Supplementary Materials

Influence of Base Catalyzed Organosolv Fractionation of Larch Wood Sawdust on Fraction Yields and Lignin Properties

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1. Preliminary fractionation experiments

A total of five preliminary experiments were performed to choose the solvent type, temperature- and catalyst range for the experimental design. Additionally, the impact of the alcohol-to-water ratio on the chemical fractionation was studied. The experimental conditions are summarized in table S1. An increase in catalyst concentration (PT_2 versus PT_4) leads to an undesired decrease in both pulp and cellulose yields. At the same time however, the residual lignin content is significantly reduced from 5.59 to 2.97%i.w. The same tendency can be observed, when increasing the temperature from 443 to 453 K (PT_1 versus PT_4). However, in the case of temperature, the decrease is slightly more severe in case of pulp yield (-5% vs. -3%) and residual lignin content (-4% vs -3 %). Thus, the preliminary experiments clearly show the need for an experimental design, to maximize yields as well as overall fractionation performance. Changing the methanol content from 50 to 70% v/v, a decrease in pulp and cellulose yield can be observed, according to PT_3 and PT_4. At the same time, it leads to a distinctly diminished delignification performance, which may be attributed to the lower amounts of formable OH^- ions at higher alcohol loading, decreasing lignin solubility. Comparing PT_4 to PT_5, pulping with ethanol or methanol leads to almost identical pulp yields. A slightly better delignification is achieved using ethanol, at the expense of a slightly lower cellulose yield. As this study was aimed both at most efficient fractionation as well as highest yields, methanol was chosen as the organic solvent. The safety aspects of ethanol versus methanol were not considered, such as decreased toxicity and vapor pressure of the former, as the pulping processes were performed on lab-scale in a high pressure / high temperature reactor.

Table S1. Results of the preliminary fractionation experiments. The, residence time, anthraquinone loading and liquid-to-solid ratio were held constant a 1 h, 0.1%w/w and 8.0 v/w respectively.

Parameters [a]	PT_1	PT_2	PT_3	PT_4	PT_5
Sawdust (g)	31.69	31.69	31.79	31.85	31.85
Solvent ( )	MeOH	MeOH	MeOH	MeOH	EtOH
Temperature (K)	443	453	453	453	453
AlkOH : H_2O (%v/v)	50	50	70	50	50
NaOH (%w/w)	30	20	30	30	30
Pulp yield (g)	15.67	15.07	13.72	14.25	13.97
Pulp yield (%i.w.)	66.24	64.06	57.73	61.15	60.22
Cellulose yield (%i.w.)	83.51	83.27	74.83	79.15	76.50
Residual lignin (%i.w.)	7.09	5.59	6.21	2.97	2.50

[a] i.*w.*, on initial wood content; *CH*, carbohydrates

2. Results for the tests of normality prior to ANOVA

Table S2. Results from Shapiro-Wilk test for normality

	Pulp yield	Cellulose yield	Residual sugar	Lignin yield	Residual CH
W value	0.8866	0.8051	0.7810	0.8390	0.8433
p-value	0.3161	0.053	0.046	0.052	0.086

3. Results from ANOVA analysis for the selected factorial models

Table S3. ANOVA analysis for the response pulp yield

Source	Sum of squares	df	Mean square	F-Value	p-value	
Model	24.53	3	8.18	707.13	< 0.0001	significant
Temperature	19.05	1	19.05	1647.42	< 0.0001	
MeOH:H_2O	1.89	1	1.89	163.47	0.0010	
NaOH	3.59	1	3.59	310.50	0.0004	
Residual	0.0347	3	0.0116			
Lack of fit	0.0264	1	0.0264	6.39	0.1272	not significant
Pure error	0.0083	2	0.0041			
Cor Total	24.57	6				

Table S4. ANOVA analysis for the response cellulose yield

Source	Sum of squares	df	Mean square	F-Value	p-value	
Model	469.94	3	156.65	872.79	< 0.0001	significant
Temperature	262.44	1	262.44	1462.22	< 0.0001	
MeOH:H_2O	106.50	1	106.50	593.39	0.0002	
NaOH	101.00	1	101.00	562.75	0.0002	
Residual	0.5384	3	0.1795			
Lack of fit	0.0166	1	0.0166	0.0635	0.8245	not significant
Pure error	0.5219	2	0.2609			
Cor Total	470.48	6				

Table S5. ANOVA analysis for the response residual carbohydrate

Source	Sum of squares	df	Mean square	F-Value	p-value	
Model	31.59	3	10.53	3999.05	0.0003	significant
Temperature	23.62	1	23.62	8969.47	0.0001	
MeOH:H_2O	6.15	1	6.15	2335.59	0.0004	
NaOH	1.82	1	1.82	692.09	0.0014	
Curvature	4.51	1	4.51	1711.99	0.0006	significant
Pure error	0.0053	2	0.0026			
Cor Total	36.11	6				

Table S6. ANOVA analysis for the response lignin yield

Source	Sum of squares	df	Mean square	F-Value	p-value	
Model	475.39	3	158.46	1448.03	0.0007	significant
Temperature	311.17	1	311.17	2843.46	0.0004	
MeOH:H_2O	137.59	1	137.59	1257.32	0.0008	
NaOH	26.63	1	26.63	243.30	0.0041	
Curvature	30.94	1	30.94	282.73	0.0035	significant
Pure error	0.2189	2	0.1094			
Cor Total	506.55	6				

