Kinetics of the $AlCl_3$ catalyzed xylan hydrolysis during Methanosolv pulping of beech wood

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Supplementary Information

Determination of the wood composition

First the wood chips are freeze milled. They milled chips pass a sieve with 180 µm mesh size. About 5 g of the chips are extracted with 150 ml cyclohexane and 75 ml ethanol for 120 min in a soxhlet apparatus. After the extraction the chips are several times washed with cyclohexane and ethanol. The washed chips are dried at 105°C over night and weight. The mass difference is given as the amount of extractives.

About 500 mg of the extractives free chips are hydrolysed using the method of Saeman. The chips are suspended in sulfuric acid (12 M) at room temperature for 45 min. Then 84 ml of MilliQ water is added and the mixture is refluxed for 3.5 h. The suspension is filtrated. From the filtrate an UV-VIS-spectrum is measured. Evaluating the spectrum at a wavelength of 205 nm using an absorption coefficient of 113 $l \cdot g^{-1} \cdot cm^{-1}$ the amount of the acid soluble lignin ASL is determined.

The filtration residue is washed several times with water and dried at 105°C over night and is called as Klason-Lignin.

The carbohydrates are determined as following described. The filtrate is adjusted to a pH of 9 with 26 wt-% ammonia solution. Then 200 µl of the aqueous sample is poured into a 10 ml glass sample tube. Then 2 ml of a fresh prepaired $NaBH_4$-solution in DMSO (c = 0.5 M) is added and the solution is stirred at 60°C for 1 h. The sample tubes are placed in a cold water bath and 100 µl of an internal standard *myo*- inositol, 200 µl glacial acetic acid, 400 µl 1-Methyl-imidazole and 4 ml acetic anhydride are added. The reaction mixture is stirred for 10 min at room temperature. The solution is poured into a separating funnel and the sample tube is washed two times with 5 ml MilliQ water. After cooling down 4 ml of Chloroform is added and the layers were separated. The organic layer is again washed twice with 10 ml MilliQ water and dried over magnesium sulfate and measured by an GC “Agilent 5890”. The column is “RT 2330”. The injection- and the FID- temperature are 275°C and the oven temperature is 240°C. The carrier gas is helium with a flow rate of 1 $ml \cdot min^{-1}$ and the split ratio is 1:35.

