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New insights into the catalytic cleavage of the lignin β-O-4 linkage in multifunctional ionic liquid media

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Ionic liquids are attractive reaction media for the solubilisation and depolymerisation of lignin into value-added products. However, mechanistic insight related to the cleavage of specific linkages relevant for efficient lignin depolymerisation in such solvents is still lacking. This study presents important insight into the scission of the most abundant lignin β-O-4 motif in Brønsted acidic ionic liquids. Using relevant model compounds, cleavage products were identified and undesired side reactions examined carefully. Stabilization of reactive intermediates was achieved in ionic liquids comprising both Brønsted acidic function as well as stabilized nanoparticles that comprise hydrogenation activity in order to supress undesired side reactions. Especially, the *in situ* hydrogenation of the aldehyde intermediate originating from acid catalysed cleavage of lignin beta-O-4 model compounds into more stable alcohols was investigated. This is the first time that such products have been systematically targeted in these multifunctional reaction media in relation to lignin depolymerization.

Introduction

Before the widespread use of fossil carbon sources at the beginning of 20th century, carbon based compounds such as terpenes, methanol, and acetone were derived from wood.[1] Due to the finite nature of fossil carbon resources the focus has shifted again to the use of renewables.[2] Implementation of lignocellulosic biomass for the chemical industry ideally requires valorisation of all its components.[2a,3] Lignin, a major component of lignocellulosic biomass (15-35 wt%), could serve as renewable source of aromatic bulk and fine chemicals.[3a,4] However, lignin depolymerization to aromatic monomers has thus far proven challenging, due to its amorphous and recalcitrant nature.[5] In lignin, aromatic monomers are randomly cross-linked via C-C and C-O bonds (Figure 1).[6] The most abundant linkage is the β-O-4 alkyl-aryl ether.[5a,6] Effective cleavage of this bond is seen as the key strategy for low temperature lignin depolymerisation into desirable monomeric aromatic compounds in relatively high yields.[4c,7] To this end, new strategies have been developed using representative β-O-4 model compounds, for which results are summarized in recent reviews.[3b,4c,5b,7b-c] In particular, several studies have recently highlighted the need for stabilization of reactive cleavage products in order to supress recondensation reactions, that lead to decreased monomer yields.[8]

Ionic liquids (ILs) have many desirable characteristics for implementation as green reaction media, such as negligible vapour pressure, chemical inertness, tuneable polarity, acidity, basicity and tuneable miscibility with other solvents.[9] Moreover, ILs have been reported as excellent solvents for the notoriously hard to dissolve lignin fractions[10] and have shown great potential for the fractionation of lignocellulose components[9c,11] Therefore, the development of lignin depolymerisation methodologies in ILs is very attractive.

One particularly intriguing field is the synthesis of nanoscale metal catalysts of controlled size and shape, namely metal(0) nanoparticles (M-NPs).[12] M-NPs stabilized in ILs have been shown by us and others to possess a variety of attractive properties for use in catalysis[13] and have found several interesting synthetic applications recently.[14] A recent development showed that ionic liquids may act in particular cases not only as solvent, stabilizing and protecting agent for the formed nanoparticles, but selected ions are suitable to act as very mild reducing agents.[13b-c,15] In particular cases even common ILs derived from imidazolium ([BMIM]NTf$_2$ or [BMIM]OAc$_2$) are capable to act as mild reducing agents. The advantage of this approach is that external reducing agents as additives such as hydrogen, hydrazine or metal borohydrides are unnecessary. Moreover, the reducing process is slower than in presence of hydrogen which implies that the local metal(0) concentration is kept low, avoiding a fast particle growth leading to undesired large particles, but allowing the synthesis of small particles. The nanoparticle catalysts can be directly used for application in catalysis, such as hydrogenation of arenes[13b,15c], (partial) hydrogenation of C-C[15a] as well as carbon hetero multiple-bonds[15c,16], C-C bond cleavage[15b] and C-N coupling reactions.[14b,16] The incorporation of functional groups into the IL-moiety allows the modification of the metal surface with ligands, thus controlling the (chemo)selectivity as for example in hydrogenation reactions.[15a-c,16,17] In particular the controlling of the (chemo)selectivity via catalyst surface modification is of particular interest also for biomass refinery. Efficient hydrodeoxygenation of phenol to cyclohexane was demonstrated using a combination of metal nanoparticles dispersed in IL and Brønsted ionic liquids.[18]

The key novelty in our approach is to use such a catalytic system for the cleavage of lignin linkages and the subsequent stabilization of reactive intermediates via in-situ reduction, provided that aromatic ring hydrogenation is not prevalent. Furthermore, ILs would allow for biphasic reactions and separation of the reaction components (Figure 2).[17]

Brønsted acids are often used to facilitate fractionation of lignocellulose as this leads to bond scission leading to partial depolymerisation of lignin.[11d,19] In this context, Brønsted acidic properties of ILs have also been studied for facilitating depolymerisation of lignin into aromatic subunits.[10d,11b,20] In order to study lignin acidolysis with Brønsted acidic ILs, several groups have employed lignin β-O-4 model compounds.[19a,21] Effective cleavage of the β-

O-4 linkage was found using 1-H-3-methylimidazolium chloride ([HMIM]Cl) at 150 °C by addition of a small amount of water[21a] or by employing catalytic amounts of Lewis acidic metal chlorides, such as $AlCl_3$ in combination with 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) to presumably form ([BMIM][$AlCl_4$]).[21b] Here, up to 80% of one of the cleavage products (guaiacol **3**) could be obtained. A separate study found no direct relation between cleavage activity and the IL acidity.[21c] The results indicated different prevalent cleavage pathways for coordinating and non-coordinating anions (Scheme 1). In these studies, Hibbert ketones[22] were suggested to be the secondary products. However, exact structures and quantities were not established. Additionally, the formation of higher molecular weight products was indicated.