Table S7. ANOVA analysis for the response lignin yield

Source	Sum of squares	df	Mean square	F-Value	p-value	
Model	2.92	3	0.97	57.14	0.0172	significant
Temperature	2.46	1	2.46	144.71	0.0068	
MeOH:H_2O	0.42	1	0.42	24.80	0.0380	
NaOH	0.03	1	0.03	1.90	0.3018	
Curvature	0.78	1	0.78	46.08	0.0210	significant
Pure error	0.03	6	0.02			
Cor Total	3.74	6				

2. Results from multiple regression analysis

Table S8. Multiple regression analysis – pulp yield

Regression Statistics	
Multiple R	0.9992
R Square	0.9986
Adjusted R Square	0.9971
Standard Error	0.1075
Observations	7

ANOVA

	df	SS	MS	F	Significance F
Regression	3	24.5348	8.1783	707.1297	0.0001
Residual	3	0.0347	0.0116		
Total	6	24.5696			

	Coefficients	Standard Error	t Stat	P-value
Intercept	120.0280	2.4547	48.8980	1.8834×10^{-5}
Temperature	-2.1825	0.0054	-40.5885	3.2909×10^{-5}
MeOH:H2O	-0.6875	0.0027	-12.7856	0.0010
NaOH	-0.9475	0.0108	-17.6209	0.0004

Table S9. Multiple regression analysis – cellulose yield

Regression Statistics	
Multiple R	0.9994
R Square	0.9989
Adjusted R Square	0.9977
Standard Error	0.4237
Observations	7

ANOVA

	df	**SS**	**MS**	**F**	**Significance F**
Regression	3	469.9449	156.6483	872.7851	0.0001
Residual	3	0.5384	0.1795		
Total	6	470.4833			

	Coefficients	Standard Error	t Stat	P-value
Intercept	485.8721	9.6698	50.2462	1.7346×10^{-5}
Temperature	-8.1	0.0212	-38.2389	3.9345×10^{-5}
MeOH:H2O	-5.16	0.0106	-24.3596	0.0002
NaOH	-5.025	0.0424	-23.7223	0.0002

Table S10. Multiple regression analysis – residual lignin

Regression Statistics	
Multiple R	0.9354
R Square	0.8750
Adjusted R Square	0.7500
Standard Error	1.2266
Observations	7

ANOVA

	df	**SS**	**MS**	**F**	**Significance F**
Regression	3	31.5925	10.5308	6.9996	0.0722
Residual	3	4.5135	1.5045		
Total	6	36.1060			

	Coefficients	**Standard Error**	**t Stat**	**P-value**
Intercept	113.8840	27.9966	4.0678	0.0268
Temperature	-2.43	0.0613	-3.9622	0.0287
MeOH:H2O	1.24	0.0307	2.0219	0.1364
NaOH	-0.675	0.1227	-1.1006	0.3515

Table S11. Multiple regression analysis – lignin yield

Regression Statistics	
Multiple R	0.9688
R Square	0.9385
Adjusted R Square	0.8770
Standard Error	3.2228
Observations	7.0000

ANOVA

	df	**SS**	**MS**	**F**	**Significance F**
Regression	3	475.3881	158.4627	15.2569	0.0254
Residual	3	31.1589	10.3863		
Total	6	506.5470			

	Coefficients	**Standard Error**	**t Stat**	**P-value**
Intercept	-314.0578	73.5597	-4.2694	0.0236
Temperature	8.82	0.1611	5.4735	0.0120
MeOH:H2O	-5.865	0.0806	-3.6397	0.0357
NaOH	2.58	0.3223	1.6011	0.2077

Table S12. Multiple regression analysis – residual carbohydrates

Regression Statistics	
Multiple R	0.8837
R Square	0.7809
Adjusted R Square	0.5619
Standard Error	0.5225
Observations	7.0000

ANOVA

	df	**SS**	**MS**	**F**	**Significance F**
Regression	3	2.9198	0.9733	3.5651	0.1621
Residual	3	0.8190	0.2730		
Total	6	3.7388			

	Coefficients	**Standard Error**	**t Stat**	**P-value**
Intercept	37.4130	11.9259	3.1371	0.0518
Temperature	-0.785	0.0261	-3.0048	0.0574
MeOH:H2O	-0.325	0.0131	-1.2440	0.3018
NaOH	0.09	0.0522	0.3445	0.7532

3. Detailed results of the thioacidolysis-GC/MS analysis

Table S13. Detailed results of the thioacidolysis-GC/MS analysis.

	H-units μmol/g	G-units μmol/g	Vanillic-units μmol/g	Total units μmol/g	% of initial monomers
MWL [a]	20	845	82	947	100.0
Kraft (-)	-	25	10	35	3.7
Kraft (+)	-	58	12	70	7.4
EOS (-)	-	136	298	434	45.8
EOS (0)	-	156	209	365	38.6
EOS (+)	-	24	127	151	16.0
SP_1 (-/+/-)	-	69	9	78	8.2
SP_2 (-/-/+)	-	29	10	39	4.1
SP_3 (+/-/-)	-	16	9	25	2.6
SP_4 (+/+/+)	-	18	8	26	2.7
CP_1 (0/0/0)	-	30	14	44	4.6
CP_2 (0/0/0)	-	34	13	47	5.0
CP_3 (0/0/0)	-	32	13	45	4.8
CP_{1-3}	-	32	13	45	4.8
Avg ± SD	-	2	>1	2	0.2