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# Electrochemical depolymerisation of lignin in a deep eutectic solvent

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Lignocellulosic biomass is an important renewable resource that could substitute fossil feedstocks as a raw material for high value chemicals production. While the cellulosic fraction of biomass gives access to saccharides only, lignin could possibly give access to low molecular weight aromatic compounds. Strong alkalinity of the reaction medium is necessary in order to dissolve lignin and to obtain an electrically conducting solution. However, strong alkalinity is supposed to be one of the reasons for consecutive oxidations to undesired organic acids and carbon dioxide. The high pH also limits the use of only a few metals as electrode materials. We report the use of pure deep eutectic solvents (DES) in order to dissolve lignin in combination with electrochemical oxidative depolymerisation. We also present successful extraction of the products through liquid-liquid extraction and their characterization by size exclusion chromatography and GC-MS, proving that a successful depolymerisation of lignin was achieved. Guaiacol and vanillin were the two most abundant detected products.

## 1Introduction

### Lignin valorisation

Lignin is the most abundant potential renewable source for aromatic building blocks. Traditionally, industrial processes that use plant polysaccharides utilise lignin as energy source by means of combustion. The advent of biorefineries that convert cellulosic biomass into liquid transportation fuels will likely produce more lignin than necessary for energy production[1]. For these reasons, the valorisation of lignin into high value compounds, such as fuel, additives or fine chemicals, is a fundamental requirement for a positive energy balance of future biorefinery concepts[2]. Lignin depolymerisation is a very promising process which can generate valuable products starting from lignin as raw material. The primary purpose of depolymerization is to convert the complex lignin molecules into small molecules (monomers or oligomers) for further applications[3]. Pyrolysis is used to obtain bio-oil from the lignin that can be used as fuel[4,5]. Enzymatic processes have been at the moment mostly suggested for wood delignification and cleavage of lignin model compounds[6]. Homogeneous as well as heterogeneous catalysis has been investigated to obtain a successful depolymerisation of lignin's structure. Frequently, metallic catalysts are combined with high temperature and pressure[7]. For instance, ruthenium, iron, copper and vanadium have been proposed for the depolymerisation of lignin[8–10]. However, catalyst recovery and catalyst aging are often a serious technical impediment to achieve a sustainable and technically viable process. Electrochemical depolymerisation is a potential approach for highly sustainable conversions because only electrons serve as reagent, while the catalyst remains immobilized on the electrode surface. For these reasons, such conversions can be considered as reagent-free, avoiding reagent waste and are possibly performed at mild process conditions[11]. Still the choice of the catalyst is limited by the pH at which the lignin is solubilized. In particulare, high pH values limit the choice of the metallic electro-catalyst.

### Electrochemical depolymerisation of lignin

The state of the art solvent for the solubilisation of lignin is a sodium hydroxide solution as Kraft lignin is not soluble at neutral pH. This solution is suitable for the electrochemical reaction due to its sufficiently high conductivity. Typical lignin bonds such as carbon-carbon bonds and carbon-oxygen bonds can be cleaved through the catalytic properties of the appropriate potential of the working electrode[12]. Current bottlenecks for the process are lack of selectivity, low yields at mild conditions and further oxidations of products. Several attempts of electrochemical depolymerisation of lignin have been reported, mainly using strong alkaline media. Parameters such as electrode material, temperature and reactor configuration were systematically studied although product overoxidation remained an issue[12,13]. In-situ removal of

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desired depolymerization reaction products through nanoporous membranes integrated into an electrochemical reactor eliminates this problem, avoiding further oxidations. [14] Electrode porosity influences depolymerisation kinetics significantly[15].

The alkalinity of the solution gives sufficient conductivity to perform the electrochemical process, however only those metal-based catalysts can be used which are stable at this high pH, as for instance, nickel. [16] Catalyst development would benefit from solvent systems which give access to milder conditions (room temperature, neutral pH), where more metal or metal oxides can be investigated and utilised. Two possible depolymerisation mechanisms have been proposed. The first mechanism considers a direct electron transfer at the electrocatalyst anode surface (nickel). The second mechanism involves depolymerisation in aqueous phase or in a solvent partially containing water. With the second mechanism the depolymerisation could take advantage of an indirect oxygen atom tranfer and of an activated oxygen mechanism. In any case the mechanisms governing the electrochemical depolymerisation of lignin are yet unclear[15,17–19].