Identification and quantification of the secondary reaction products is important as in lignin only one set of products is formed that contains the both functional groups from the model compounds cleavage reactions (alkyl and phenolic side). Therefore, significant amounts of products can only be obtained from lignin if “both sides” of the model compound are obtained in reasonably high yield after cleavage.[6a] The pathways observed in ILs relate closely to established mechanistic insight on acid catalysed conversion in mixtures of water and organic solvents.[22b-c,23] The main difference is the observation of the apparent stability of the vinyl ethers in ILs.[21d]

In this work, we aimed to establish further insight into acid mediated depolymerisation of lignin in multifunctional ILs. Furthermore, in situ stabilization of reactive intermediates in these multifunctional reaction media was envisioned in order to obtain stable cleavage products. For this purpose, the cleavage of lignin β-O-4 model compound **1** was studied in detail with Brønsted acidic ILs, **IL-H$^+$1** and **IL-H$^+$2** as catalysts (Figure 3). Additionally, homogenously dispersed metal nanoparticles in IL were prepared and evaluated as hydrodeoxygenation catalyst to stabilize the acid catalysed cleavage product **2**, hereby forming more stable **4** or potentially **5**.[8a] Ionic liquid 1-butyl-2,3-dimethylimidazolium *N*,*N*-bis(trifluoromethylsulfonyl)imide ([BM_2Im]NTf_2, **IL1**) was selected for its demonstrated ability to stabilize homogenously dispersed ruthenium nanoparticles, which have been previously shown excellent for in situ hydrogenation reactions.[13b] (<- ANSWER COMMENT 1 REFEREE 2) This ionic liquid has the added advantage that it contains no acidic imidazolium proton[24], which is expected to provide controlled acidity in the reaction medium.

Results and discussion

Cleavage of β-O-4 model compounds using IL-H$^+$ in IL1

Cleavage activity of **IL-H$^+$1** was tested on β-O-4 model compound **1** with **IL1** as reaction medium (Scheme 2). The reaction conditions were optimized for the yield of guaiacol **3**. As expected, no conversion of **1** was detected in the absence of **IL-H$^+$1** demonstrating the lack of acidic protons in the **IL1** reaction medium. Upon addition of **IL-H$^+$1** high substrate conversion was detected. Increasing the temperature led to higher selectivity for **3** at short reaction times, indicating a fast cleavage reaction and slow decomposition of the reaction products (Figure 4). The reaction appeared fast compared to previously reported systems in 1,4-dioxane[8a] and water.[22b,23,25] The maximum yield of **3** was 42% upon using 10 mol% **IL-H$^+$1** in **IL1** after 1 minute at 140 °C. Application of 2-phenoxy-1-phenylethanol as substrate provided similar yields of phenol compared to **3**.

Unlike in the ionic liquid system employed by Ekerdt *et al*, we found no positive effect of the addition of water.[21a] Our previous work, using triflic acid in 1,4-dioxane, showed excellent yields of **3**.[8a] In order to test the potential of biphasic reactions with **IL1** mixtures of 1,4-dioxane were tested as reaction medium (Figure 5). This clearly showed a positive effect of the addition of 1,4-dioxane. The exact nature of this positive effect is unknown, but this might be related to the stabilization of the reaction products. It should be noted that a 1:1 mixture of 1,4-dioxane : IL results in a single phase while a biphasic system is observed at ratios of 3:1 and greater. (<- ANSWER COMMENT 1 REFEREE 1)

A lower substrate concentration was beneficial for obtaining higher yields of **3** (Figure 6). This effect has likely to do with the stability of the products in the reaction mixture. The yield of **3** could be increased to 61%, at a substrate concentration of 0.1 M, 140 °C and using 5 mol% **IL-H$^+$1** (Figure 7). Increasing the temperature to 160 °C did not improve the yields of **3** after 5 minutes. When **IL-H$^+$2** was used as Brønsted acid, the yields of **3** were very similar (around 60%, Figure 8). However, in contrast to **IL-H$^+$1**, the application of **IL-H$^+$2** did lead to slightly improved yields of **3** at temperatures above 140 °C. At a reaction time of 5 minutes over 70% **3** could be obtained at 180 °C and 200 °C. This could be further improved to 74% **3** at 200 °C by decreasing the reaction time to 2 minutes. **IL-H$^+$2** has less Brønsted acidity compared to **IL-H$^+$1**, might therefore cause less product decomposition. Overall, the yields of **3** following cleavage **1** with **IL-H$^+$2** at 200 °C at low reaction times are an improvement over earlier reported reactions of β-O-4 model compounds in acidic IL or IL media.[19a,21]

Side reactions involving cleavage products

Apart from **3**, typically complex mixtures of products were observed by HPLC (Figure 9a). Using **IL-H$^+$2** at elevated temperature provided much cleaner reaction mixtures as well as less coloured solutions (Figure 9b). Identification by LC-MS analysis revealed the dehydration product **6** as a mixture of E- and Z-isomers, which were previously reported as major products starting from β-O-4 model compounds in ionic liquid media.[21c-d] The observation of **6** reveals that, although substrate conversion is high, not all of the dimer is in fact cleaved, even at high temperatures. This is likely caused by the stabilization of carbocation intermediates obtained upon dehydration in the ionic medium.[10c,19a,26] Although this explains why selectivity towards **3** never reaches 100%, it does not provide evidence on the fate of the second cleavage product that consequently has to be formed upon release of **3**. Column chromatography allowed for isolation of 2-phenylnapthalene **7** from the reaction mixture. Formation of **7** was confirmed using an authentic sample, which also allowed for quantification. Formation of up to 10% was found in reactions that gave relatively high amounts of **3** at high reaction temperature and time. Up to 20% of **7** could be obtained at prolonged reaction times (1 hour). Additionally, when HOTf or $MeSO_3H$ were applied as Brønsted acid in **IL1** relatively high amounts of **7** were observed (up to 20%). **7** originates from acid mediated aldol condensation of aldehyde **2** and subsequent condensation and dehydration (Scheme 3).[27] These results highlight the dehydration potential of these catalytic systems. Other signals found by HPLC may relate to other products originating from aldol condensation reactions or other condensation reactions of **2** (e.g. condensation of **3** and **2**, which would be in line with the observation of the decomposition of **3**). Furthermore, side products can originate from the condensation reaction between the carbocation intermediate and aromatics in the product mixture. Products related to **7** obtained from lignin would be functionalized (phenolic) polycyclic aromatic compounds. Tuning the properties of the IL system to prefer such pathways for the formation of polycyclic aromatics from lignin is an interesting future direction to explore. (<- ANSWER COMMENT 2 REFEREE 1)