Graphs for the determination of the kinetic parameters E_A, a, m and k_0

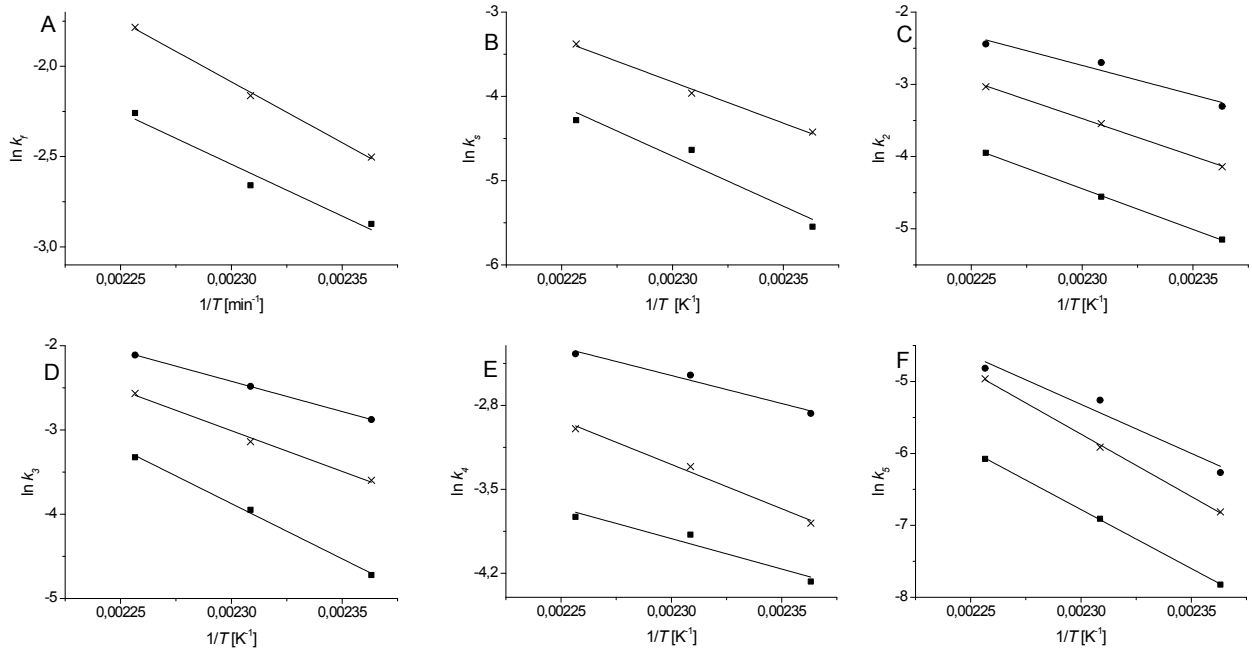


Fig. S1: Arrhenius plots at two different catalyst concentrations for A: reaction pathway f and B: reaction pathway s, and at three different catalyst concentrations for C: reaction pathway 2; D: reaction pathway 3; E: reaction pathway 4; F: reaction pathway 5. ■ 0.01 M $AlCl_3$; X 0.02 M $AlCl_3$; ● 0.04 M $AlCl_3$.

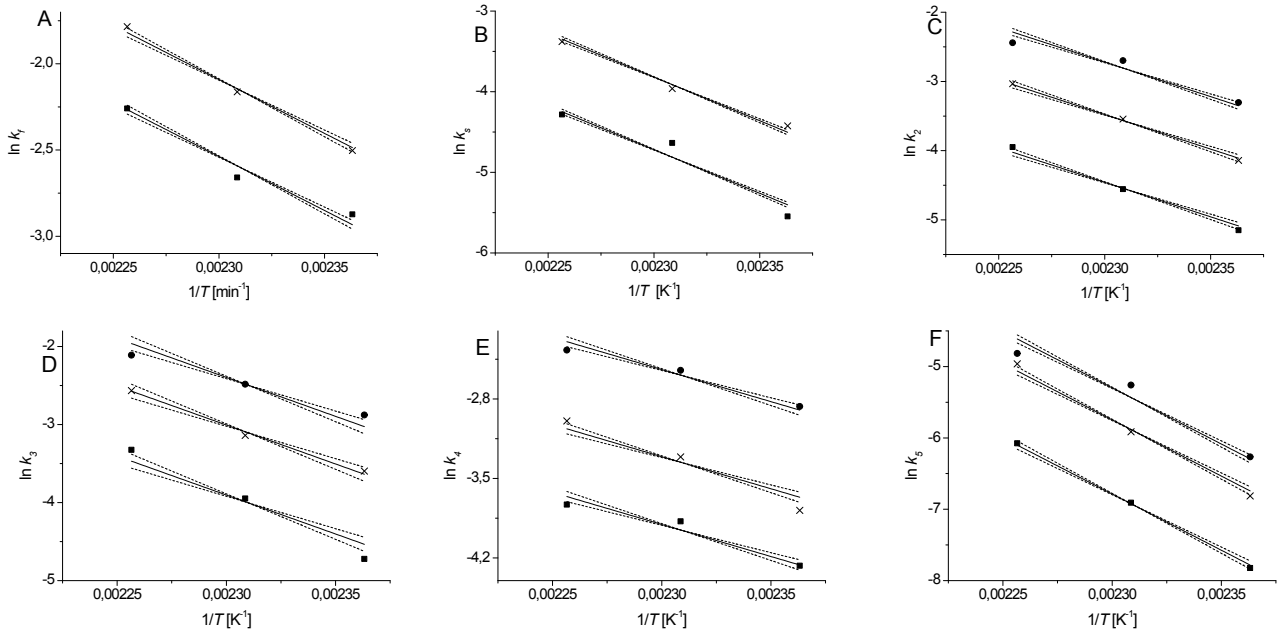


Fig. S2: Arrhenius-plots to determine the parameter a. The activation energy is set as constant. The solid lines are the plots using the mean activation energies of *Tab. 3*. The dotted lines are the plots using the mean activation energies ± the mean errors of *Tab. 3*. A: reaction f and B: reaction s, C: pathway 2; D: reaction 3; E: reaction 4; F: reaction 5. ■ 0.01 M $AlCl_3$; X 0.02 M $AlCl_3$; ● 0.04 M $AlCl_3$.

