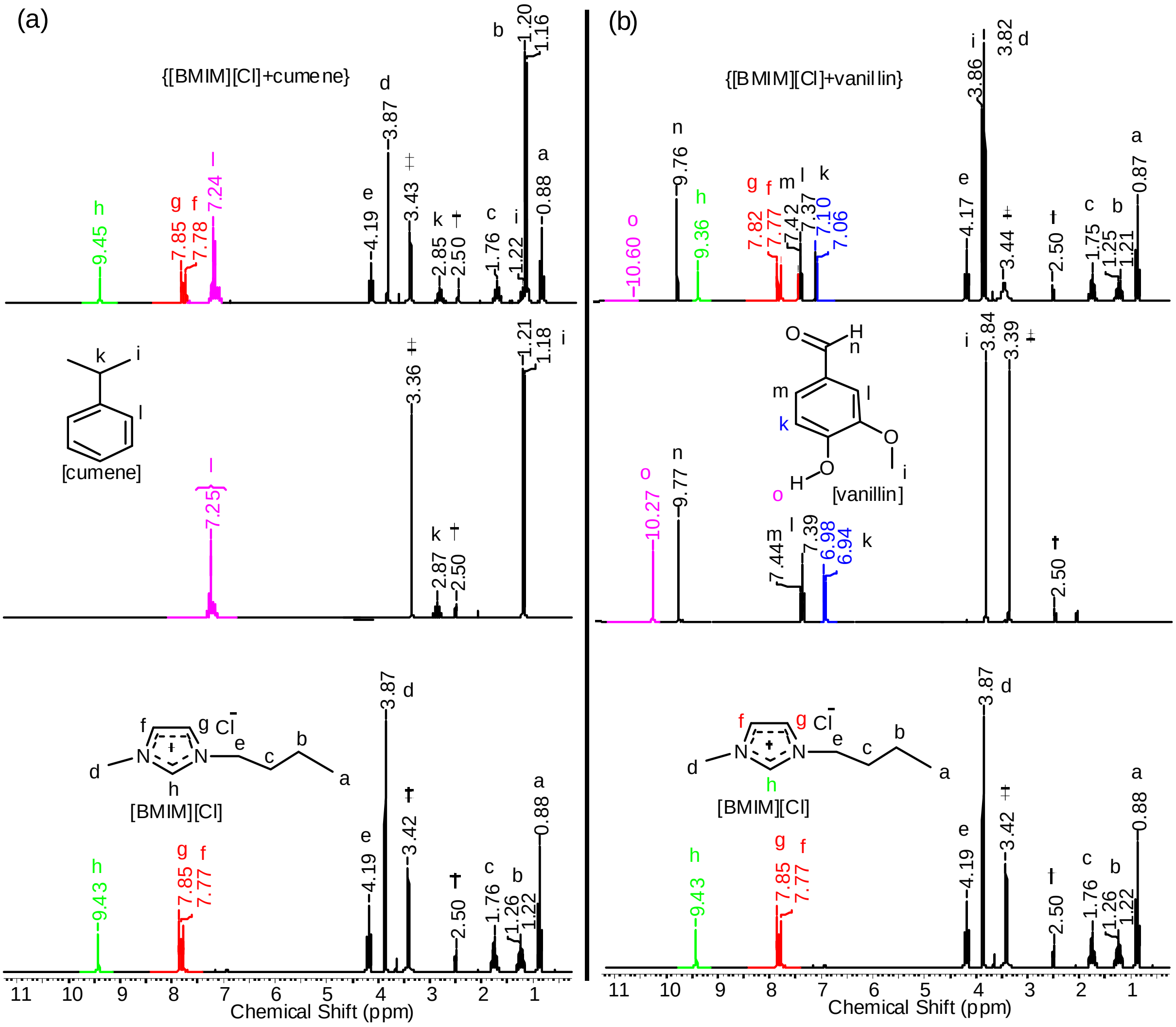
electron density on imidazolium, ${}^{+}\delta$ character is weakened and accordingly negative shift is spotted. These results yet again endorse the fact that –OH groups interact with imidazolium. Albeit from 1D NMR and RAMAN studies it was apprehended that –OH groups interact with immidazolium, however to find out the mode of interaction; either parallel or perpendicular (ESI, Fig. 23S†), studies on 2D (NOSEY) NMR were undertaken for a mixture of vanillin and IL as this technique allows to gather information for an interaction between H-H (inter or intra molecular) if they are in the close vicinity (<5Å) with each other. As observed (Fig. 7c), we could only detect intra-molecular H-H interaction and consequently it is believed that predominantly –OH and immidazolium interact with each other in a perpendicular mode.