Hence, we investigate deep eutectic solvents as they are able to solubilise lignin [20] and are suitable for electrochemical processes such as electrodeposition[21]. Yet another issue needs to be resolved with aqueous solutions. If the solvent system is water based, electrochemical oxidation of lignin in aqueous solutions may suffer from simultaneous parasitic oxygen evolution, resulting in reduced current utilisation[22]. Hence, a mostly non-aqueous solvent system is desired for lignin valorisation. Here, we report potentially important new solvents for the lignin depolymerisation process.

### Deep eutectic solvents

Deep eutectic solvents (DESs) are mixtures of two or more compounds, often in the solid state as pure chemicals, that reach their eutectic point at room temperature causing the mixture to be liquid and homogeneous[17]. Recently, deep eutectic binary mixtures have been noticed to fulfil different criteria such as easiness of preparation, non-toxicity, biodegradability, non-flammability and low price and they have proved to solubilise lignin[23]. DESs also have similar electrochemical and rheological properties compared to ionic liquids (ILs)[24]. Contrary to ILs, DESs are considered to be not reactive with water[25]. ILs have been considered widely in biorefinery concepts, however their recovery needs to be close to complete, otherwise process economics suffer [26,27]. Hence, cheap IL-like solvent systems are interesting to be identified for several applications in biorefinary fractionations and lignin valorisation[28]. Significant issues in the utilisation of the DESs are the recovery and possible side reactions due to the degradation of the binary mixture[29].

### Product recovery

Recovery of the depolymerisation products is yet another important step during the process development. Membrane processes become increasingly important, in particular when they are integrated into a reactor concept. In biorefinery applications, membrane processes currently grow out of their infant state[30]. Selective extraction processes are often today's choice in order to recover the depolymerisation products. When using new solvent systems for the electrochemical cleavage of lignin also the subsequent extraction processes needs to be considered. Fractionation of lignin using different organic solvents has been widely used in order to characterise lignin fractions based on the different molecular weights. Depending on the fraction of interest and on the downstream analytics, appropriate solvents can be chosen[31]. We report below that the classical organic extractants will fulfil many of the required properties for the new DES systems used during the depolymerisation experiments.

## 2 Materials and Methods

### Electrochemical depolymerisation

Kraft Lignin (370959, Sigma Aldrich) was used. Two DES systems were prepared by using ethylene glycol, urea and choline chloride (Sigma Aldrich). All chemicals were used as received. DESs were prepared by mixing the choline chloride with urea (Urea-ChCl) or with ethylene glycol (EtGly-ChCl). The mixing was performed at room temperature or by slightly heating in order to accelerate initial melting of the salts. The used molar ratio was 1:2 in order to reach the eutectic point, resulting in a liquid, clear solution.

The electrochemical depolymerisation of lignin in DES was carried out in an undivided cell using a three-electrodes configuration. Nickel (99.9 % purity, Alfa Aesar) was used as electrocatalyst. The geometric surface area of the electrode was 2.5 $cm^2$. Ag/AgCl was used as reference electrode. Chosen oxidation potential were 0.5 and 1.0 V. These values were obtained analysing the electrochemical window of the DES by means of cyclic voltammetry. At higher voltages than 3V high thermal losses were noticed (warm up of the DES). The electrochemical experiments were performed at room temperature for 24 hours using 5 $g\ l^{-1}$ as lignin concentration.

### Lignin recovering and liquid-liquid extraction

Lignin was recovered from the DES by means of a dilution 1:4 with a 0.01 M $H_2SO_4$ (Sigma Aldrich) solution. The precipitated insoluble lignin was dissolved in 1 M sodium hydroxide (NaOH, 99%, Sigma Aldrich) for SEC analysis. The soluble lignin fraction was extracted from the supernatant with a liquid-liquid extraction (LLE) using ethyl acetate (EA) (99.8% purity, Sigma Aldrich) as organic phase. Produced aromatic compounds were extracted with methyl isobutyl ketone (MIBK) (99.5% purity, Sigma Aldrich) with a LLE for further analysis. The two phases were brought in contact by mixing the samples for 5 hours. After extraction the two phases were accurately phase separated by centrifugation and the organic phase was divided from the water phase. Ideally, lignin should be easily separated from the DES system, as well from as the products. Simple dilution of the lignin DES system with water was identified as an efficient method to separate the lignin and, theoretically, to reuse the DES. However, the recycling of the DES goes beyond the aim of this work.