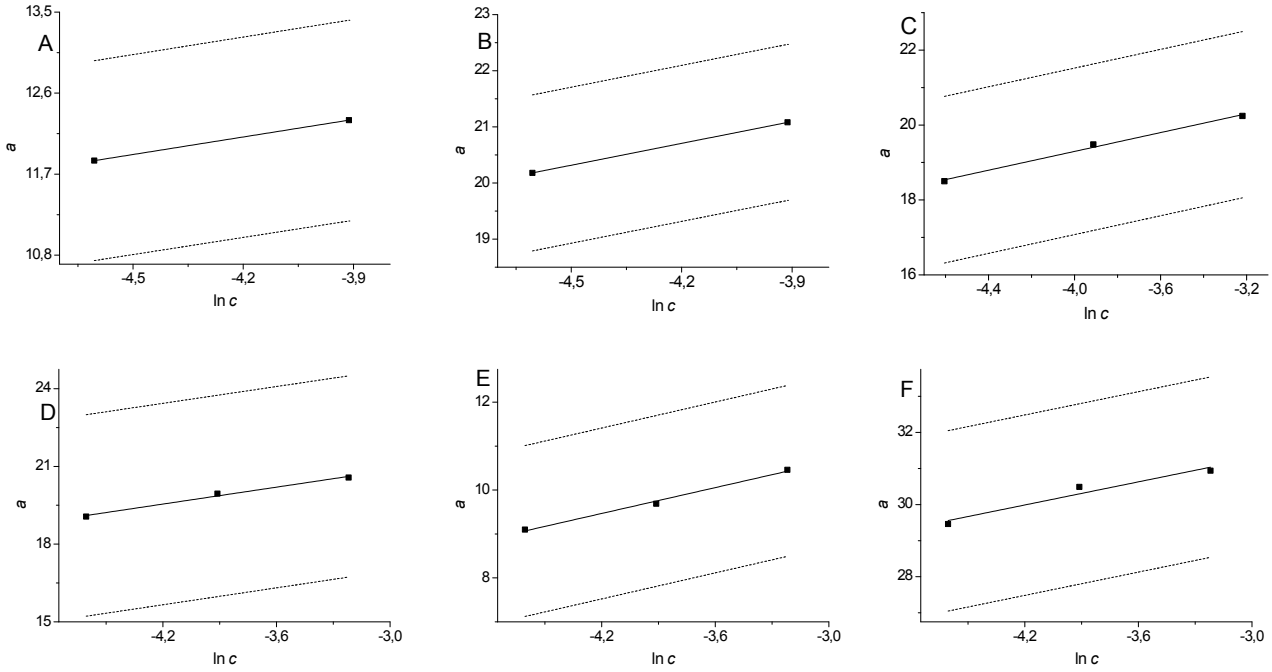


Fig. S3: Plots of the parameter *a* against the logarithm of the catalyst concentration. The slope of the linear fits leads to the parameter *m* and the intercept leads to the logarithm of the pre-exponential factor ln k_0.The solid line are the calculated *a* values and the dotted lines are the calculated values ± the mean error. A: reaction f and B: reaction s, C: pathway 2; D: reaction 3; E: reaction 4; F: reaction 5.

NMR- and mass spectra

To determine the byproducts in the $AlCl_3$ catalyzed methanosolv pulping of beech wood NMR- spectra and a GC-MS-chromatogram are recorded. The experimental procedure is already described in the manuscript. The NMR-spectra of the extracted distillate are shown in *Fig. S4* and *Fig. S5*. The GC-chromatogram is shown in *Fig. S6*. In this chromatogram can be three main signals at 4.05 min, 6.78 min and 8.87 min seen. In *Fig. S7 – Fig. S9* the corresponding mass spectra are shown.