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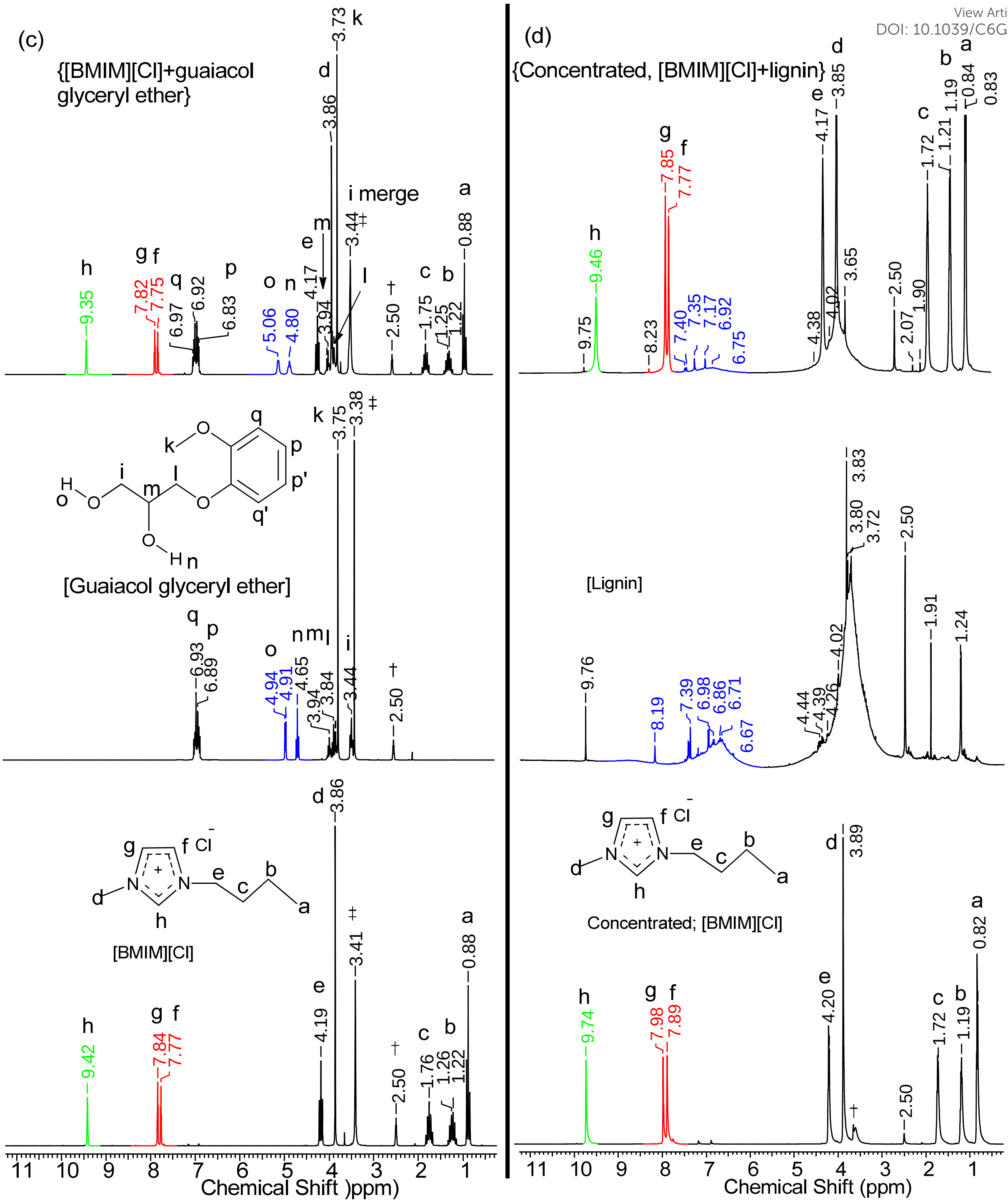

Fig. 6 1D ^{1}H NMR spectra. a) neat [BMIM][Cl], neat cumene and mixture of [BMIM][Cl] & cumene; b) neat [BMIM][Cl], neat vanillin and mixture of [BMIM][Cl] & vanillin; c) neat [BMIM][Cl], neat guaiacol glyceryl ether and mixture of [BMIM][Cl] & guaiacol glyceryl ether; d) neat [BMIM][Cl], neat lignin and mixture of [BMIM][Cl] & lignin. All the spectra were recorded in DMSO-d$_6$.