### Analytics

Size exclusion chromatography (SEC) was used to measure the average molecular weight of the different lignin fractions. Average molecular weight ($\overline{M_w}$) and polydispersity (D = $\overline{M_w}/\overline{M_n}$, where $\overline{M_w}$ is the weight average molecular weight and $\overline{M_n}$ the number average molecular weight) were evaluated. Measurements were performed using an Agilent 1200 system equipped with a refractive index detector at a wavelength of $\lambda = 280$ nm. Eluent solution was prepared with water (HPLC grade, Carl Roth) with addition of 0.1 mol $L^{-1}$ sodium hydroxide (NaOH, 99 % , Sigma Aldrich) and 0.01 wt% sodium azide ($NaN_3$, extra pure, Merck KGaA). The internal standard was a 12.5 mg $mL^{-1}$ glucose monohydrate solution (biochemistry, Merck KGaA). One precolumn (8x50 mm) and three MCX gel columns (8x300 mm) were used at a flow rate of 1.0 mL $min^{-1}$ at 40 °C. The diameter of the gel particles was 5 µm, the nominal pore widths were 1000 Åfor the three columns. Calibration was performed using narrowly distributed poly(styrene sulfonate) standards (Polymer Standards Service).

Gas chromatography mass spectrometry (GC-MS) (Agilent 6890 and N-Agilent 5975 MSD) equipped with a J&W 122-0132 DB-1MS capillary column (30 m, 0.25 mm n.d., film 0.25 mm) was performed in order to detect the monomers and oligomers produced during the electrochemical depolymerisation and subsequent extraction. Helium was applied as carrier gas with an initial flow of 0.8 ml $min^{-1}$. The initial temperature of the GC oven was 50 °C for 1 minute, thereafter the temperature was increased until 120 °C with a rate of 15 °C/min and finally 280 °C were reached with a rate of 25 °C/min. The two temperatures were kept constant for 6 and 2.5 minutes, respectively. All identified products by GC-MS measurement were quantified by external calibration curves. All identified products were purchased by Sigma Aldrich, purest available grade.

## 3Results and Discussion

### Solubility and conductivity

Figure 1 shows the solubility (left y-axes) and conductivity (right y-axes) of lignin dissolved in different solvents. The solubility of lignin in 1 M NaOH was used as a reference since this solvent is the benchmark for electrochemical depolymerisation of lignin. The solubility of lignin in 1 M NaOH was found to be around 75 g $L^{-1}$. The solubility in Urea-ChCl is 85 % of the solubility in NaOH. EtGly-ChCl shows the best solubility of lignin with a final value of 100 g $L^{-1}$. EtGly-ChCl was still able to dissolve lignin, however 100 g $L^{-1}$ was chosen as final concentration since the increase of the viscosity made the solution difficult to handle. EtGly-ChCl was chosen as solvent for the electrochemical experiments based on better lignin solubility and better conductivity in comparison with Urea-ChCl. Improvement of the conductivity for EtGly-ChCl was achieved by adding 10 % water without affecting the solubility of lignin. At the same time the addition of water decreased the viscosity of the DES-Lignin solution. Water-free DES and DES-Water solvent allow electrochemical processes in which oxygen evolution reaction is absent or marginal, hence not being the main mechanism for lignin depolymerisation. Further optimisation of these solvent systems is beyond the scope.

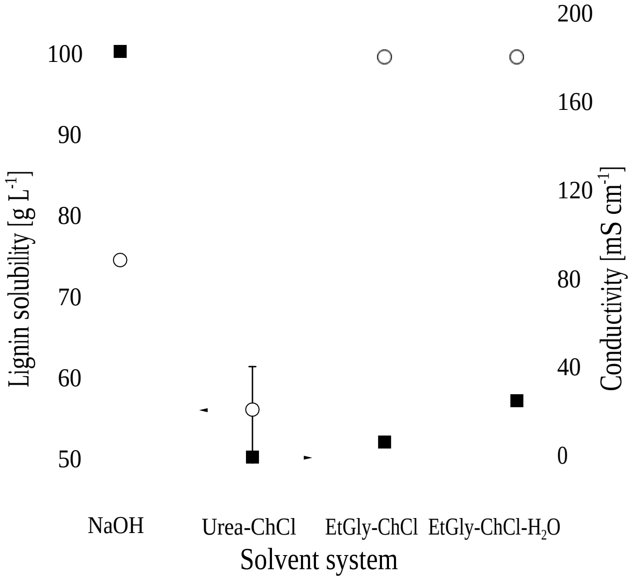

**Fig. 1** Lignin solubility and conductivity of 1M NaOH, Urea-ChCl, EtGly-ChCl and EtGly-ChCl dissolved with 10 % $H_2O$