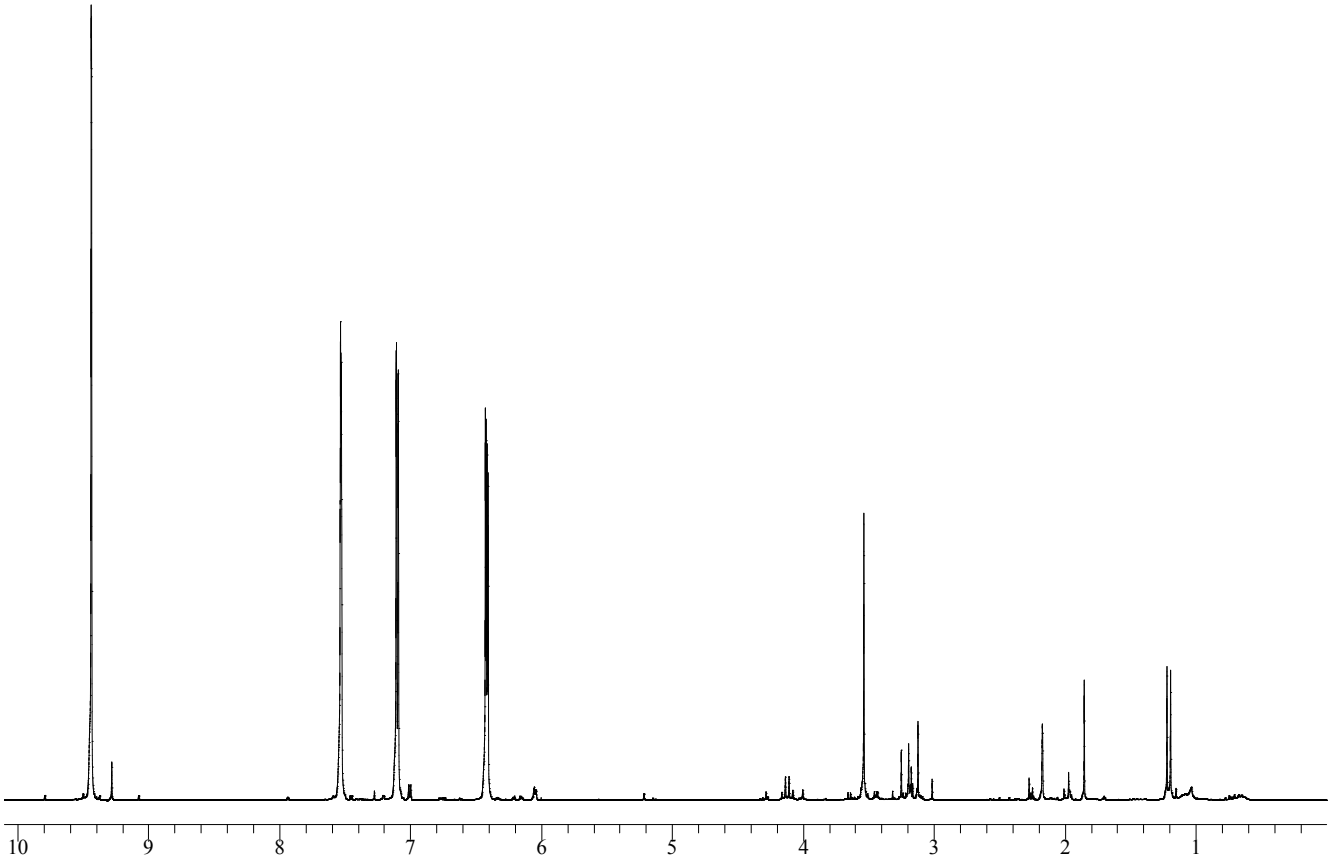


Fig. S4: ^{1}H-NMR-spectrum of the extracted distillate.