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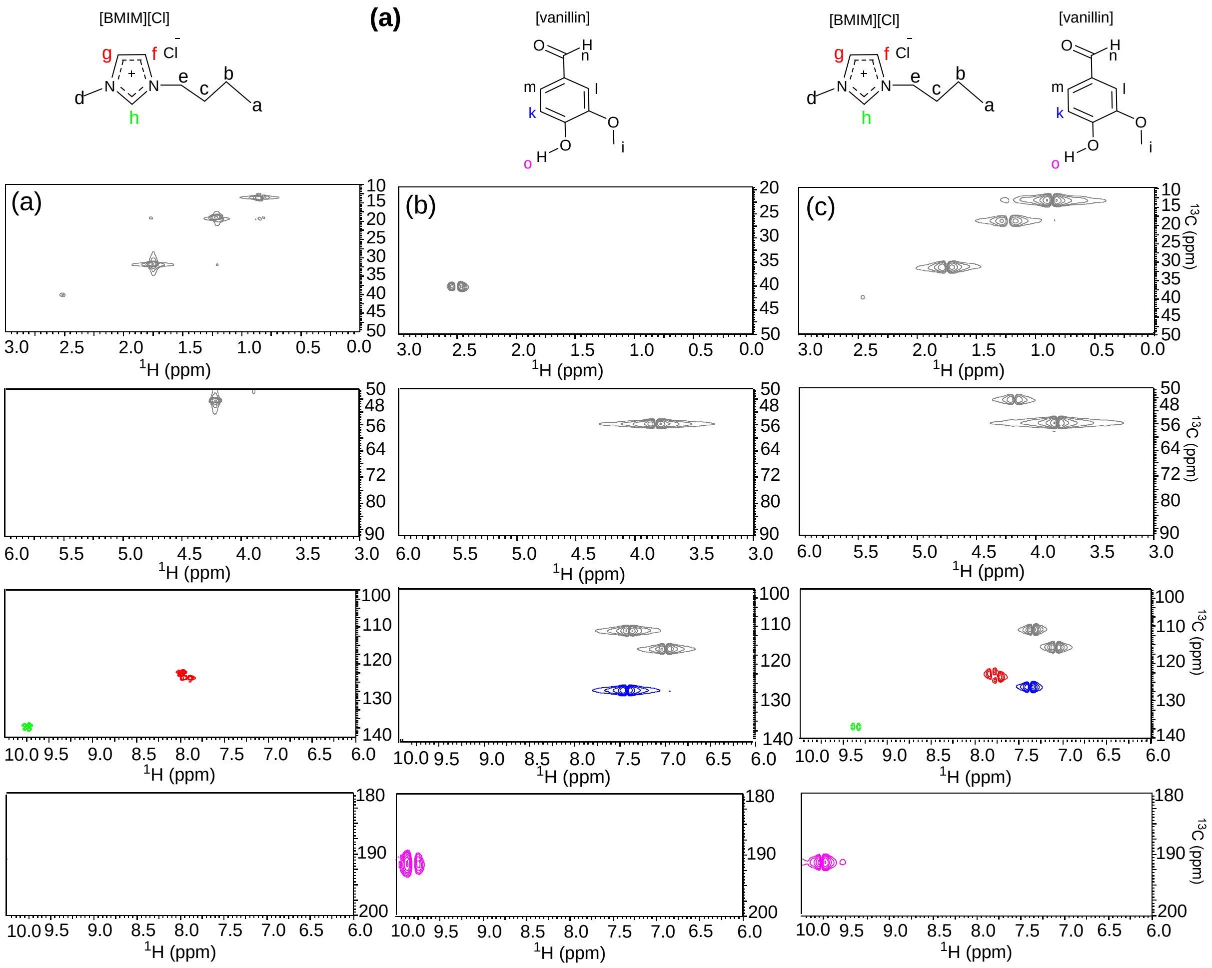

