

Birch fractionation in γ -valerolactone with the emphasis on pulp properties: prehydrolysis, acid-catalyzed, and alkaline-catalyzed concept

Marianna Granatier ^a, Huy Quang Lê ^a, Eva Carmona González ^a, Herbert Sixta ^{*a}

^aSchool of Chemical Engineering, Department of Biosystems and Bioproducts, Aalto University, Vuorimiehentie 1, 02150 Espoo, Finland

*Author in charge of correspondence. E-mail: herbert.sixta@aalto.fi

Contents

Table S1 Summary of reaction conditions and composition of individual samples. Reaction time =120 min, $m_{\text{GVL}}=7.5$ g	2
Table S2 Mass balance of one-stage acid and alkaline GVL pulping. The values are calculated as the average. Reaction conditions: 180°C, 120 min, 50 wt% GVL, L:W= 10	3
Table S3 Chemical composition and macromolecular properties of pulps obtained from birch sawdust 1-stage acid GVL pulping. Reaction conditions: 120 min, L:W 10 kg/l, 50 %wt GVL	4
Figure S1 Molecular mass distribution of unbleached GVL pulp in comparison with commercial bleached PHK birch pulp (dw/dlog(MW): differential mass fraction)	5

Table S1 Summary of reaction conditions and composition of individual samples. Reaction time =120 min, $m_{\text{GVL}}=7.5$ g

Sample	T [°C]	pH _{initial}	H ₂ SO ₄ [kg/t]	H ₂ SO ₄ ^a [mol/L]	NaOH [kg/t]	NaOH ^b [mol/L]
Reference	180	3.96	0	0	0	0
1	180	3.88	0.02	0.00003	0	0
2	180	3.24	0.2	0.0002	0	0
3	180	2.36	1.9	0.002	0	0
4	180	1.20	5.9	0.006	0	0
5	180	1.00	10.9	0.01	0	0
6	180	0.84	13.6	0.02	0	0
7	180	4.21	0	0	0.02	0.00005
8	180	6.00	0	0	1.9	0.005
9	180	8.62	0	0	192.1	0.5
10	180	1.46	3.9	0.004	0	0
11	180	1.53	6.1	0.006	0	0
12	180	1.38	7.4	0.008	0	0
13	180	1.34	10.7	0.01	0	0
14	150	1.48	5.7	0.006	0	0
15	150	1.25	10.1	0.01	0	0
16	150	1.01	20.6	0.02	0	0
17	150	0.80	34.4	0.04	0	0
18	120	1.49	11.1	0.01	0	0
19	120	1.10	14.5	0.02	0	0
20	120	0.82	30.0	0.03	0	0
21	120	0.61	51.1	0.05	0	0
22	180	4.36	0	0	0.02	0.00005
23	180	5.98	0	0	1.6	0.005
24	180	8.69	0	0	156	0.5

^{a,b} Total concentration of H₂SO₄ and NaOH in pulping liquor

Table S2 Mass balance of one-stage acid and alkaline GVL pulping. The values are calculated as the average. Reaction conditions: 180°C, 120 min, 50 wt%

Sample	Solid phase [%odw]			Liquid phase [%odw] ^a								Total [%odw]
	H ₂ SO ₄ [kg/t]	NaOH [kg/t]	Yield [% odw]	C ^b	H ^c	L ^d	C	H	L	Fur. ^e	OA ^f	
Wood	-	-	-	41.6	32.0	23.8	-	-	-	-	-	97.4
Reference	-	-	55.8	39.7	10.6	5.5	0.3	11.4	18.7	0.4	2.0	91.9
1	0.02	0	56.5	40.1 ± 0.3	10.9 ± 0.4	5.6 ± 0.2	0.3	12.5	21.5	0.3	1.4	92.7
2	0.2	0	55.1	39.5 ± 0.5	10.3 ± 0.1	5.4 ± 0.1	0.3	12.4	20.1	0.4	0.4	88.6
3	1.9	0	50.6	39.6 ± 0.2	7.9 ± 0.5	3.3 ± 0.3	0.5	14.1	21.8	0.6	0.6	88.3
4	5.9	0	36.7	34.5 ± 0.5	1.0 ± 0.2	1.2 ± 0.1	3.2	11.6	20.4	6.4	7.1	85.5
5	10.9	0	24.8	16.5 ± 0.6	0.2 ± 0.3	8.1 ± 0.4	8.9	5.1	22.1	13.6	5.7	80.3
6	13.6	0	17.2	12.6 ± 0.5	0.1 ± 0.3	7.5 ± 0.3	11.5	2.5	18.6	15.5	6.1	74.6
7	0	0.02	51.7	38.2 ± 1.3	9.2 ± 0.4	4.4 ± 0.1	0.3	11.8	20.8	0.6	0.3	85.5
8	0	1.9	59.4	39.8 ± 0.1	12.4 ± 1.1	7.3 ± 0.8	0.3	10.7	19.0	0.3	0.4	90.1
9	0	192.1	73.6	39.5 ± 0.3	22.0 ± 0.4	12.2 ± 0.4	0.1	1.7	14.3	0.1	3.9	93.8

GVL, L:W= 10

^aSpent liquor combined with washing water; ^b Cellulose; ^c Hemicellulose; ^d Lignin, ^e Furfural, ^f Organic acids (acetic acid, levulinic acid)

Table S3 Chemical composition and macromolecular properties of pulps obtained from birch sawdust 1-stage acid GVL pulping. Reaction conditions: 120 min, L:W 10 kg/l, 50 %wt GVL