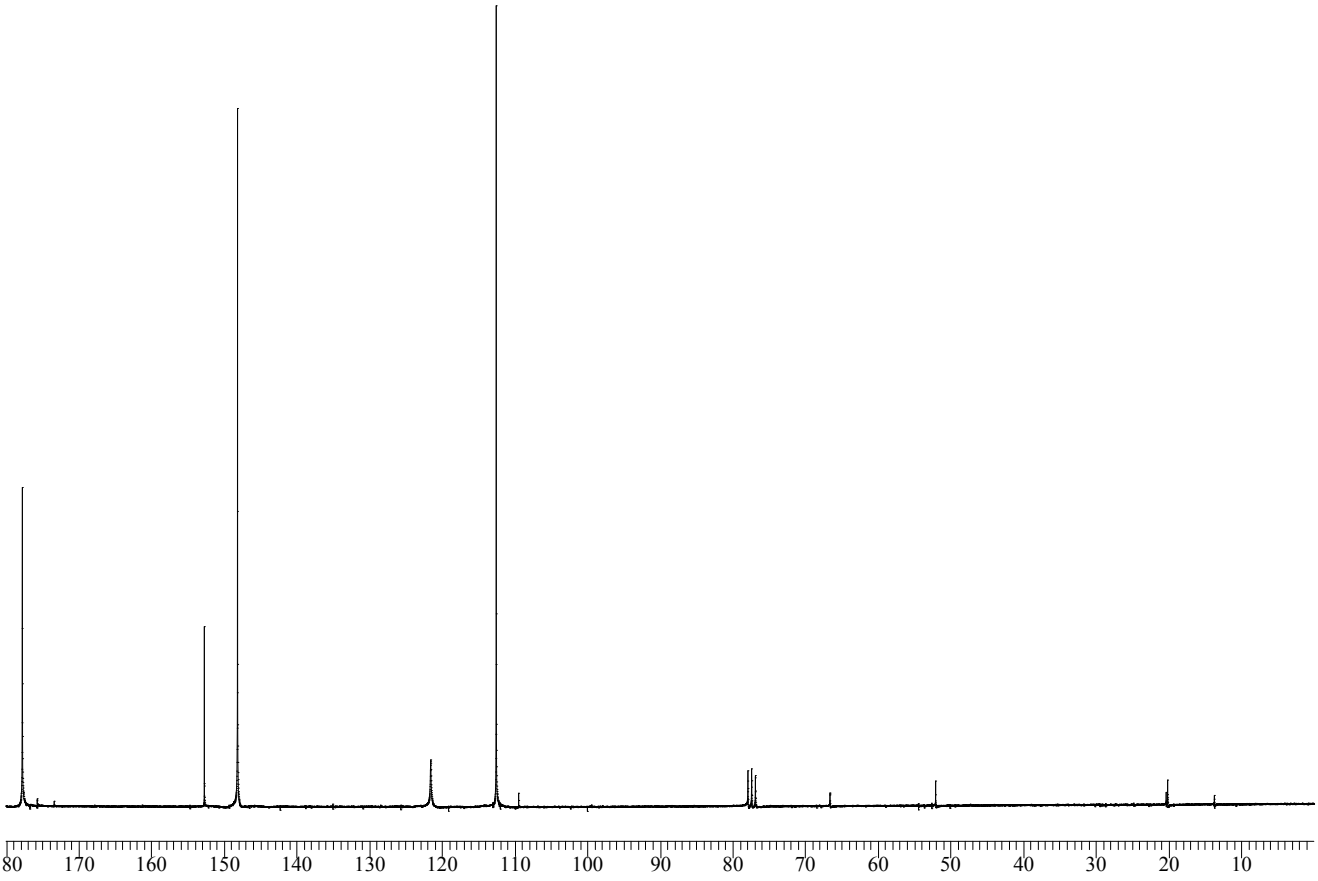


Fig. S5: ^{13}C-NMR-spectrum of the extracted distillate.

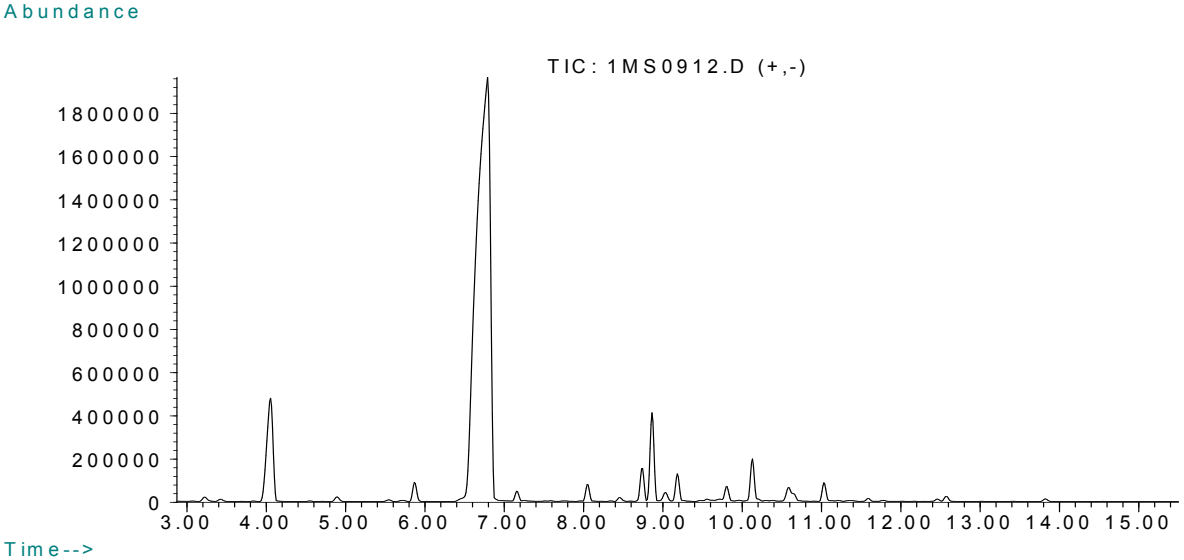


Fig. S6: GC-chromatogram of the extracted distillate.