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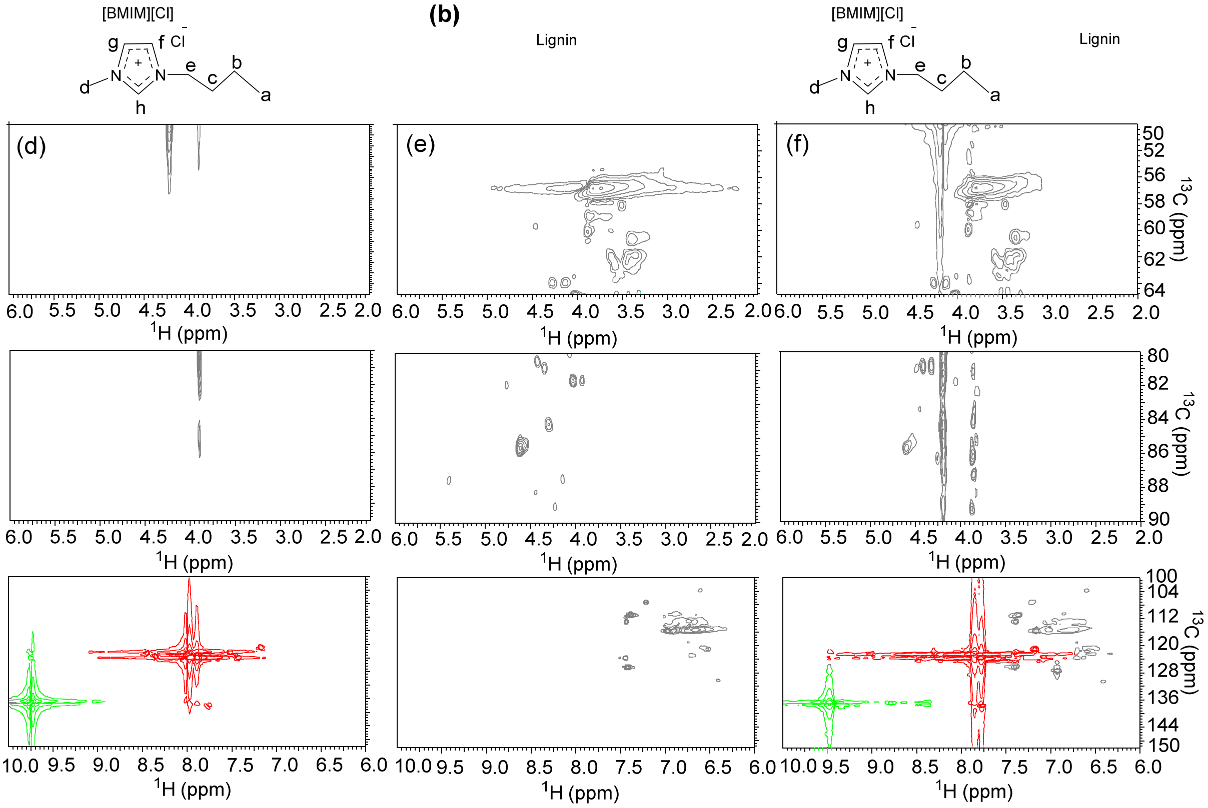

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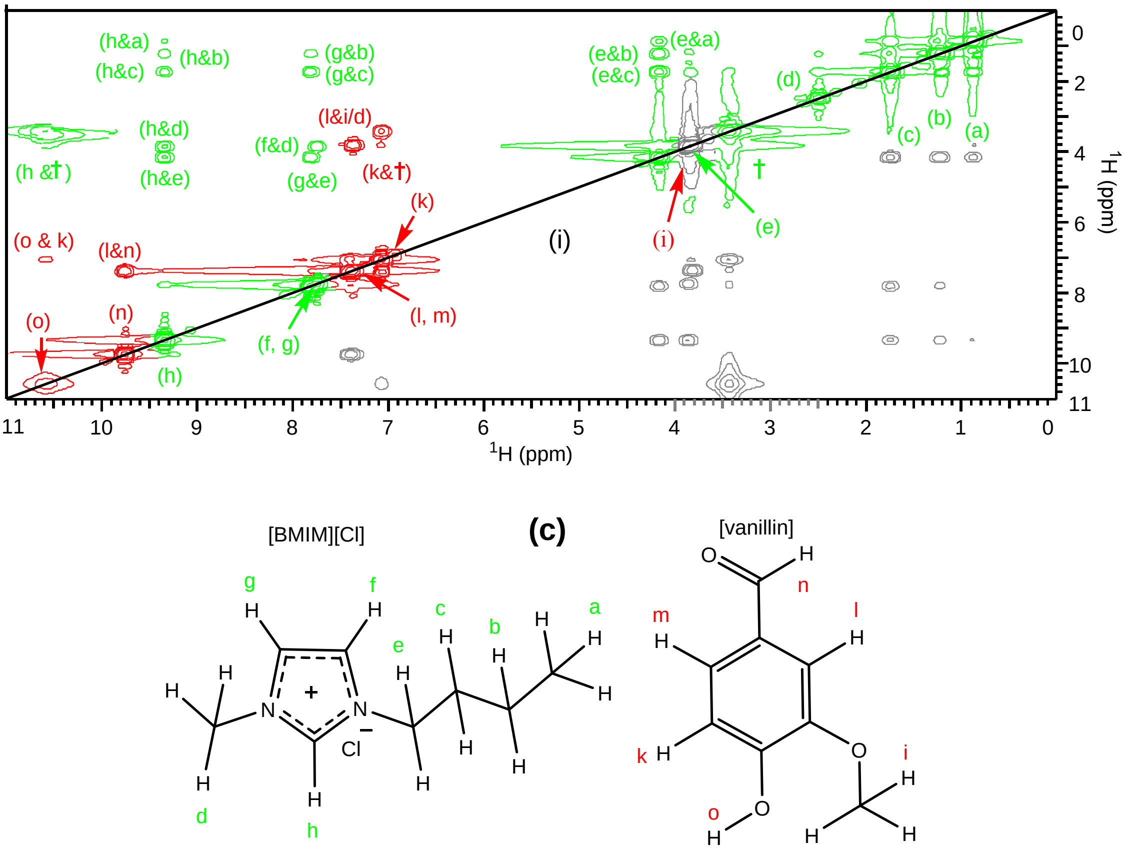