Trapping the aldehyde cleavage product with ethylene glycol

Recently, we reported on a novel methodology to increase the yields of the cleavage products by trapping the aldehyde **2** with ethylene glycol to obtain the corresponding acetal **8**.[8a] Moderate yields of **8** were also obtained upon the addition of ethylene glycol to the cleavage reaction of **1** in **IL1** using **IL-H$^+$1** as catalyst (Scheme 4, Figure 10). In line with the results presented above, lower catalyst loadings led to higher yields of the products **8** and **3**. Increased reaction times resulted in significantly lower yields. From these observations it can be concluded that **8** is not a stable product in this reaction medium. A similar degradation of **8** was previously observed in toluene at the same temperature with triflic acid as Brønsted acid catalyst.[8a] Using triflic acid in the ionic liquid medium led to very low yields of **8** (<20%) even after 5 minutes. No formation of **7** was observed in the reaction using ethylene glycol as well as increased yield of **3**. These observations indicate that another decomposition pathway for **2** could be Friedel-Crafts hydroxyalkylation of **3**. These results highlight the need for direct conversion of reactive aldehydes formed upon cleavage of the lignin β-O-4 linkage.

Synthesis and characterization of ruthenium nanoparticles

Ruthenium nanoparticles were employed to stabilize the reaction products by in-situ hydrogenation of the formed aldehyde product to the corresponding alcohol. For this purpose, ruthenium nanoparticles were dispersed in **IL1** according to a literature procedure developed for similar ionic liquids by heating of a $Ru(cod)(methylallyl)_2$ solution.[14a] The formation of homogeneously dispersed ruthenium nanoparticles (Ru-NP@**IL1**) was confirmed by TEM measurements and the size distribution was determined, showing an average size of 3.0 ± 0.3 nm (Figure 11). These results are comparable to nanoparticles homogeneously dispersed in related ionic liquids.[14a]

Cleavage in bifunctional ionic liquid reaction media

Cleavage of **1** combined with in situ hydrogenation of the reactive aldehyde intermediate to **2** was performed using Ru-NP@**IL1** as hydrogenation catalyst (Scheme 5). Several products were anticipated through sequential dehydration and hydrogenation steps based on earlier experience with in situ hydrogantion reactions following acid mediated cleavage of **1**.[8a]

Initial experiments were performed overnight using **IL-H$^+$1** as Brønsted acid catalyst in **IL1**. Low **IL-H$^+$1** loading (<1 mol%) resulted in high conversion of **1**. However, the main products corresponded to **1** in which the β-O-4 ether was not cleaved and the aromatic rings were hydrogenated. Additionally, small amounts of aromatic monomeric products that were formed were completely “over-reduced” to the corresponding cyclohexane compounds. Increasing the amount of **IL-H$^+$1** gave moderate yields of **9** at reaction times from 1 to 4 hours (Figure 12a). Surprisingly, at these high loadings incomplete conversion was observed after 1 hour. Increasing the reaction time resulted in full conversion and a small increase in the yields of **3** and **9**. Lowering the amount of **IL-H$^+$1** did not lead to improved yields of **3** and **9**. These experiment indicate that the addition of the Ru-NP@**IL1** lowers the overall rate of cleavage of **1**, which is greater in **IL-H$^+$1** alone, thus the two catalyst affect each other. (<- ANSWER COMMENT 3 REFEREE 1) In conjunction with the ethylene glycol trapping experiments, the application of a stabilization strategy that converts the reactive aldehyde **2** in situ, leads to near equimolar yields of the two cleavage products. Small amounts (up to 15%) of **11** and ring hydrogenation products of **11** and **1** were also detected as side products. Saturated compound **11** is the result of sequential dehydration and hydrogenation of **1** and was previously found to be resistant to acid catalysed cleavage.[8a,28] Additionally, hydrogenated monomeric compounds **9h** and **10h** were observed as minor products (<3%) as well as small amounts (<1%) of further dehydration and hydrogenation of **9** to **10**. This stands in contrast to earlier reports from comparable reactions in 1,4-dioxane with triflic acid and 5% Ru/C, where **10** was a major product.[8a] Consistent with the cleavage reaction of **1** with **IL-H$^+$1**, the yields of **3** could be increased to over 60% upon application of a mixture of **IL1** with 1,4-dioxane (Figure 12b). Under these conditions, moderate yields of **9** were obtained even at lower ruthenium loading, while similar amounts of non-cleaved dimers were observed. At lower concentrations of **IL-H$^+$1**, significant amounts of **2** were found in the mixture. This is in contrast to the reaction without 1,4-dioxane were only traces of **2** (<2%) were detected. The observed amounts of **2** are counter-intuitive, yet remarkable, as **2** is typically unstable under acidic conditions. This could be caused by several factors. For example, **2** might be separated from the acidic **IL1** layer by solvation in the 1,4-dioxane layer. Additional measurements with authentic standards in a 1,4-dioxane : IL (4:1) biphasic mixture confirmed the preference of 2-phenylacetaldehyde for the 1,4-dioxane layer (See SI, section 4). This likely plays a role in temporary separation of the aldehyde from the acidic IL layer and allows for more controlled hydrogenation to take place, without extensive recondensation due to the buildup of the aldehyde in the IL phase. (<- ANSWER COMMENT 1 REFEREE 1) Additionally, 1,4-dioxane might effectively reduce the acid strength of the reaction medium leading to the suppression of side reactions.[8a]