### Analysis of the lignin after the electrochemical depolymerisation

Figure 2 shows SEC chromatograms of lignin after 0, 7 and 24 h of electrochemical depolymerisation. All curves show three characteristic peaks, one representing the high molecular weight (HMW) fraction (with a maximum around 3000 Da) and two peaks representing the low molecular weight (LMW) fraction (with maxima around 105 and 45 Da). The line of the 0 h sample represents lignin without electrochemical depolymerisation. Figure 2a and 2b show the electrochemical process using pure EtGly-ChCl as solvent for the lignin at 0.5 and 1 V as anodic potentials. Chromatograms after 7 h show that lignin did not change its molecular weight distribution since the two curves overlap each other almost perfectly. A slight shift towards left and a decrease in intensity for the HMW can be noticed after 24 h of electrochemical depolymerisation. At the same time an increase of the two LMW peaks occurs. LMW peaks are due to a wide range of possible products coming from the depolymerisation. Figure 2c and 2d show chromatograms for the electrochemical depolymerisation in the DES-water solvent, again using respectively 0.5 and 1 V as anodic potentials. A more pronounced shift towards lower molar masses and a decrease in intensity can be noticed for the HMW peak. Furthermore, a strong increase in intensity for the LMW peaks can be seen, indicating a successful depolymerisation of the lignin. Changes in the chromatograms are already clearly visible after 7 h reaction time for both potentials. The strongest signal for the LMW peaks is observed after 24 h of electrochemical depolymerisation indicating a stronger depolymerisation at