Fig. 7 2D (HSQC) NMR and 2D (NOSEY) NMR. (a) 2D (HSQC) NMR of neat [BMIM][Cl], neat vanillin and mixture of [BMIM][Cl] & vanillin; (b) 2D (HSQC) NMR of neat [BMIM][Cl], neat lignin and mixture of [BMIM][Cl] & lignin. (c) 2D (NOSEY) NMR of mixture of [BMIM][Cl] & vanillin. All the spectra were recorded in DMSO-d_6.

This is evident since steric hindrance between alkyl chains, methoxy group etc. would destabilize parallel arrangement. Moreover, aromatic rings would repel each other and this will lead to almost perpendicular interaction. These results also match well with the results obtained with 1D ^{1}H NMR of cumene analysis where no shift in δ values was noticed because of absence of –OH groups and that there is a least prospects of pi-pi interaction between aromatic rings in cumene and immidazolium owing to perpendicular interaction.

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Based on the results a mechanistic pathway (Fig. 8) is advocated wherein it is proposed that BAILs interact with lignin molecules via ‘O’ of –OH groups and make a virtual binding with the substrate. This helps in easy supply of H^+ available with BAIL for protonation of ‘O’ of ether linkages which exist in lignin with almost 70% of all linkages. Once this is achieved, cleavage of C-O-C bond and attack of water on the cation will take place to yield hydrolysis products with higher concentration of –OH groups which is again discussed through FT-IR study. For more details on the mechanism please refer ESI (Section S4.4.c).