Brønsted acid catalyst **IL-H$^+$2** was also assessed for the cleavage of **1** in combination with Ru-NP@**IL1** (Figure 13). In this case with 20 mol% **IL-H$^+$2** no significant amounts of **9** and **3** were found. Significant amounts of **11** and hydrogenated substrate were detected instead. By increasing the amount of **IL-H$^+$2** to 40 mol% cleavage products of **1** were observed as well as residual **2**. Further increasing the amount of **IL-H$^+$2** led to additional formation of **9** and **3**. Again, yields of **3** and **9** could be increased by the addition of 1,4-dioxane. Up to 53% **9** was obtained. The cleavage of **1** with **IL-H$^+$2** showed optimal cleavage product formation at temperatures above 140 °C. Therefore, in situ hydrogenation was performed at 180 °C. Repetitively, the cleavage activity of the bifunctional catalytic system was surprisingly low compared to the cleavage reactions without Ru-NP@**IL1**. Complete substrate conversion was obtained after 5 minutes at 180 °C while in the presence of Ru-NP@**IL1 a**fter 1 hour the reaction was still incomplete (compare figures 8 and 14 entries for 180 °C). Leaving the reaction for 2 hours led to full conversion of **1** and increased amounts of **3** and **9** showing a progressive reaction. In these experiments significant amounts (up 15%) of **10** was observed, revealing the positive effect of the temperature on the subsequent dehydration/hydrogenation of **9**.

The above results indicate that harsher reaction conditions (temperature and acid strength) are required for effective cleavage of **1** with **IL-H$^+$2** in the presence of Ru-NP@**IL1**. The hydrogenation activity of Ru-NP@**IL1** were relatively low under these conditions. However, extended reaction times at temperatures of 140 °C or higher seemed to increased ring hydrogenation as well as other undesired side reactions. To overcome this, relatively short temperature bursts at 180 °C were applied followed by further reaction at lower temperature to allow for consecutive hydrogenation of any remaining **2** (Figure 14). Similar yields of **3** were obtained when compared to a reaction at 180 °C for two hours, indicating a fast cleavage reaction. Conform expectations improved yields of **9** (up to 64%) were observed. This supports the hypothesis that cleavage is relatively fast and the hydrogenation is relatively slow. Additionally, under these conditions, less side products were observed that arise from ring hydrogenation of the substrate as well as **11**. Despite of using the "temperature burst"-method, the Brønsted acidity and the loading of the hydrogenation catalyst could not be reduced.

The fate of the ruthenium nanoparticles

In order to better understand the low hydrogenation activity under reaction conditions, the hydrogenation of **2** alone by Ru-NP@**IL1** was studied. The nanoparticles performed well in reported hydrogenation reactions (Table S1).[14a] Additionally, hydrodeoxygenation of phenol and cyclohexanol was successful in the presence of **IL-H$^+$1** although with lower activity (Table S2). In most of the reactions using **1** as substrate agglomeration of the ruthenium nanoparticles was observed. This effect was not observed by solely heating the Ru-NP@**IL1** to high temperatures. However, when the same experiment was repeated in the presence of the substrate, significant agglomeration was observed. This indicated a possible deactivation of the ruthenium nanoparticles, which could not be recycled in these reactions. (<- ANSWER COMMENT 2 REFEREE 2) Hydrogenation of **2** by Ru-NP@**IL1** in the absence and presence of **IL-H$^+$2** was followed in time (Figure 15). In the absence of Brønsted acid **2** was initially converted to **9**, however hydrogenation activity significantly decreased over time to stall at a maximum 41% yield of **9** after 3 hours. In the presence of **IL-H$^+$2**, **2** was quickly converted. However, selectivity to **9** was low reaching a maximum of 32% after 30 minutes. The initial rate was higher with 24% of **9** formed in the first 10 minutes compared to 6% of **9** in the absence of **IL-H$^+$2**. Thus, the Brønsted acid catalyst appears to have a positive influence on the hydrogenation activity, an effect that has been previously observed for ruthenium hydrogenation catalysts.[30] (<- ANSWER COMMENT 3 REFEREE 1) This explains that when short and high temperature bursts were applied the best results for the yield of **9** were obtained. Under these conditions **1** rapidly cleaved and the produced **2** rapidly hydrogenated to **9** before the catalyst loses its activity.

Conclusions

This study demonstrates that stabilization of the reactive intermediates formed upon acid catalysed cleavage of lignin model compounds in ionic liquids is a desirable strategy. For the first time proof of principle is provided for the in situ catalytic conversion of these instable fragments, taking advantage of modular, multifunctional nature of this alternative reaction media.

The acid catalysed cleavage of the β-O-4 lignin model compound **1**, using Brønsted acidic IL media, confirmed earlier observations, that good selectivity to guaiacol **3** can be achieved.[21a-b] Isolation of 2-phenylnapthalene **7** from the reaction mixture revealed 2-phenylacetaldehyde **2** as the secondary cleavage product in agreement with studies in conventional reaction media.[8a,22b,23,25] Further efforts focused on stabilization of **2** in situ to obtain acetals or alcohols. By addition of ethylene glycol, **2** was converted to 2-benzyl-1,3-dioxolane **8** in equimolar amounts to **3**. By employing bifunctional reaction media containing both a Brønsted acid catalyst and Ru-NP@**IL1** as hydrogenation catalyst, good yields of 2-phenylalcohol **9** could be obtained. This is the first time good combined yields of monomer products were obtained from a reactions in ionic liquids.

Relating the selective and efficient depolymerization of lignin as an aromatic polymer with predominantly β-O-4 linkages, phenolic products that resemble a combination of both **2** and **3** would be obtained upon acid catalysed cleavage. Therefore, good selectivity for both types of products is essential for successful application of such methodology on lignin. Thus, the present study explains the low monomer yields in early attempts of lignin depolymerisation in ionic liquid media[10d,11b,19a,] which in model compounds only provided good yields of one cleavage product.[19a,21a]

Future studies should focus on improving stability of these catalytic systems in order to prevent agglomeration of the metal nanoparticles in the presence of the substrate. Additionally, aromatic ring hydrogenation activity should be minimized. Further tailoring the acidity of the reaction medium, and the nature of the nanoparticles, for example copper-based NP@**IL** should lead to improved catalytic systems for effective dissolution and depolymerisation of lignin. This could be combined with efficient product separation in an IL/organic biphasic system.

