

# Supplementary Materials

## Influence of Ethanol Organosolv Pulping Conditions on Physicochemical Lignin Properties of European Larch

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### Preparation of milled wood lignin [1,2]

In detail, ground larch sawdust (<0.5 mm) was extracted with acetone for 8 h followed by ethanol for another 8 hours in a Soxhlet apparatus. After throughout drying, 20 g of the ground extractive-free sawdust were wetted with toluene and ground in a planetary ball mill (S100, Retsch, Germany) for a total of 130 h at 96 rpm. The grinding protocol was set to 15min of grinding followed by 5 min of rest, to reduce possible thermal degradation of the milled wood lignin. A porcelain ball to biomass weight ratio of 20:1 was chosen, using 5 mm yttria-stabilised zirconia balls. This procedure was performed two times due to the limited size of the zirconia oxide milling cup (Fritsch, Germany). Toluene was removed via a rotary evaporator under reduced pressure and the milled wood was stored in a desiccator overnight. Afterwards, the dried milled wood was extracted two times with 1 L of dioxane-water 9:1 (v/v) in a 2 L round bottom flask under constant shaking in the dark at room temperature. After filtration, the combined filtrate containing the dissolved crude lignin was concentrated on a rotary evaporator and freeze-dried overnight. The crude milled wood lignin was dissolved in 90% (v/v) acetic acid and precipitated into water. The precipitate was filtered, dried and dissolved again in a 2:1 (v/v) 1,2-dichloroethane-ethanol mixture and precipitated into ethyl ether. The precipitate was washed with petrol ether and dried in vacuum for 24 h to yield the purified milled wood lignin.

### 1. <sup>31</sup>P nuclear magnetic resonance analysis (<sup>31</sup>P NMR)

Derivatization of the lignin samples with 2-chloro-4,4',5,5'-tetramethyl-1,3,2-dioxaphospholane (TMDP, Sigma-Aldrich, France) was performed according to Granata et al. [3]. Lignin samples (20 mg) were dissolved in 400 µL of a mixture of anhydrous pyridine and

deuterated chloroform (1.6:1 v/v). Then were added 150  $\mu\text{L}$  of a solution containing cyclohexanol (4.7  $\text{mg mL}^{-1}$ ) and chromium(III) acetylacetonate (3.60  $\text{mg mL}^{-1}$ ), which served as internal standard and relaxation reagent respectively and 75  $\mu\text{L}$  of TMDP. NMR spectra were acquired on a Bruker Biospin Avance III 400 MHz spectrometer. A total of 128 scans were acquired with a delay time of 6 s between successive pulses. The spectra were processed using Topspin 3.1. All chemical shifts are reported relative to the product of TMDP with cyclohexanol, which has been observed to give a doublet at 145 ppm referenced from the water-TMDP signal (132.2 ppm). The content of carboxylic acid hydroxyl groups (in  $\text{mmol g}^{-1}$ ) was calculated on the basis of hydroxyl groups contained in the internal reference cyclohexanol and by integration of the spectral region of 136.6 to 133.6 ppm.

## 2. ATR-FTIR peak assignment according to literature [4–6]

*Table S 1: Peak Assignment of ATR-FTIR of larch organosolv samples according to literature [4-6]*

Peak in Figure 1	Peak Assignment	Wavenumber [ $\text{cm}^{-1}$ ]
1	O-H stretching	3420
2	C-H stretching in $\text{CH}_3/\text{CH}_2$	2930
3	C-H stretching in $\text{CH}_3/\text{CH}_2$	2855
4	C=O stretching in unconjugated systems	1700
5	Aromatic skeletal vibrations	1600
6	Aromatic skeletal vibrations	1510
7	C-H deformation in $\text{CH}_3/\text{CH}_2$	1455
8	Aromatic skeletal vibrations plus C-H in-plane deform.	1420
9	Phenolic hydroxyl groups plus aliphatic C-H stretch in $\text{CH}_3$	1360
10	Ring vibration, guaiacyl units (G)	1264
11	C-C stretch plus C-O stretch plus C=O stretch	1215
12	Aromatic C-H in plane, G units	1140
13	C=O stretch in conjugated systems	1126
14	C-O-C stretching	1085
15	Aromatic C-H in plane, G units plus C-O deform in prim. OH plus C=O stretch	1030
16	Aromatic C-H out-of-plane, G units	850
17	Aromatic C-H out of plane, G units	813

## References

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