
Acetosolv Pretreatment of Wood for Biorefinery Applications

Supplementary Information

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Fitting of Non-Recovered Fraction

Evaluation of the non-recovered fraction as a function of the catalyst concentration represents a first step towards the quantification of the influence of catalyst concentration. Our function resembles the logistic function chosen by [Dong et al. \(2017\)](#) and [Chang et al. \(2021\)](#) for the modeling of pretreatment phenomena during formic acid pretreatment of wheat straw and sugarcane bagasse, respectively. Since time and temperature were not varied for the acetosolv experiments, they are not included in the function. Furthermore, we assume that the biomass cannot be solubilized completely during pretreatment but instead we consider a maximum limit of non-recovered fraction after pretreatment $w_{\text{nr,max}}$. A similar assumption has already been made to model incomplete lignin solubilization during acetosolv pretreatment ([Vázquez et al., 1995](#); [Zhao and Liu, 2013](#)). Each fit includes all samples (i.e., DoD 0 to DoD 4) in concentrated acetosolv liquids (filled symbols) except for the two samples with DoD 4 for phosphoric acid, which are excluded due to the high standard deviations. To correlate the non-recovered fraction w_{nr} with the concentration of each catalyst acid c_{cat} , we use the following logistic function:

$$w_{\text{nr}} = \frac{w_{\text{nr,max}}}{\left(1 + e^{-w_{\text{nr,max}} \cdot k \cdot c_{\text{cat}}} \cdot \left(\frac{w_{\text{nr,max}}}{w_{\text{nr},0}} - 1\right)\right)}. \quad (\text{S1})$$

The parameters $w_{\text{nr,max}}$ and $w_{\text{nr},0}$ refer to the maximum value of the non-recovered fraction and the non-recovered fraction at a catalyst concentration of 0 (i.e., pretreatment without catalyst acid), respectively. k denotes the steepness of the increase of the non-recovered fraction with catalyst acid concentration. All parameter values are determined individually for each catalyst acid. Overall, the logistic function of Eq. (S1) represents the experimental data well as indicated by the high coefficients of determination. The fitted values for the three parameters depending on the type of catalyst acid are given in Tab. S1.

The estimated maximum non-recovered fraction is similar for all three catalyst acids: for complete disintegration, a maximum of approximately 40 wt % of beech wood is removed. Thus, this parameter is independent of the catalyst acid but is specific for beech or for acetosolv-pretreated beech. A comparable

Table S1: Fitting parameters for Eq. (S1).

	HCl	H ₂ SO ₄	H ₃ PO ₄
$w_{\text{nr,max}}$ (g g ⁻¹)	0.397	0.397	0.374
k (L mol ⁻¹)	238	1.58×10^4	16.9
$w_{\text{nr},0}$ (g g ⁻¹)	0.0532	6.45×10^{-8}	0.01997

overall limit has been observed by Parajó et al. (1993) with 50 wt % recovered fraction after acetosolv pretreatment of eucalyptus wood. The fluctuation of points around the upper limit of the non-recovered fraction might be due to the fact that especially at higher DoDs very small particles are formed, which are not hold back uniformly during filtration. Analogously, the estimated values for $w_{\text{nr},0}$ in case of hydrochloric and sulfuric acid are in the range of the non-recovered fraction determined in the experiment without catalyst (see Tab. S2), while the value for sulfuric acid appears rather low. Nevertheless, this parameter should have a fixed value independent of the type of catalyst acid for a general analysis. In contrast, an increasing value of k correlates with a decreasing amount of catalyst acid required to achieve disintegration. Hence, this parameter indicates the strength of the employed acetosolv liquids resulting from the acidity of the catalyst acid and/or the influence of the water content. A generalization of this analysis could aid to further describe acid properties of the investigated electrolyte solutions.