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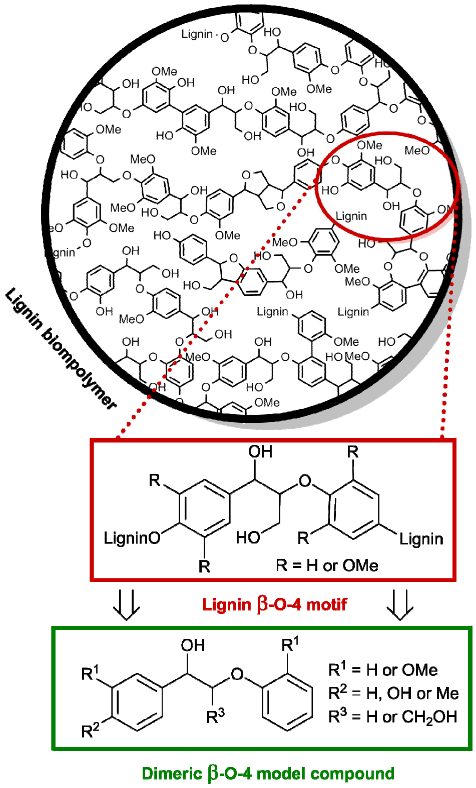


Figure 1. Lignin structure highlighting the β-O-4 linkage and model compounds representing this motif.

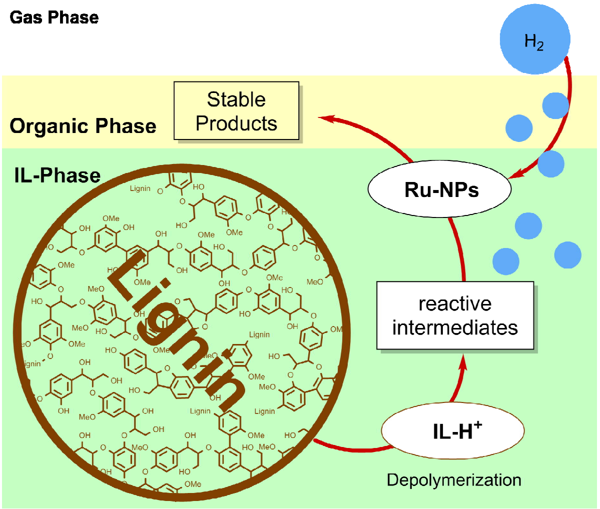


Figure 2. Concept of lignin depolymerisation in ionic liquid followed by conversion of reactive intermediates using Ru-NPs and H_2 and separation of products.

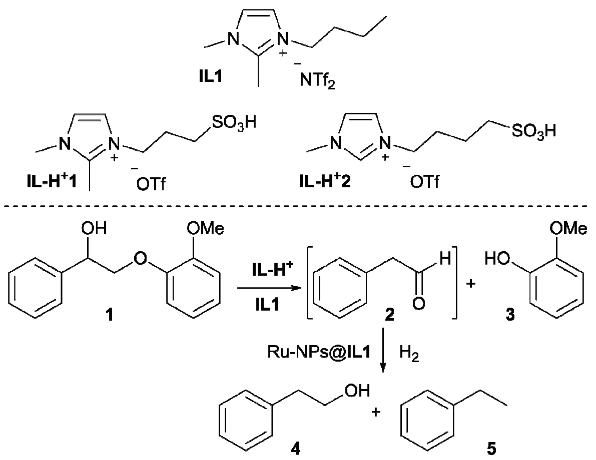


Figure 3. Ionic liquid medium and Brønsted acidic ionic liquids used in this study and approach to cleavage and conversion of reactive intermediate.

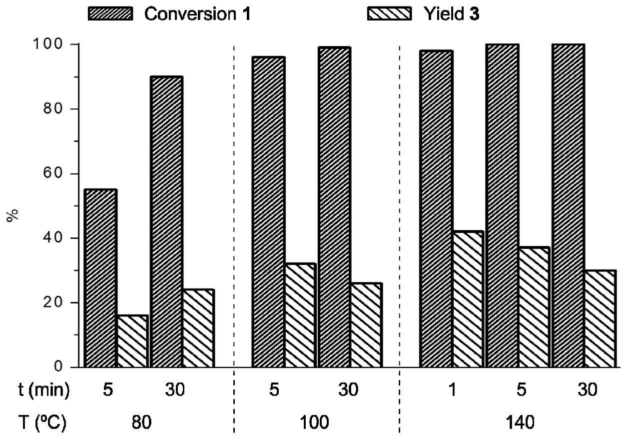


Figure 4. Conversion of **1** and yield of **3** in the cleavage of compound **1** (0.1 mmol) with **IL-H$^+$1** (0.01 mmol) in **IL1** (500 μL) at different reaction times and temperatures.

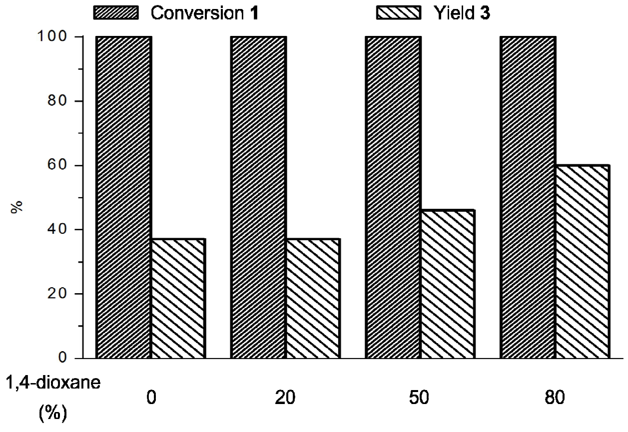


Figure 5. Conversion of **1** and yield of **3** in the cleavage of compound **1** (0.1 mmol) in mixtures of **IL1** and 1,4-dioxane (0.2 M) with **IL-H$^+$1** (0.01 mmol) at 140 °C and 5 min.