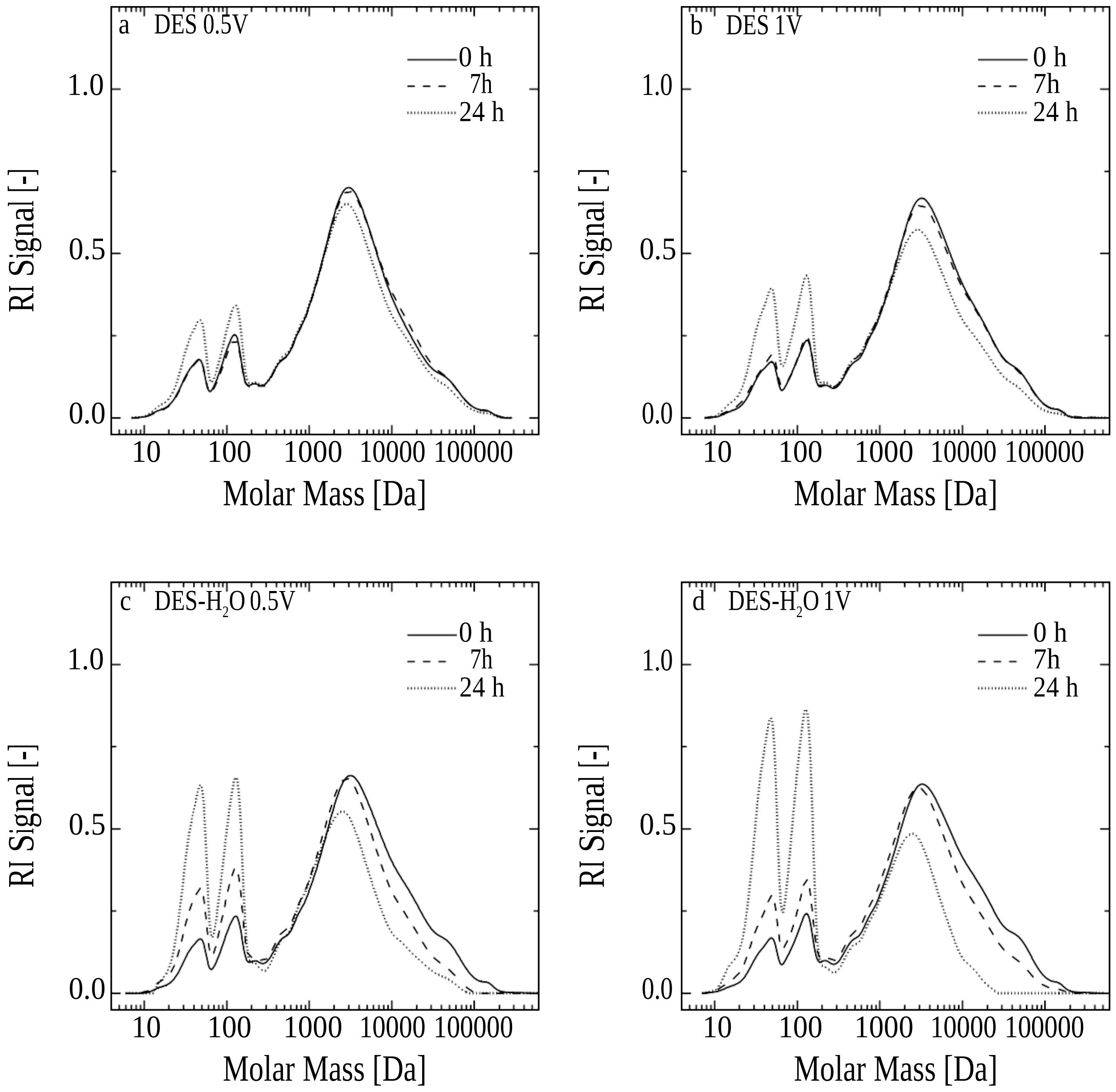

**Fig. 2** SEC results after the depolymerisation of lignin in DES at (a) 0.5 V and (b) 1.0 V and in DES dissolved with 10 % water at (c) 0.5 V and (d) 1.0 V (—— untreated lignin, – – – lignin after 7 h and · · · · lignin after 24 h of electrochemical depolymerisation)

the end of the experiment.

Table 1 presents the average molecular weights of the lignin over time of electrochemical depolymerisation. Interestingly, both experiments in pure EtGly-ChCl show in the first hours of electrochemical depolymerisation higher values of average molecular weights, indicating that the polymerisation of the lignin occurs. Depolymerisation starts between 2 and 5 h and it reaches a final value of depolymerisation respectively of 80 % and 65 % compared to the starting molecular weight for the 0.5 V and 1 V experiments after 24 h. Both experiments in DES-water show a decrease in molecular weight already after 1 h of depolymerisation and the last measured value was around 30 % of the starting molecular weight, achieved after 24 h of electrochemical depolymerisation for both 0.5 and 1 V.

Figure 3 presents a visual overview of untreated lignin (0 h) and of lignin after electrochemical depolymerisation (7 and 24 h). The colour of the solution after 0, 7 and 24 h of depolymerisation in EtGly-ChCl with a 0.5 V and b 1 V and in EtGly-ChCl dissolved with 10 % $H_2O$ with c 0.5 V and d 1 V. The colour difference between 0 and 7 h of electrochemical depolymerisation is visible for the experiments performed at 1 V (Figure 3b and 3d). In time the colour of the solution becomes brighter: this is even more visible by comparing 0 and 7 h with 24 h of electrochemical depolymerisation. By comparing these results and by combining them with the molecular weight distribution of Figure 2, it can be concluded that the brighter the colour of the extracted solution is, the lower the molecular weight distribution is.

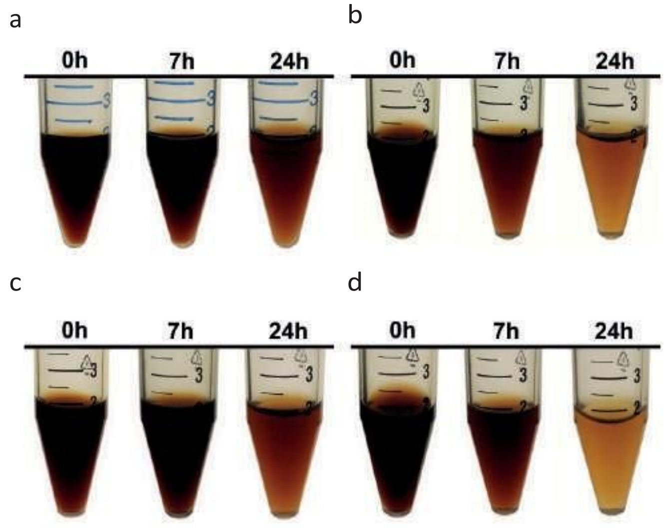

**Fig. 3** Visual difference of the lignin solution after 0, 7 and 24 h of electrochemical depolymerisation with (a) 0.5 V and (b) 1 V and in DES with (c) 0.5 V and (d) 1 V in DES with 10 % water