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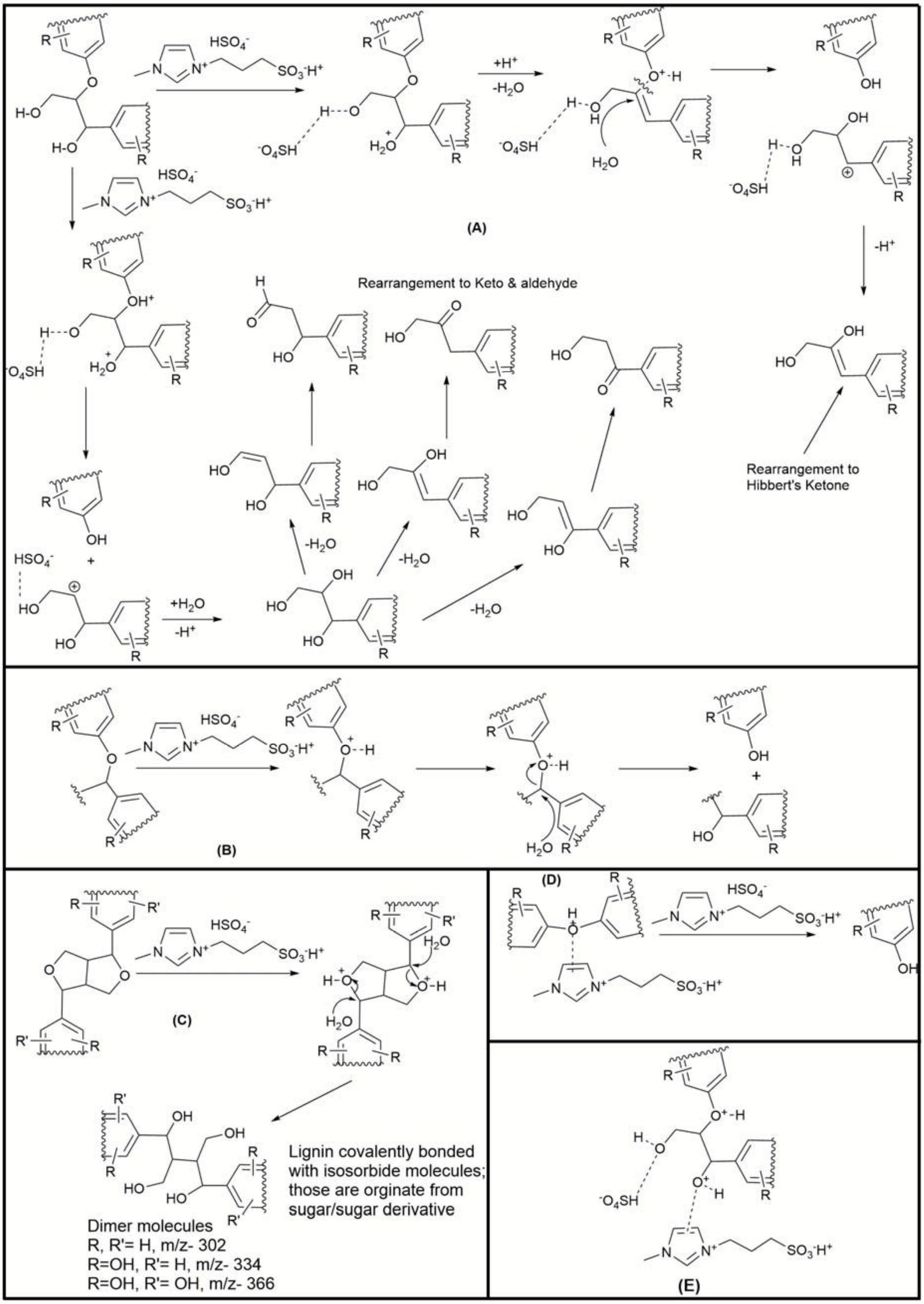

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Fig. 8 The proposed mechanism. (A) β-O-4, (B) α-O-4, (C) 4-O-5, (D) α-O-γ linkage present in the lignin molecules to form monomers and dimer units and (E) interaction of lignin with [C_3SO_3HMIM][HSO_4] BAIL.

Conclusions.

The superior activity with high atom efficiency accomplished with recyclable BAILs under milder conditions for yielding 78% THF soluble products from (real) lignin is correlated to their interaction with each other via transfer of electron density from ‘O’ of –OH groups present on lignin to imidazolium ring. This conclusion is substantiated by meticulous studies performed with the help of RAMAN and 1D & 2D (HSQC/NOSEY) NMR. These characterizations also helped comprehend the mode of interaction as (preferably) perpendicular. The FT-IR, NMR and GC-MS techniques could assertively identify the formation of different products with diversity in functional groups and a unique temperature dependent product and lignin stability study was monitored using thermal and chromatographic techniques. After compilation of all the data, hydrolysis mechanism is proposed for depolymerisation of lignin through protonation of C-O-C linkages. The work described here should assist tuning reaction conditions for proficient conversions.

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Footnote.

†Electronic supplementary information (ESI) available. Methods, synthesis of ILs, Characterizations of IL, lignin, reaction mixture, organic solvent soluble products, identification of products.

References.

