Supporting information to "Liquid/liquid extraction of biomass-derived lignin from Lignocellulosic pretreatments"

Extract SEC elugrams for Kraft lignin

Fig SI 1 shows the SEC elugrams for Kraft lignin corresponding to Fig. 3 in the manuscript. Interesting to note is that the high molecular-weight fractions of Kraft lignin (elution times between 19 and 24 ml) are extracted more easily than their OrganoCat counterparts. Similar to the OrganoCat lignin, a shift in molecular weight between extract pH 13 and 14 occurs. This is especially interesting, as Kraft lignin has been fractionated from wood by a strongly alkaline solution in the first place.

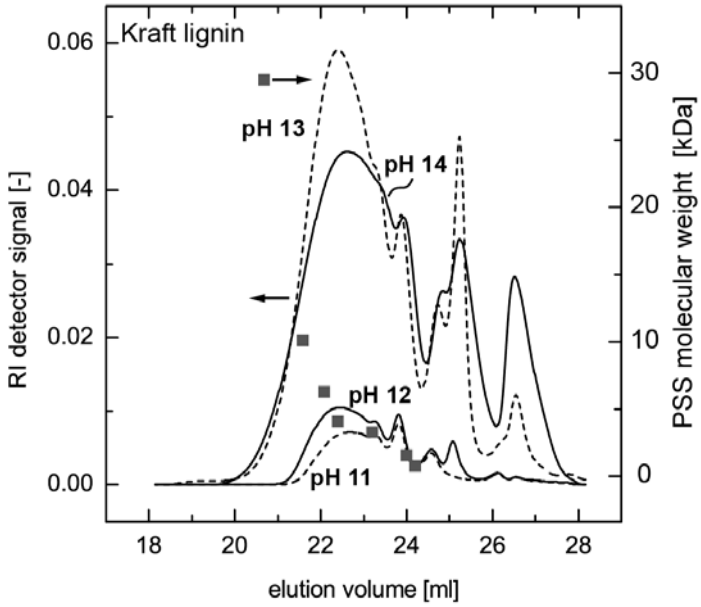

Fig SI 1 SEC Elugrams of extracted Kraft lignin for pH 11 to 14.

Molecular weights of extracted lignin samples

Table SI 1 shows the molecular weights corresponding to the presented SEC elugrams (Fig. 3 and Fig. SI 1). The calibration is based on narrowly distributed polystyrene-sulfonate (PSS) standards. The signals of both detectors have been evaluated. As can be seen from the data, the RI detector shows in general lower molecular weights than its UV counterpart, due to UV-inactive low-molecular weight fractions in the lignin sample. This effect is more pronounced in the OrganoCat lignin.

Table SI 1 Molecular weight of the lignin samples extracted at different pH values compared to a narrowly distributed poly styrene sulfonate standard. UV and RI detector signals have been evaluated separately.

	Kraft lignin		**OrganoCat lignin**	
Extract pH	M_w^{UV} [Da]	M_w^{RI} [Da]	M_w^{UV} [Da]	M_w^{RI} [Da]
11	1649	1683	603	345
12	1999	1835	923	519
13	2638	2233	2910	2409
14	2333	1898	1867	1486

NMR sample preparation and measurement method

The mixtures with known amounts of 2-MTHF in pH 13 NaOH were prepared as follows: A certain volume of 2-MTHF was given in a flask and either 40 or 50mL pH 13 NaOH, prepared from purified millipore water, was added with a volumetric pipette. The flasks were shaken thoroughly and remained a constant 30°C for at least 1 h. The aqueous phase was carefully removed from the flasks in the water bath using the following procedure in order to assure that no 2-MTHF residues can be found in the sample. The syringe was initially filled with air, which was expelled while passing the organic phase, and the withdrawn sample was transferred after removing the needle. The mixtures of NaOH in 2-MTHF were prepared similarly, except that the NaOH solution being weighed directly into the flask and a certain volume of 2-MTHF was subsequently added. Then the organic phase was withdrawn and analyzed.

In order to prevent proton exchange of the sample with the deuterated solvent, inserts for the NMR tubes were used. Inside an ordinary NMR tube, containing the sample, a smaller tube with DMSO-d6 was inserted. DMSO-d6 was chosen as deuterated solvent, because its ^{1}H-NMR signal interferes neither with the signals of 2-MTHF nor NaOH. In a preliminary test, ^{1}H-NMR spectra were acquired both at 400MHz and 600MHz, yet the resolution was found to be sufficient at 400MHz. The spectra were recorded on a Bruker AV III 400 spectrometer using deuterium frequency field lock.

Figs SI 2 and 3 show sample ^{1}H-NMR spectra for the partially saturated aqueous and organic phases.