SEC analysis of the soluble lignin obtained from the liquid liquid extraction was performed, in order to gather the complete information regarding the change of the molecular weight of the lignin. Table 1 presents the molecular weight of the lignin and of the extracted lignin. The molecular weight distribution of the soluble lignin was found to be smaller in comparison to the insoluble lignin, confirming an effect of the electrochemistry on both solu-

**Table 1** Molecular weight for lignin ($\overline{M_w}$) and lignin extract ($\overline{M_w}$ extract) at different depolymerization time

| | Time [h] | $M_w$ [Da] | $M_w$ extract [Da] |
|---|---|---|---|
| DES 0.5 V | 0 | 7569 | 388 |
| | 1 | 7794 | |
| | 2 | 8536 | |
| | 5 | 7901 | |
| | 7 | 7460 | 251 |
| | 24 | 6077 | 66.6 |
| DES 1 V | 0 | 8655 | 323 |
| | 1 | 10131 | |
| | 2 | 9220 | |
| | 5 | 8913 | |
| | 7 | 8931 | 288 |
| | 24 | 5618 | 178 |
| DES-Water 0.5 V | 0 | 9519 | 306 |
| | 1 | 9377 | |
| | 2 | 8577 | |
| | 5 | 5731 | |
| | 7 | 5065 | 228 |
| | 24 | 3288 | 122 |
| DES-Water 1 V | 0 | 9466 | 356 |
| | 1 | 8751 | |
| | 2 | 8829 | |
| | 5 | 7257 | |
| | 7 | 6403 | 225 |
| | 24 | 2598 | 92.5 |