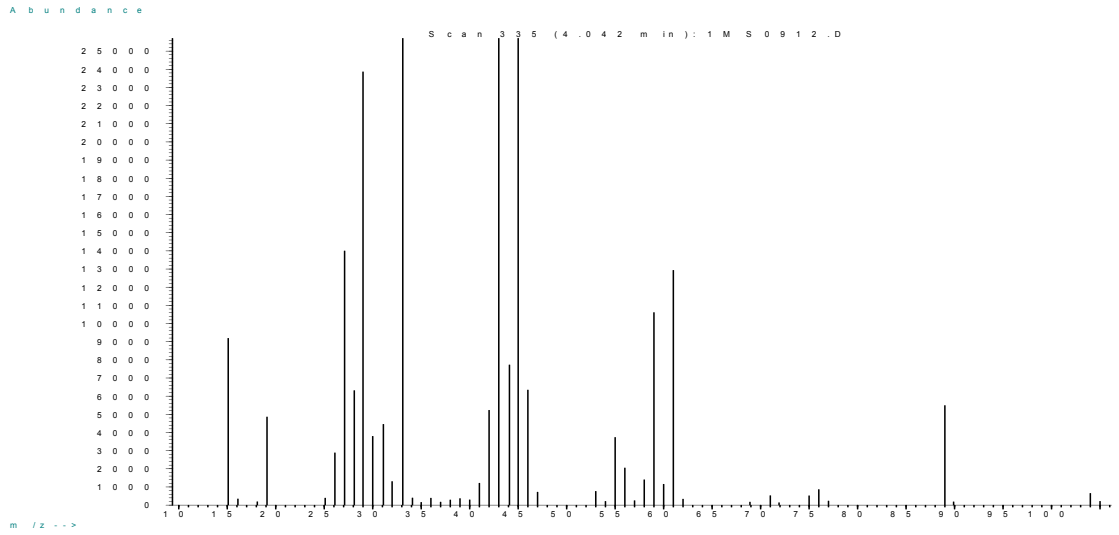


Fig. S7: Mass spectrum of methyl lactate with the retention time of 4.05 min.

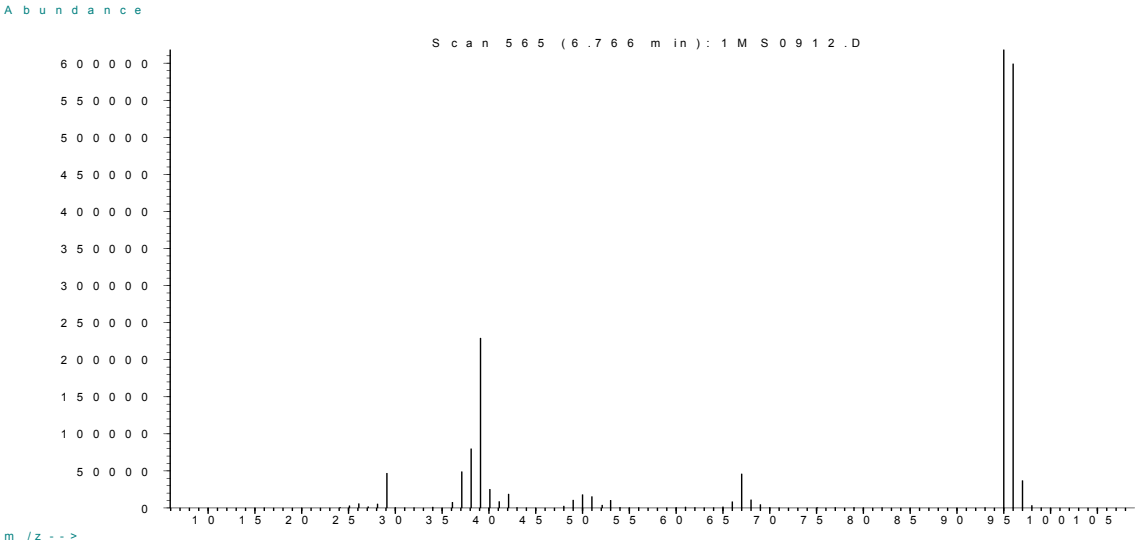


Fig. S8: Mass spectrum of furfural with the retention time of 6.78 min.