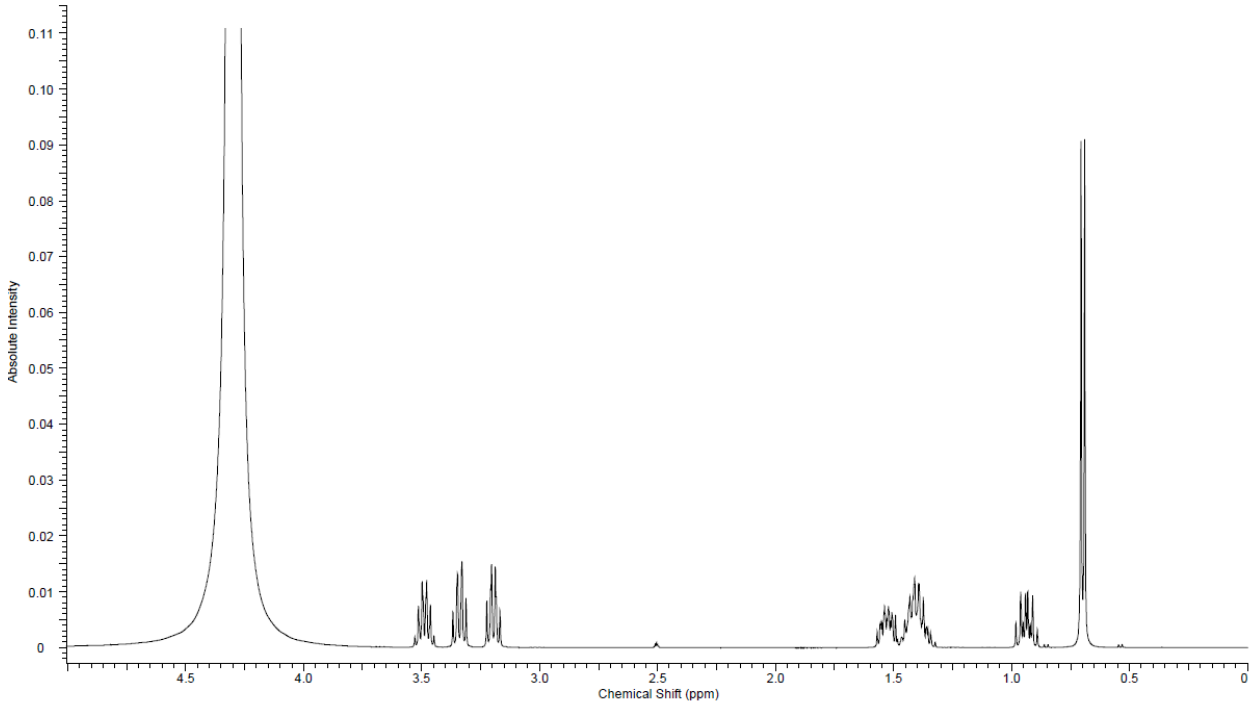

Fig SI 2 1H-NMR spectrum for an alkaline solution spiked with 2-MTHF

The singlet peaks with a chemical shift between 4.08 ppm and 4.50 ppm can be assigned to the proton of the hydroxide ion of aqueous NaOH, whereas the protons of the methyl group of 2-MTHF show a clear doublet peak between 0.67 ppm and 0.72 ppm. The other 2-MTHF peaks are not regarded for further analysis. The chemical shift of the peak maximum is determined and a range of ±0.2 ppm for the hydroxide ions and ±0.02 ppm for the CH3-group is chosen for integration. The ratio between the peak areas is then calculated as a signal that represents the amount of 2-MTHF in the aqueous NaOH solution.