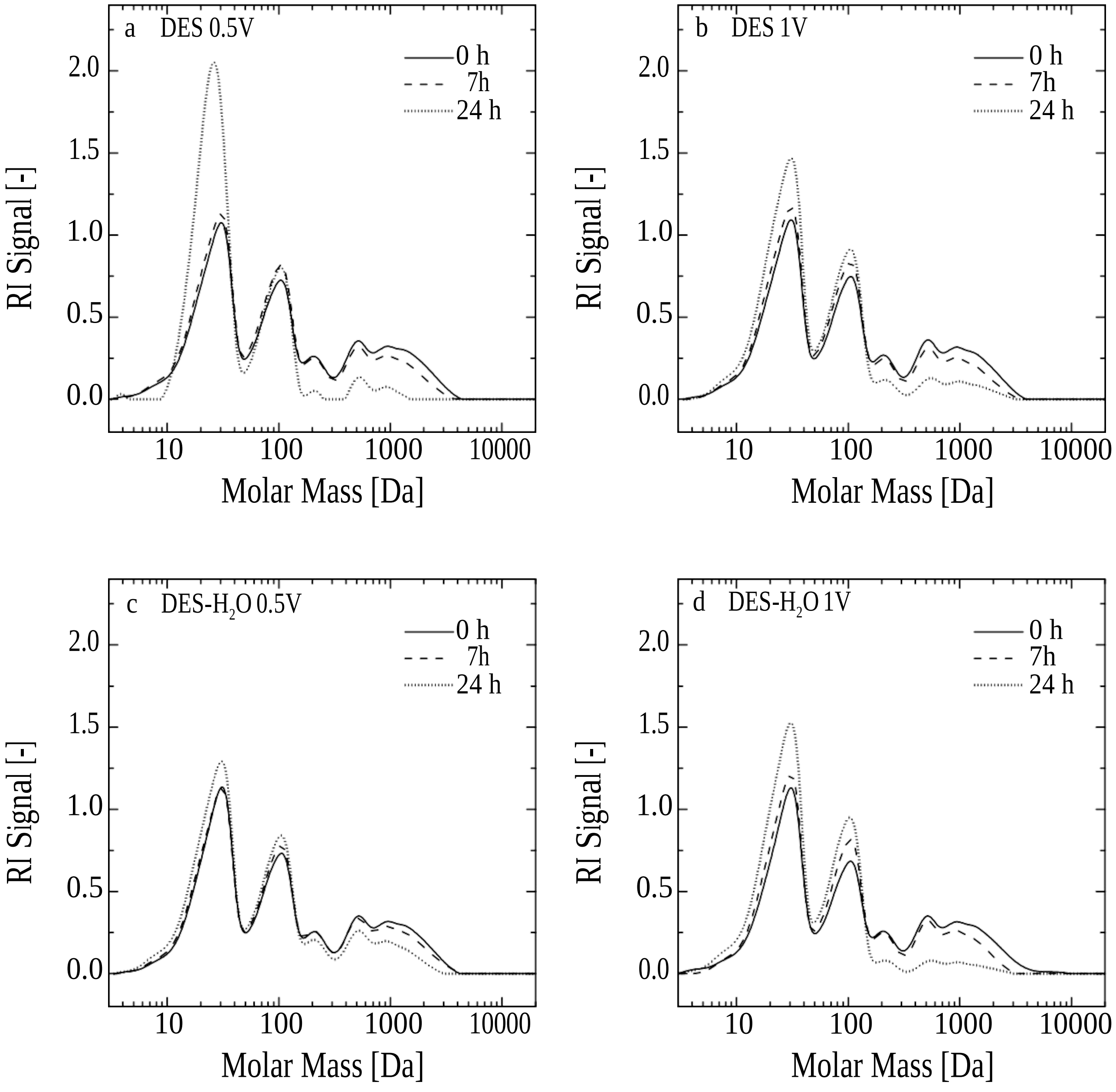

**Fig. 4** SEC results of the extract from the liquid liquid extraction after the depolymerisation of lignin in DES at (a) 0.5 V and (b) 1.0 V and in DES dissolved with 10 % water at (c) 0.5 V and (d) 1.0 V (—— untreated lignin, – – – lignin after 7 h and · · · · lignin after 24 h of electrochemical depolymerisation)

ble and insoluble lignin. Figure 4 presents the chromatograms for the soluble lignin after 0, 7 and 24 h of electrochemical depolymerisation for the experiments in pure DES and in DES-water at the two different anodic potentials (0.5 and 1 V) corresponding to the chromatograms of the insoluble lignin showed in Figure 2. It can be noticed that the intensity of the LMW peaks is higher already in the 0 h sample for all chromatograms. The decrease in the molecular weight of the soluble lignin confirmed what was already observed from the SEC analysis of the insoluble lignin and it is in accordance with the depolymerisation process.

### GC-MS results

Due to the lack of selectivity of the electrochemical process, the product spectrum of depolymerisation products is broad. The product spectrum contains oligomers and monomers, for example vanillin, guaiacol and syringol. The depolymerisation products were extracted from the supernatant by means of a liquid liquid extraction using MIBK as a selective extractant. Table 2 presents the list of identified products consulting the NIST online database[32]. A relatively small amount of the total number of peaks of the GC chromatogram could be identified. A quantification of the total product spectrum is known to be a very difficult task.

Figure 5 presents the relative mass of products yielded during the electrochemical depolymerisation. A starting amount of phenols is present already in the untreated lignin and this is depicted by the relative value 1. The experiment in DES at 0.5 V (Figure 5 a presents a decrease of the relative mass in time for the products, indicating a consecutive oxidation during the depolymerisation. An increase of 10 % in relative mass can be seen in the other three experiments (Figure 5 a and b). The increase in products was observed in the first three hours of electrochemical depolymerisation for DES 1 V and DES-water 0.5 and 1 V. In the remaing time of the depolymerisation process the total amount of products slowly decreased (in case of DES 1 V) or rapidly decreased (for both experiment in DES-water solvent). Experiments in DES dissolved with 10 % water present the highest increase (10 % in relative products), corresponding to approximately 2 wt% yield referred to the starting amount lignin. While this consecutive oxidation seems to be a severely limiting hurdle for the process, we have demonstrated that the in-situ removal will be a viable option to avoid overoxidation[14].

Guaicol, vanillin, acetovanillone and syringaldeyhde were the most abundant quantified products, representing for all the experiments almost the totality of the identified products. Guaiacol and vanillin were the two most abundant detected compounds with relative yields of 30-38% for guaiacol and 34-37% for vanillin. Acetovanillone and syringaldehyhde showed relative yields respectively of 9% and 12%. The relative yields did not show significant changes during the reaction time.