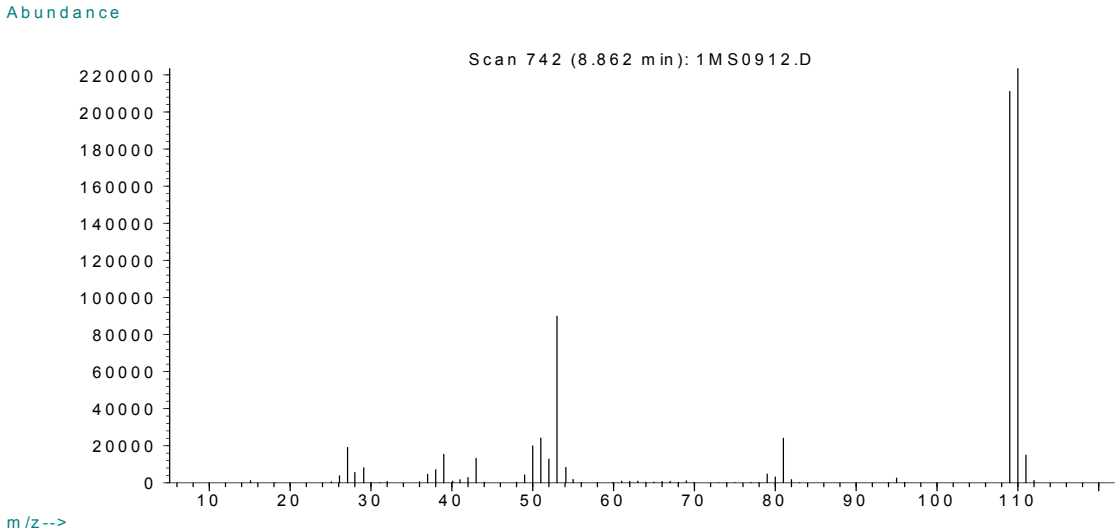
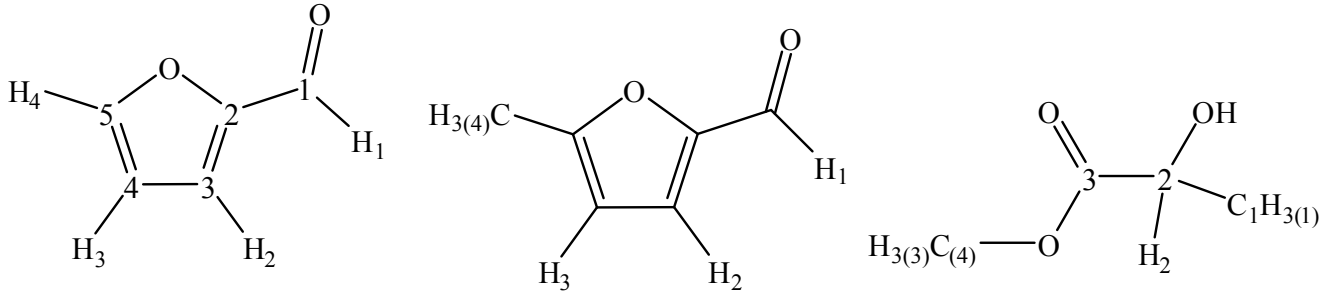


Fig. S9: Mass spectrum of methylfurfural with the retention time of 8.87 min.

Evaluating these spectra three components can be clearly identified. The structures of these components are shown in *Fig. S10* and the spectral data are given below.For methylfurfural no ^{13}C-data are given. The intensity of the signals (*Fig. S5*) is too low to give a qualified analysis.



furfural methylfurfural methyl lactate

Fig. S10: Identified components from the NMR- and the MS-spectra.

Furfural: ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 6.42 (dd, 3-H_1), δ = 7.10 (dd, 2-H_1), δ = 7.53 (m, 4-H_1), δ = 9.44 (s, 1-H_1) ppm.
$^{4}J_{2,4}$ = 0.70 Hz, $^{3}J_{3,4}$ = 1.69 Hz, $^{3}J_{2,3}$ = 3.58 Hz.

^{13}C-NMR (CDCl3, 250 MHz): δ = 112. 5 (4-C), δ = 121.6 (3-C), δ = 148.1 (5-C), δ = 152.7 (2-C), δ = 177.8 (1-C) ppm.

Methylfurfural: ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 2.17 (s, 4-H_3), 6.05 (d, 3-H_1), 7.01 (d, 2-H_1), δ = 9.28 (s, 1-H_1) ppm.
$^{3}J_{2,3}$ = 3.58 Hz.

Methyl lactate: ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 1.21 (d, 1-H_3), δ = 3.54 (s, 3-H_3), 4.12 (q, 2-H_1) ppm.
$^{3}J_{1,2}$ = 6.95 Hz.