Compositional Changes after Pretreatment

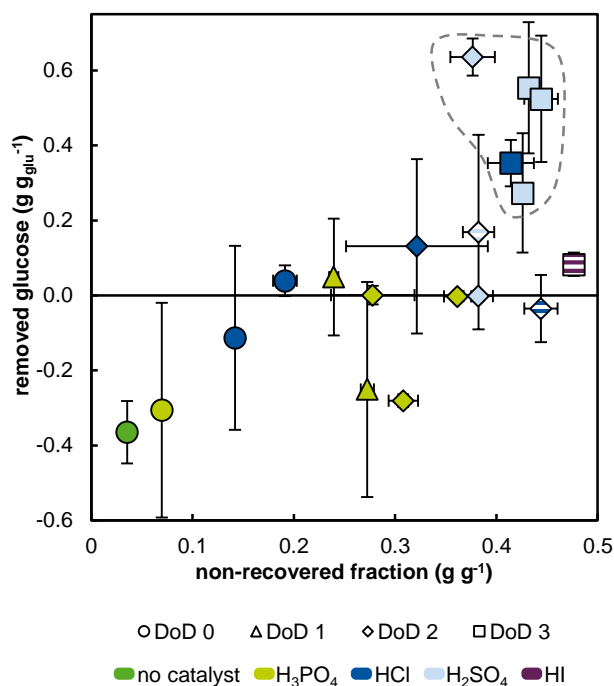


Fig. S1: Glucose removed during pretreatment with acetic acid-based liquids (filled symbols) and acetic acid–water-based liquids (striped symbols) versus non-recovered fraction. The content of cellulose as glucose in native beech is 41.8 wt %. The area delineated by the dashed curve highlights experiments with an extraordinary high fraction of lignin remaining in the pretreated material and at the same time a high amount of glucose removed during pretreatment. The shape and color of the symbols indicate the DoD and the employed catalyst acid, respectively (see legend). Error bars are shown only for measurements with standard deviation above symbol size.

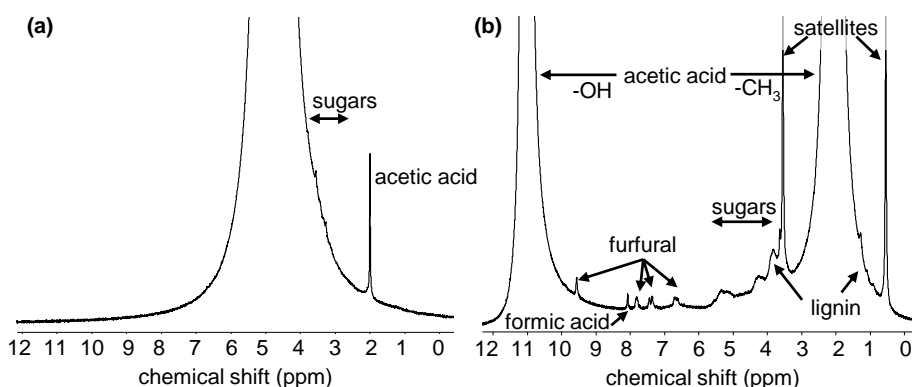


Fig. S2: NMR spectra of pretreatment liquids after pretreatment with signals of dissolved components: **(a)** Pretreatment liquid consisting of water and sulfuric acid ($234.48 \text{ mmol L}^{-1}$) and **(b)** acetosolv pretreatment liquid consisting of acetic acid and sulfuric acid ($21.78 \text{ mmol L}^{-1}$).

Figure S2 (a) shows a sample spectrum of a reference experiment with only water and sulfuric acid catalyst. Here, only slight signals of sugars between 3 ppm and 4 ppm (mostly covered by the dominant water peak around 4.75 ppm) and acetic acid around 2 ppm are visible. The acetic acid peak is visible for all experiments, whereas the sugar signals are more pronounced at higher concentrations of catalyst acid in water.

Figure S2 (b) shows a sample spectrum of an acetosolv pretreatment liquid after pretreatment including signals of the dissolved biomass components. Dominant peaks arise from the acetic acid methyl and hydroxyl group. The peak of the latter is superimposed with the hydroxyl peak of other components, mainly water and catalyst acid. Due to the low concentration of dissolved components, their signal intensities are much smaller than the solvent peaks. The poor signal to noise ratio at these low concentrations would lead to high errors in a quantitative analysis (e.g., via peak integration). Nevertheless, peaks of some dissolved wood components (sugars, lignin) and degradation products (furfural, formic acid) are clearly visible, which allows for a qualitative analysis of dissolved components complementing the component analysis of the recovered fraction. Owing to the low resolution of the spectrometer, all sugar signals are superimposed between 3.8 ppm and 5.6 ppm and visual differentiation between the different types of sugars (glucose, xylose, mannose) is not possible. The signals of the solubilized lignin are clearly visible and only partially superimposed with the main peak of lignin arising at 3.8 ppm and further lignin peaks around 1.3 ppm. Similar signals have been observed for measurements of lignin with low-field NMR spectroscopy (Rönnöls et al., 2019). Between 9.5 ppm and 6.5 ppm, four peaks of furfural arise and around 8.1 ppm is the signal of formic acid.