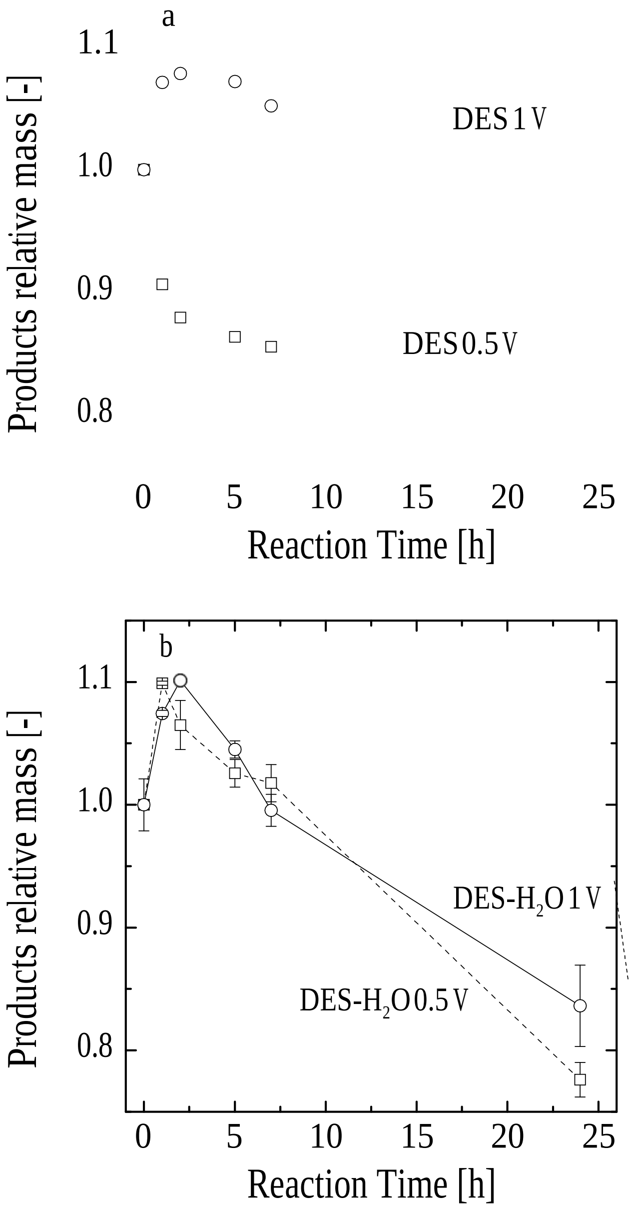

**Fig. 5** Products relative mass over reaction time of the depolymerisation of lignin at 0.5 and 1.0 V in (a) DES and in (b) DES dissolved with 10 % water (○ and – – – 0.5 V, Q and – 1 V)

## 4Conclusions and Outlook

DES systems are proposed as an alternative to NaOH and ILs as electrolyte for the lignin degradation processes. DESs are cheap, biodegradable and easy to handle and interest in using these sol-

**Table 2** Identified products for electrochemical depolymerisation of lignin in deep eutectic solvent using GC-MS

| | Compound | Chemical Formula |
|---|---|---|
| 1 | $\alpha$-Methylstyrene | $C_9H_{10}$ |
| 2 | Guaiacol | $C_7H_8O_2$ |
| 3 | P-Cumenol | $C_9H_{12}O$ |
| 4 | Phenil acetic acid | $C_8H_8O_2$ |
| 5 | Syringol | $C_8H_{10}O_3$ |
| 6 | 4-Hydroxybenzaldehyd | $C_7H_6O_2$ |
| 7 | Eugenol | $C_{10}H_{12}O_2$ |
| 8 | Vanillin | $C_8H_8O_3$ |
| 9 | 4-Hydroxyacetophenone | $C_8H_8O_2$ |
| 10 | Acetovanillone | $C_9H_{10}O_3$ |
| 11 | Di-butylhydroxytoluol | $C_{15}H_{24}O$ |
| 12 | Syringaldeyhde | $C_9H_{10}O_4$ |
| 13 | Acetosyringone | $C_{10}H_{12}O_4$ |
| 14 | Bisphenol-A | $C_{15}H_{16}O_2$ |

vents for biomass fractionation is growing. The development of processes for the valorisation of lignin in the fractionation solvent is crucial. We reported a proof of principle for lignin electrochemical depolymerisation. The process can be performed in DES (pure or diluted) and a subsequent liquid-liquid extraction of the products can be successfully performed. Molecular weight of lignin decreases due to the electrochemical processes producing low molecular weight products, as shown in the SEC measurement. GC-MS identified vanillin and guaiacol as the most abundant produced phenolic compounds. Quantification of the depolymerisation products and optimisation of the process parameters, such as electrode material, stability and DES recycling are the next important steps that need to be taken into account for the electrochemical depolymerisation of lignin in this new class of solvents.

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