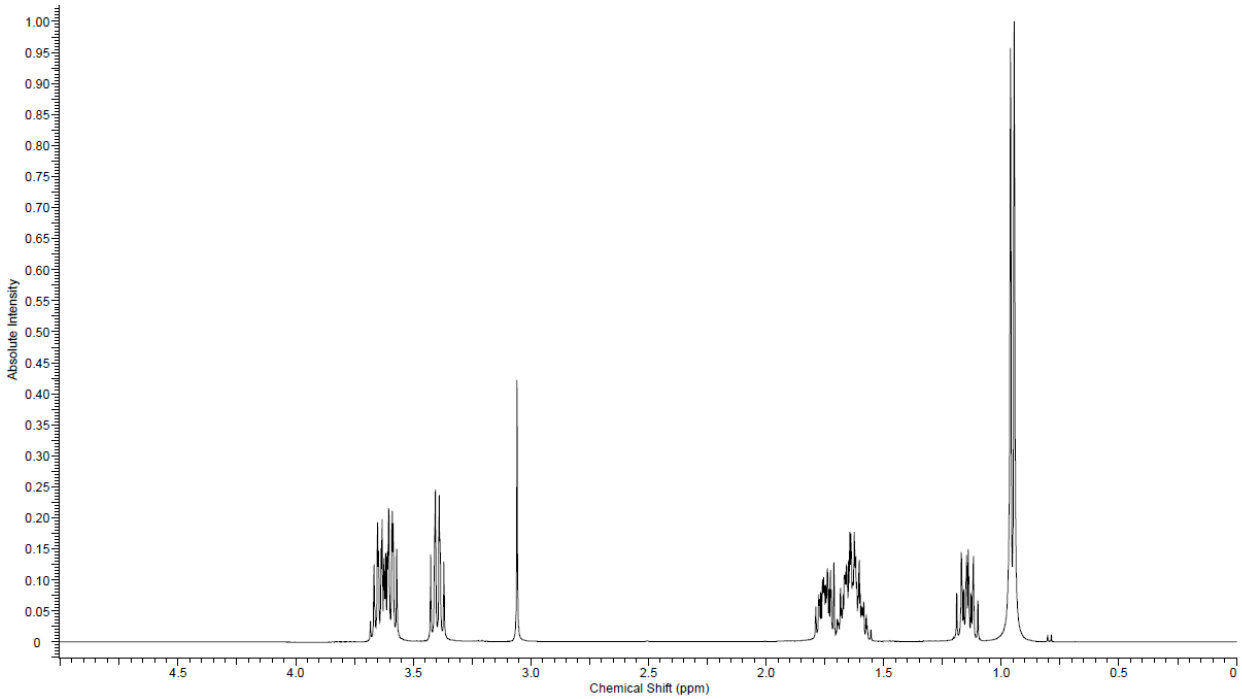

Fig SI 31H-NMR spectrum for 2-MTHF spiked with an alkaline solution

The solubility of NaOH in 2-MTHF can be calculated using a similar approach. Firstly, the peak maxima are determined and then the bounds of integration are chosen within a range of ±0.04 ppm for the CH_3-group of 2-MTHF and ±0.02 ppm for NaOH in water. It is noteworthy that the hydroxide peak shows a strong shift from 2.33 ppm for low concentrations to 3.27 ppm for high concentrations.

Fig SI 4 show the calculated ratios of the evaluated peaks for the saturated organic and aqueous phases. The data points corresponding to the regime where the amount of dissolved substance increases have been fitted with a linear regression line with an intercept of zero. The regime where the maximum solubility has been reached was fitted with a regression line without constraints. The intercept of the respective lines has then been calculated. The calculated intercept is relatively sensitive to measurement deviations, so that there are better suited methods for the detection of miniscule influences of salt concentration on the miscibility. For the detection of major trends however, as was the aim in this work, the measurements are relatively facile to perform and evaluate.

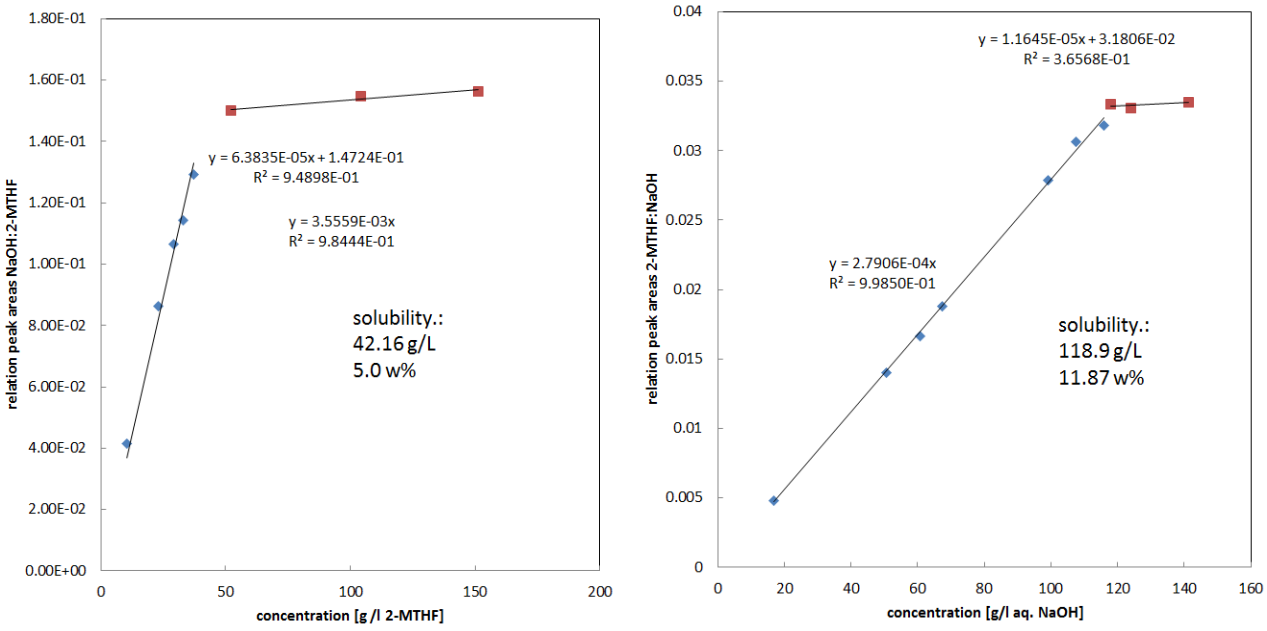

Fig SI 4 Relation of the characteristic integrated peak areas of 2-MTHF and aqueous sodium hydroxide plotted against respective concentration of the two phases. The left graph shows dissolved aqueous sodium hydroxide in 2-MTHF, the right graph 2-MTHF in aqueous sodium hydroxide. Linear regression lines with their equations are noted next to the lines.