Table S2: Experimental conditions for acetosolv experiments. Note that the non-recovered fraction w_{nr} as well as the glucose (glu) and xylose (xyl) yields refer to the initial amount of dry biomass, while the acetyl content refers to the recovered fraction. The fraction of removed components refers to the respective fraction of glucose, xylose + mannose and lignin in native beech.

pretreatment liquid			pretreatment samples									
catalyst	c_{cat} (mol L ⁻¹)	mole fractions (mol mol ⁻¹)			DoD	w_{nr} (g g ⁻¹)	removed components (g g ⁻¹)			acetyl (g g ⁻¹)	yield (g g ⁻¹)	
		cat	H ₂ O	AA			glu	xyl + man	lignin		glu	xyl
-	0	0	0.0326	0.9674	0	0.0354	-0.3648	-0.2664	-0.0749	0.0643	0.0448	0.0203
HCl	0.14161	0.0077	0.0674	0.9250	3	0.4143	0.3529	0.9092	0.3223	nd	nd	nd
	0.05906	0.0033	0.0474	0.9494	2	0.3215	0.1309	0.5864	0.4088	0.0608	0.1148	0.0364
	0.01561	0.0009	0.0365	0.9626	0	0.1913	0.0392	0.3294	0.1686	nd	0.0364	0.0282
	0.00863	0.0005	0.0572	0.9424	0	0.1419	-0.1130	0.2151	0.0637	nd	0.0359	0.0299
	0.20253	0.0076	0.4969	0.4956	2	0.4439	-0.0352	0.747	0.7458	0.0441	0.2206	0.0272
H ₂ SO ₄	0.02178	0.0012	0.0329	0.9659	3	0.4318	0.5537	0.9737	0.3432	nd	0.0367	0.0144
	0.02408	0.0014	0.0227	0.9760	3	0.4258	0.2733	0.9465	0.227	nd	0.0334	0.0132
	0.01814	0.0010	0.0223	0.9767	3	0.4442	0.5243	0.9542	0.4654	nd	0.0430	0.0158
	0.00602	0.0003	0.0493	0.9504	2	0.3820	-0.0018	0.6756	0.3826	0.0805	0.0736	0.0296
	0.00505	0.0003	0.0466	0.9531	2	0.3765	0.6357	0.8644	0.5109	nd	nd	nd
	0.22659	0.0099	0.3297	0.6604	2	0.3824	0.1688	0.7588	0.8538	0.0531	0.0752	0.0093
H ₃ PO ₄	0.27338	0.0150	0.0362	0.9487	0	0.0696	-0.3060	-0.0425	0.0266	0.0601	0.0323	0.0304
	0.74114	0.0395	0.0422	0.9182	2	0.3080	-0.2808	0.4063	0.4821	nd	0.0411	0.0269
	0.64248	0.0345	0.0410	0.9245	1	0.2724	-0.2508	0.4264	0.3412	nd	nd	nd
	0.90216	0.0476	0.0442	0.9082	2	0.3616	-0.0027	0.5782	0.5908	nd	0.0435	0.0267
	0.65722	0.0347	0.0636	0.9017	2	0.2779	0.0098	0.567	0.4288	nd	nd	nd
0.46882	0.0252	0.0551	0.9197	1	0.2394	0.0487	0.4988	0.3317	nd	0.0521	0.0356	
HI	0.20114	0.0075	0.4962	0.4963	3	0.4765	0.0829	0.8078	0.8248	0.037	0.1851	0.0192

Table S3: Visibility of components solubilized in pretreatment liquid after acetosolv pretreatment of beech wood: + strong signal, o signal visible, - signal hardly visible, x component not visible in spectrum.

catalyst acid	c_{cat} (mol L ⁻¹)	lignin	sugars	furfural	formic acid
no catalyst	-	-	x	x	x
HCl	0.14161	+	o	+	-
	0.05906	+	o	+	-
	0.01561	+	x	x	x
	0.00863	+	x	x	-
	0.20253	+	o	+	x
H ₂ SO ₄	0.02178	+	+	+	+
	0.02408	+	+	+	o
	0.01814	+	+	+	-
	0.00602	+	+	-	x
	0.00505	+	+	-	-
	0.22659	+	o	o	x
H ₃ PO ₄	0.27338	+	x	x	o
	0.74114	+	-	-	-
	0.64248	+	-	-	-
	0.90216	+	-	-	-
	0.65722	+	-	x	-
	0.46882	+	-	x	-
HI	0.20114	+	o	o	x

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