^{13}C-NMR (CDCl3, 250 MHz): δ = 20.1 (1-C), δ = 52.1 (4-C), δ = 66.6 (2-C), δ = 175.7 (3-C) ppm.

Additionally to the spectra of the extracted distillate there is also a ^{1}H-NMR-spectrum of the extracted distillation residue recorded. This spectrum is shown in *Fig. S11*.

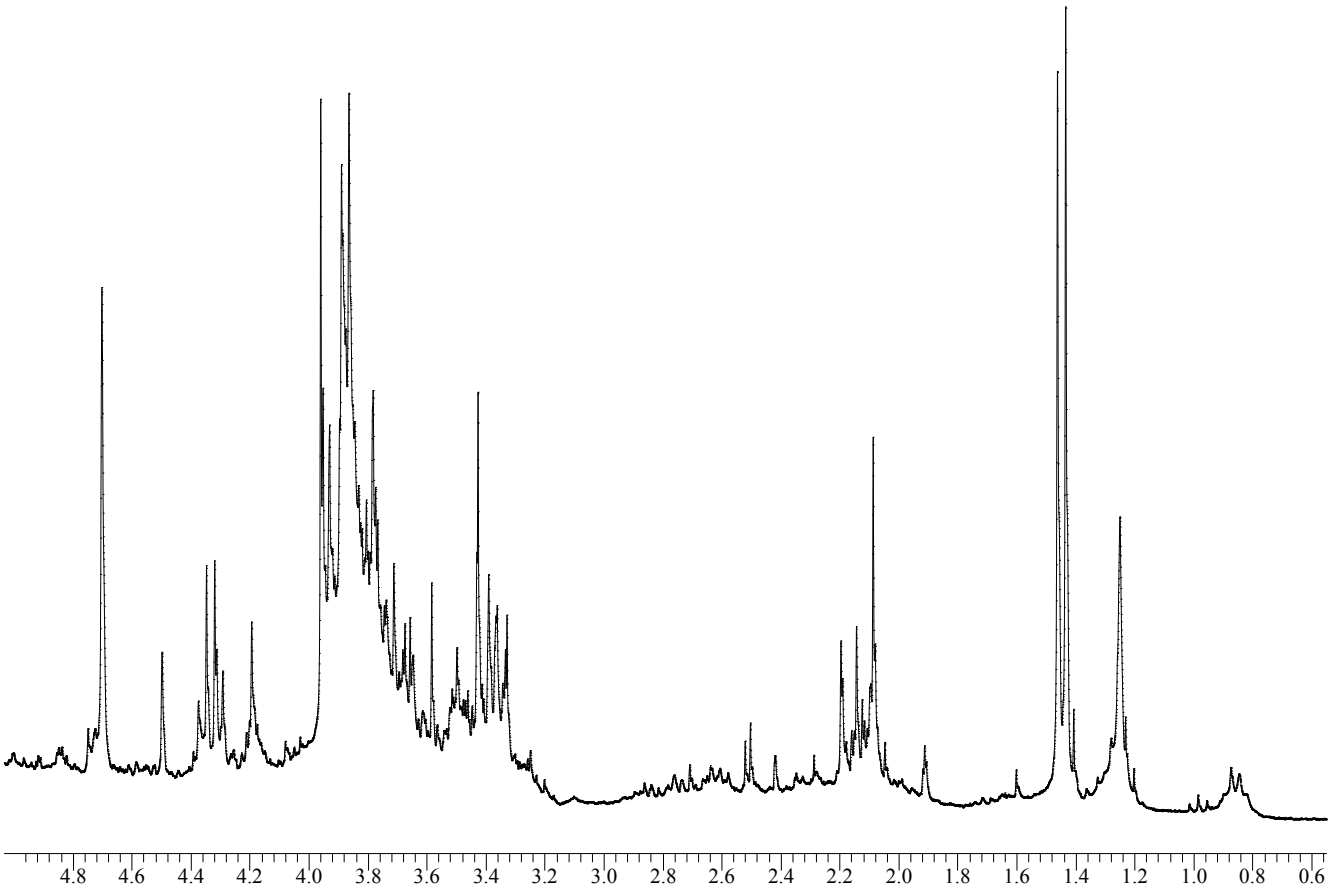


Fig. S11: ^{1}H-NMR-spectrum of the extracted distillation residue.

This spectrum is much more difficult to evaluate than the NMR-spectra of the extracted distillate. But the dublett at about 1.4 ppm and the quartett at about 4.3 ppm are the evidence for the appearance of lactic acid or one of the derivates.