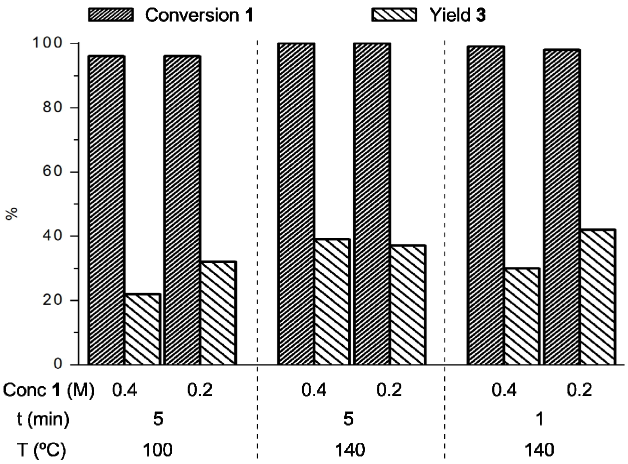


Figure 6. Conversion of **1** and yield of **3** in the cleavage of compound **1** (0.1 mmol) at different concentration in **IL1** with **IL-H$^+$1** (0.01 mmol).

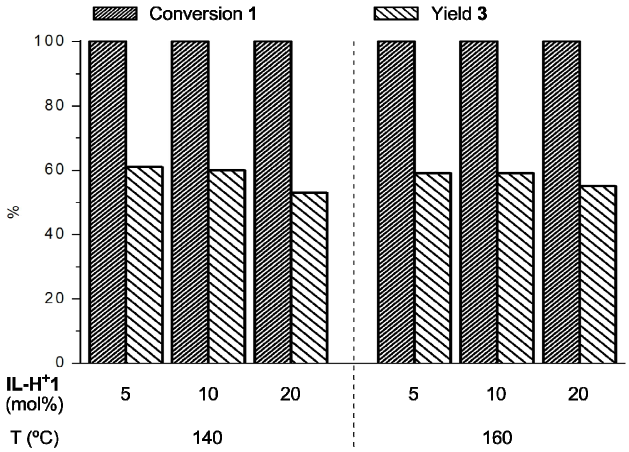


Figure 7. Conversion of **1** and yield of **3** in the cleavage of compound **1** (0.05 mmol) in **IL1** (0.1 M) at different temperatures and **IL-H$^+$1** concentrations after 5 min.

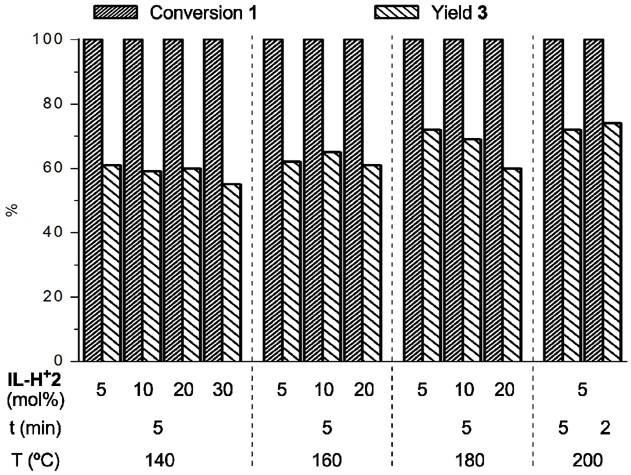


Figure 8. Conversion of **1** and yield of **3** in the cleavage of compound **1** (0.05 mmol) in **IL1** (0.1 M) at different temperatures and **IL-H$^+$2** concentrations.

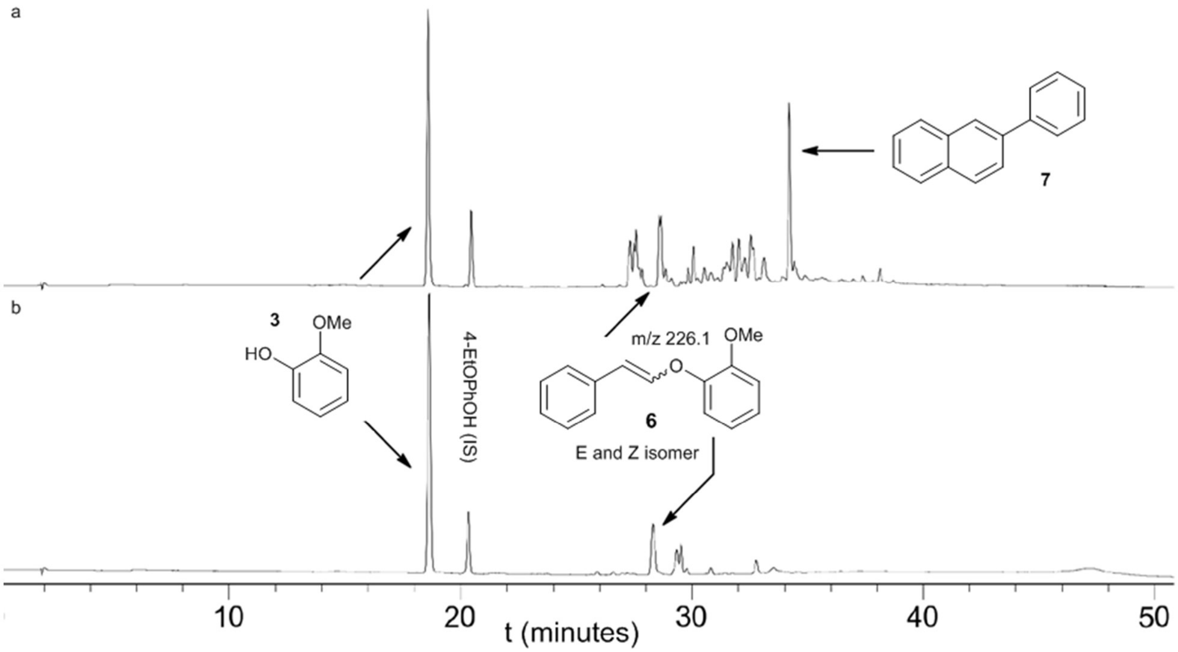


Figure 9. Representative HPLC chromatograms showing identified signals of a) 140 °C, 30 min, 0.1 mmol **1** 0.2 M in **IL1**, 10 mol% **IL-H$^+$1** b) 200 °C, 2 min, 0.05 mmol **1** 0.1 M in **IL1**, 5 mol% **IL-H$^+$2**.