1. A. J. Ragauskas, G. T. Beckham, M. J. Biddy, R. Chandra, F. Chen, M. F. Davis, B. H. Davison, R. A. Dixon, P. Gilna, M. Keller, P. Langan, A. K. Naskar, J. N. Saddler, T. J. Tschaplinski, G. A. Tuskan and C. E. Wyman, *Science*, 2014, **344**, 709-719.
2. C. Xu, R. A. D. Arancon, J. Labidi and R. Luque, *Chem. Soc. Rev.*, 2014, **43**, 7485-7500.
3. J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius and B. M. Weckhuysen, *Chem. Rev.*, 2010, **110**, 3552-3599.
4. P. C. A. Bruijnincx and B. M. Weckhuysen, *Nat Chem*, 2014, **6**, 1035-1036.
5. *Promotion of the use of energy from renewable sources and amending and subsequently repealing*, Report Directive 2009/28/EC of the European Parlament and of the Council, Europe, 2009.
6. L. C. Rodriguez and D. O Connell, *Nature*, 2011, **476**, 283-283.
7. V. M. Roberts, V. Stein, T. Reiner, A. Lemonidou , X. Li and J. A. Lercher, *Chem. Eur. J.*, 2011, **17**, 5939-5948.
8. W. W. Zmierczak and E. Chornet, U.S. Pat. No. 5,959,167, Sep. 28, 1999.
9. D. Meier, J. Berns, O. Faix, U. Balfanz and W. Baldauf, *Biomass Bioenergy*, 1994, **7**, 99-105.
10. N. Yan, C. Zhao, P. J. Dyson, C. Wang, L. T. Liu and Y. Kou, *ChemSusChem*, 2008, **1**, 626-629.
11. J. A. Onwudili and P. T. Williams, *Green Chem.*, 2014, **16**, 4740-4748.
12. Wahyudiono, T. Kanetake, M. Sasaki and M. Goto, *Chem. Eng. Technol*, 2007, **30**, 1113-1122.
13. T. L. K. Yong and Y. Matsumura, *Ind. Eng. Chem. Res.*, 2012, **51**, 11975-11988.
14. M. A. Hill Bembenic and C. E. Burgess Clifford, *Energy Fuels*, 2012, **26**, 4540-4549.
15. R. K. Sharma and N. N. Bakhshi, *Bioresour. Technol.*, 1991, **35**, 57-66.
16. A. K. Deepa and P. L. Dhepe, *ACS Catal.*, 2015, **5**, 365-379.
17. A. K. Deepa and P. L. Dhepe, *RSC Adv.*, 2014, **4**, 12625-12629.

View Article Online
DOI: 10.1039/C6GC00771F

18. N. Sun, R. Parthasarathi, A. M. Socha, J. Shi, S. Zhang, V. Stavila, K. L. Sale, B. A. Simmons and S. Singh, *Green Chem.*, 2014, **16**, 2546-2557.
19. N. Sun, H. Rodriguez, M. Rahman and R. D. Rogers, *Chem. Commun.*, 2011, **47**, 1405-1421.
20. J. Zakzeski, A. L. Jongerius and B. M. Weckhuysen, *Green Chem.*, 2010, **12**, 1225-1236.
21. K. Stärk, N. Taccardi, A. Bösmann and P. Wasserscheid, *ChemSusChem*, 2010, **3**, 719-723.
22. M. E. Zakrzewska, E. Bogel-Lukasik and R. Bogel-Lukasik, *Energy & Fuels*, 2010, **24**, 737-745.
23. B. J. Cox and J. G. Ekerdt, *Bioresour Technol*, 2012, **118**, 584 - 588.
24. A. George, K. Tran, T. J. Morgan, P. I. Benke, C. Berrueco, E. Lorente, B. C. Wu, J. D. Keasling, B. A. Simmons and B. M. Holmes, *Green Chem.*, 2011, **13**, 3375 - 3385.
25. Z. C. Zhang, *Wiley Interdiscip. Rev.: Energy Environ.*, 2013, **2**, 655-672.
26. Y. Yang, H. Fan, J. Song, Q. Meng, H. Zhou, L. Wu, G. Yang and B. Han, *Chem. Commun.*, 2015, **51**, 4028-4031.
27. G. Chatel and R. D. Rogers, *ACS Sustainable Chem. Eng.*, 2014, **2**, 322-339.
28. E. Reichert, R. Wintringer, D. A. Volmer and R. Hempelmann, *Phys Chem Chem Phys*, 2012, **14**, 5214 - 5221.
29. H. Wang, M. Tucker and Y. Ji, *J. Appl. Chem.*, 2013, **2013**, 1-9.
30. J. Long, W. Lou, L. Wang, B. Yin and X. Li, *Chem. Eng. Sci.*, 2015, **122**, 24-33.
31. J. Long, X. Li, B. Guo, L. Wang and N. Zhang, *Catal. Today*, 2013, **200**, 99-105.
32. S. Nanayakkara, A. F. Patti and K. Saito, *Green Chem.*, 2014, **16**, 1897-1903.
33. S. Nanayakkara, A. F. Patti and K. Saito, *ACS Sustainable Chem. Eng.*, 2014, **2**, 2159-2164.
34. A. G. Sergeev and J. F. Hartwig, *Science*, 2011, **332**, 439-443.
35. J. M. Nichols, L. M. Bishop, R. G. Bergman and J. A. Ellman, *J. Am. Chem. Soc.*, 2010, **132**, 12554-12555.
36. H. Nimz, *Angew. Chem. Int. Ed.*, 1974, **13**, 313-321.
37. M. P. Pandey and C. S. Kim, *Chem. Eng. Technol*, 2011, **34**, 29-41.
38. A. Rahimi, A. Ulbrich, J. J. Coon and S. S. Stahl, *Nature*, 2014, **515**, 249-252.
39. D. J. Tao, J. Wu, Z. Z. Wang, Z. H. Lu, Z. Yang and X. S. Chen, *RSC Adv.*, 2014, **4**, 1-7.
40. Y. Zhao, J. Long, F. Deng, X. Liu, Z. Li, C. Xia and J. Peng, *Catal. Commun.*, 2009, **10**, 732-736.
41. C. Xie, H. Li, L. Li, S. Yu and F. Liu, *J. Hazard. Mater.*, 2008, **151**, 847-850.
42. J. Gui, X. Cong, D. Liu, X. Zhang, Z. Hu and Z. Sun, *Catal. Commun.*, 2004, **5**, 473-477.
43. F. E. Brauns and D. A. Brauns, in *The Chemistry of Lignin*, Academic Press Inc. Published by Elsevier Inc., 1960, Ch. XVIII pp. 486-497.
44. TCI chemicals, http://www.tcichemicals.com/eshop/en/in/commodity/L0045/).
45. S. Zhao, Y. Luo, Y. Su, Y. Zhang and Y. Long, *Energy Fuels*, 2014, **28**, 5049-5056.