Sample ^a	T [°C]	H ₂ SO ₄ [kg/t]	Chemical composition [% odp]			Mw [kDa]	Mn [kDa]	PDI	DP<100 [%]	DP>2000 [%]
			C ^b	H ^c	L ^d					
PHK birch	-	-	94.0	5.5	0.5	152	56	2.7	5.4	9.7
PHK eucalyptus	-	-	95.4	4.1	0.5	229	79	2.9	23.5	3.2
AS beech	-	-	94.6	4.9	0.4	208	40	5.2	9.9	22.7
AS spruce	-	-	96.1	3.5	0.4	164	47	3.4	14.4	6.6
GVL-IP ^{e 1}	-	-	96.5	2.1	1.0	685	201	3.4	0.4	56.5
10	180	3.9	87.2	8.8	4.2	115	23	4.9	21.5	9.0
11	180	6.1	93.8	2.9	3.2	54	15	3.5	34.3	2.0
12	180	7.4	95.1	1.9	3.0	63	11	5.8	42.1	2.1
13	180	10.7	86.3	1.6	12.0	47	10	4.6	46.9	3.0
14	150	5.7	74.3	16.5	9.1	280	45	6.3	11.4	33.5
15	150	10.1	86.8	9.1	4.1	144	24	6.0	19.4	13.5
16	150	20.6	89.5	5.8	4.7	78	18	4.2	25.2	3.8
17	150	34.4	91.6	3.8	4.6	57	15	3.7	31.6	1.8
18	120	11.1	49.1	30.0	20.8	242	24	11.7	24.0	30.9
19	120	14.5	52.8	27.7	19.5	243	29	8.8	25.9	29.9
20	120	30.0	58.7	22.9	18.3	254	30	8.8	19.7	31.8
21	120	51.1	66.1	18.7	15.2	224	30	8.0	20.3	26.5

^aThe analysis of fully bleached commercial pulps followed the same protocol as the selected pulp samples, ^b Cellulose, ^c Hemicellulose, ^d Lignin, ^e Uncatalyzed GVL cook with ionic liquid post treatment of fully bleached birch pulp (15% water content), ¹ S. Shokri, S. Hedjazi, QH. Lê, A. Abdulkhani, H. Sixta, *Carbohydr Polym.* 2022, **288**, 119364

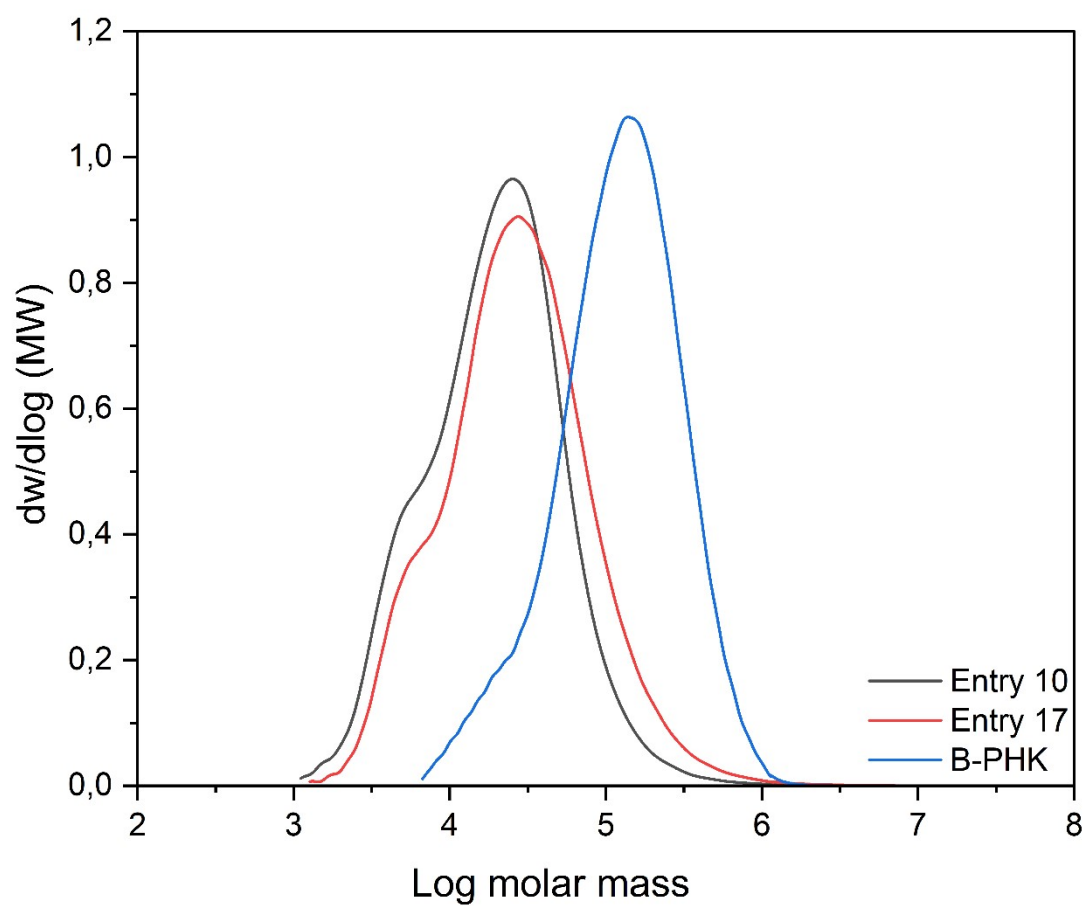


Figure S1 Molecular mass distribution of unbleached GVL pulp in comparison with commercial bleached PHK birch pulp ($dw/d\log(MW)$: differential mass fraction)