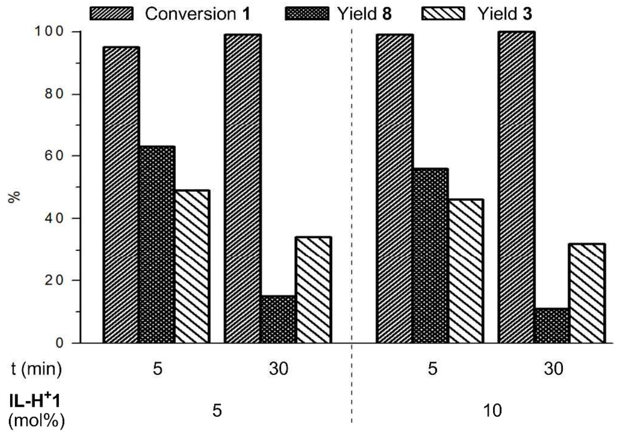


Figure 10. Conversion of **1** and yields of **3** and **8** in the cleavage of compound **1** (0.1 mmol) in **IL1** (0.2 M) at 140 °C with **IL-H$^+$1** in the presence of 8.5 µL ethylene glycol.

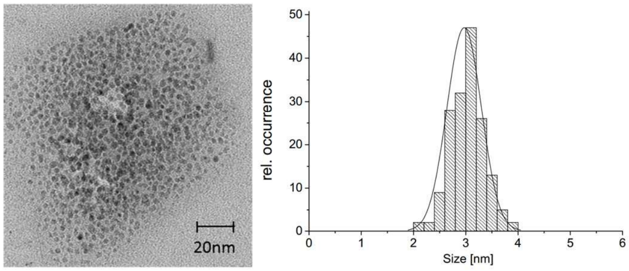


Figure 11. TEM measurement of Ru-NP@**IL1** and size distribution.

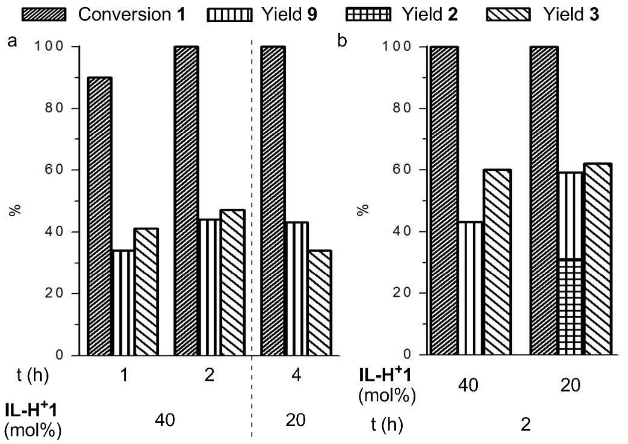


Figure 12. Conversion of **1** and yields of **2**, **3** and **9** in the cleavage of compound **1** (0.1 mmol, 0.2 M) in a) **IL1** and b) 60% 1,4-dioxane in **IL1** at 140 °C with **IL-H**$^+$**1**, 40 bar H_2, Ru-NPs@**IL1** (a) 30 mol% [Ru], b) 7.5 mol% [Ru]).

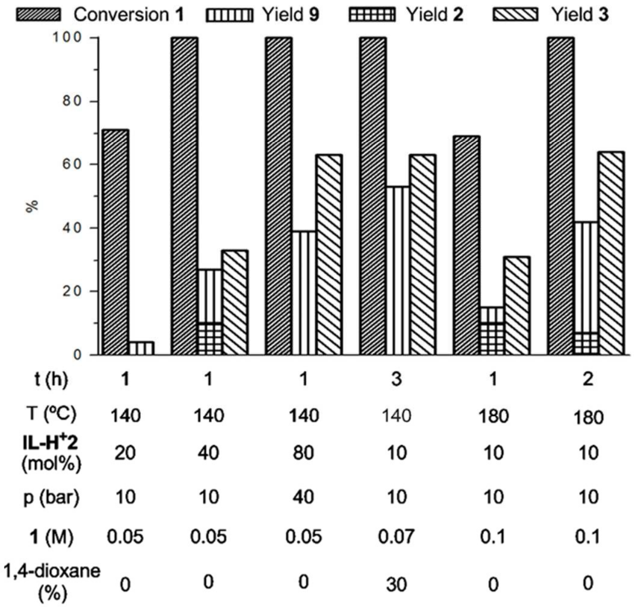
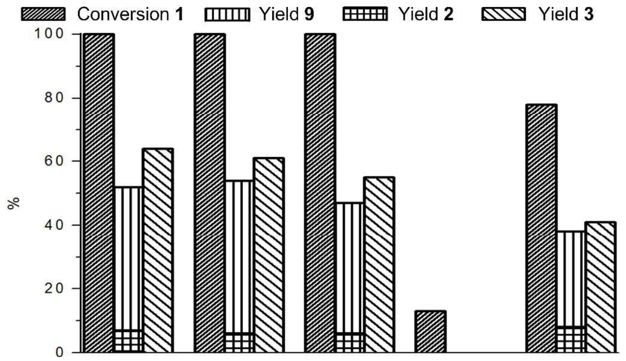


Figure 13. Conversion of **1** and yields of **2**, **3** and **9** in the cleavage of compound **1** (0.05 mmol) in **IL1** with **IL-H**$^+$**2** and Ru-NPs@**IL1** (30 mol% [Ru]).



Burst (180 ºC)					
t (min)	5	10	20	10	10
Reaction (100ºC)					
t (h)	3	2	1	3	3
IL-H$^+$2 (mol%)	40	40	40	10	20
[Ru] (mol%)	30	30	30	5	25

Figure 14. Conversion of **1** and yields of **2**, **3** and **9** in the cleavage of compound **1** (0.05 mmol, 0.1 M) in **IL1** with **IL-H$^+$2** and Ru-NPs@**IL1** using 180 °C temperature bursts at 10 bar H_2.