View Article Online
DOI: 10.1039/C6GC00771F

46. A. I. Afifi, J. P. Hindermann, E. Chornet and R. P. Overend, *Fuel*, 1989, **68**, 498-504.

47. Detroit, W. U.S. Pat. No. 3,726,850, Apr. 10, 1973.

48. A. Toledano, L. Serrano and J. Labidi, *Fuel*, 2014, 116, 617-624.

49. J. Li, G. Henriksson and G. r. Gellerstedt, *Bioresour. Technol.*, 2007, **98**, 3061-3068.

50. F. Tran, C. S. Lancefield, P. C. J. Kamer, T. Lebl and N. J. Westwood, *Green Chem.*, 2015, **17**, 244-249.

51. P. Ferrini and R. Rinaldi, *Angew. Chem. Int. Ed.*, 2014, **53**, 8634-8639.

52. J. M. W. Chan, S. Bauer, H. Sorek, S. Sreekumar, K. Wang and F. D. Toste, *ACS Catal.*, 2013, **3**, 1369-1377.

53. N. D. Bonawitz, J. I. Kim, Y. Tobimatsu, P. N. Ciesielski, N. A. Anderson, E. Ximenes, J. Maeda, J. Ralph, B. S. Donohoe, M. Ladisch and C. Chapple, *Nature*, 2014, **509**, 376-380.

54. S. Van den Bosch, W. Schutyser, R. Vanholme, T. Driessen, S. F. Koelewijn, T. Renders, B. De Meester, W. J. J. Huijgen, W. Dehaen, C. M. Courtin, B. Lagrain, W. Boerjan and B. F. Sels, *Energy Environ. Sci.*, 2015, **8**, 1748-1763.

55. M. Foston, R. Samuel, J. He and A. J. Ragauskas, *Green Chem.*, 2016, **18**, 608-621.

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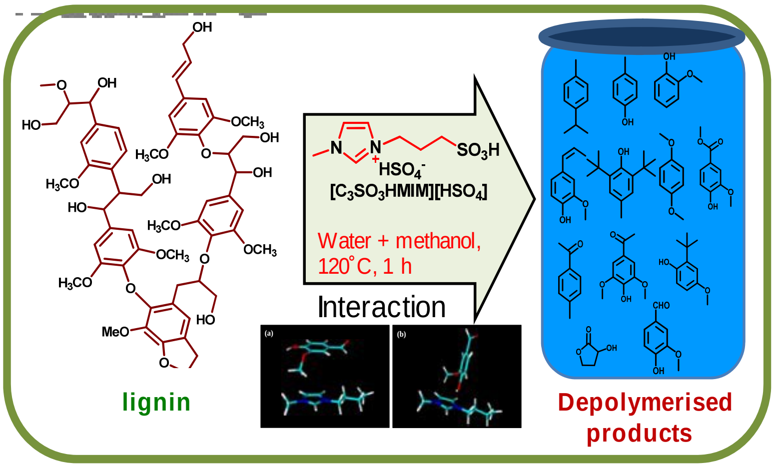
View Article Online
DOI: 10.1039/C6GC00771F



Reusable Brønsted acidic ionic liquids are shown to depolymerize lignin into value-added depolymerized products with 78% yield.