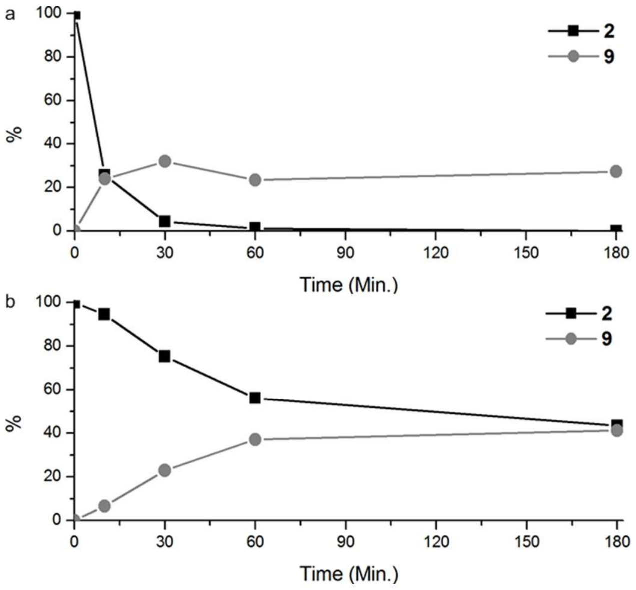
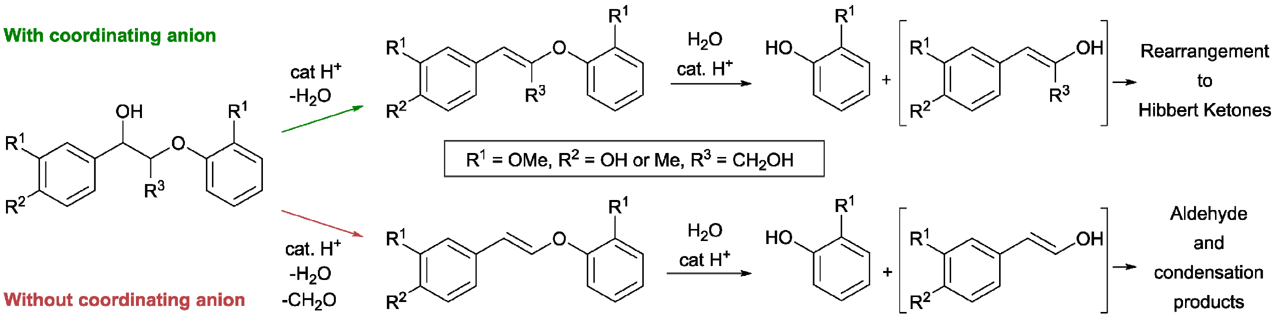
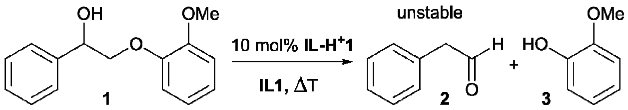


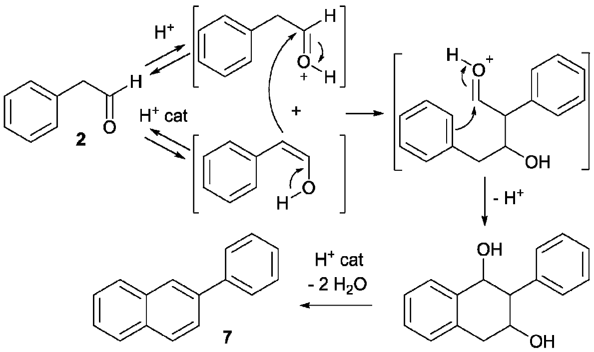
Figure 15. a) Catalytic hydrogenation of **2** with Ru-NP@**IL1**, 6 mol% [Ru], 140 °C b) in the presence of 40 mol% **IL-H$^+$2** in **IL1**.



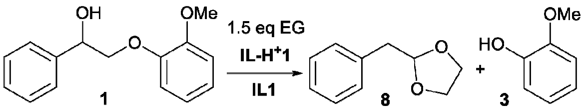
Scheme 1. Acid mediated cleavage pathways of β-O-4 model compounds, identified in ionic liquid media.[21c]



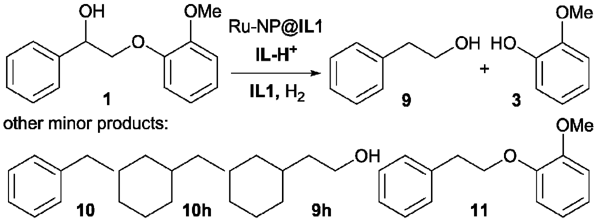
Scheme 2. Cleavage of β-O-4 model compound **1** with **IL-H$^+$1** in **IL1**.



Scheme 3. Formation of **7** via aldol condensation of **2** and subsequent condensation and dehydration.[27]



Scheme 4. Cleavage of β-O-4 model compound **1** with **IL-H$^+$1** in **IL1** in the presence of ethylene glycol (EG) to give 2-benzyl-1,3-dioxolane **8**.



Scheme 5. Cleavage of β-O-4 model compound **1** with **IL-H$^+$** in **IL1** in the presence of Ru-NP@**IL1** and hydrogen to give 2-phenylethanol **9**.

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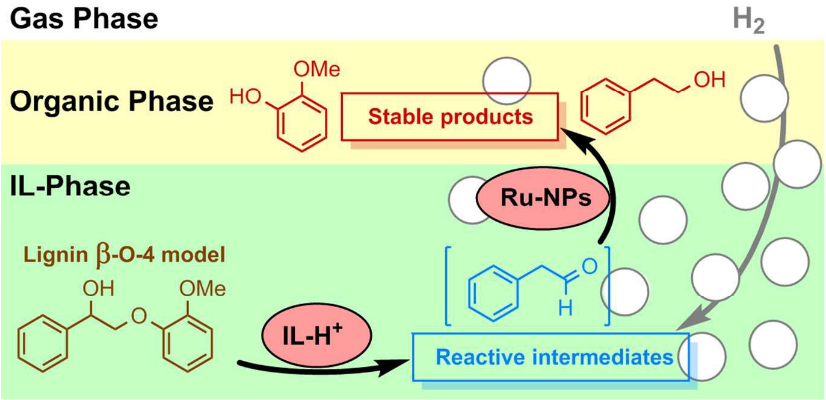

Solving the lignin β-O-4 cleavage using acidic multifunctional Ionic liquid media.