Lignin-to-liquid-solvolysis (LtL) of organosolv extracted lignin

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Number of Pages: **6**

Number of Tables: **4**

Table S1:	Experimental parameters for optimum resolution during ^{31}P-NMR analysis.
Table S2:	Extended overview of input material, reaction conditions and product output during LtL-solvolysis.
Table S3:	A structure overview with corresponding compound nomenclature from GC-MS analysis.
Table S4:	A tabulated numerical distribution overview of hydroxyl group types measured by ^{31}P-NMR.

Table S1 – Parameters for ^{31}P-NMR.

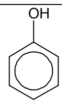
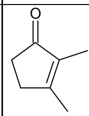
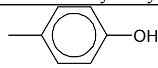
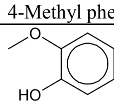
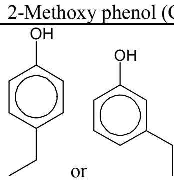
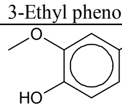
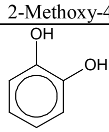
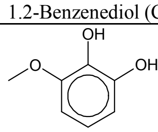
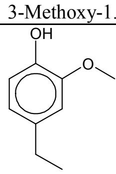
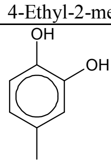
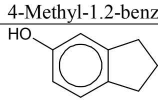
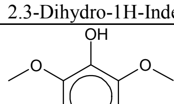
td	sw [ppm]	o1p [ppm]	o1 [Hz]	p1 [µs]	pl1 [dB]	d1 [s]	ns	aq [s]
52902	261.3222	70.273	14227.21	11.25	0.00	25	64*	0.4999238

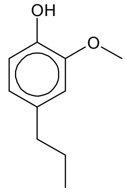
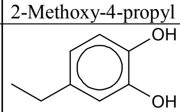
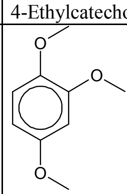
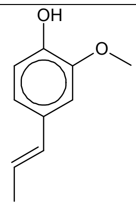
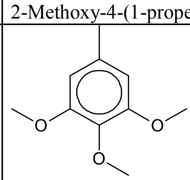
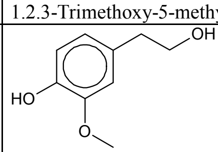
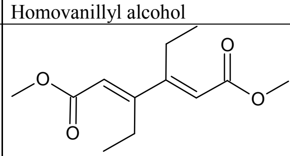
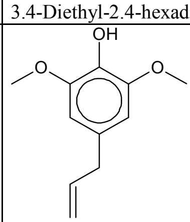
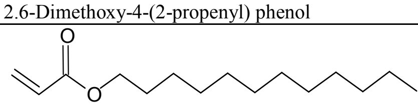
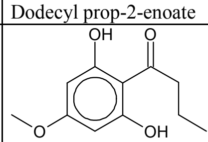
Table S2 – Extended overview of input material, reaction conditions and product output from LtL-solvolysis.

Condi-tions	Experiment	EEH--	EEH+-	EEH00I	EEH00II	EEH-+	EEH++
	Feedstock	EEH	EEH	EEH	EEH	EEH	EEH
	Time (h)	2	2	2	2	2	2
	Temperature (°C)	320	320	340	340	360	360
In	Lignin (g)	0.50	0.50	0.50	0.50	0.50	0.50
	Formic Acid (g)	0.61	1.22	0.92	0.92	0.61	1.22
	Formic Acid (mL)	0.50	1.00	0.75	0.75	0.50	1.00
	Water (g)	4.02	4.02	4.02	4.01	4.00	4.01
	Lignin percentage of mass input (%)	9.7	8.7	9.2	9.2	9.8	8.7
	Total mass input (g)	5.13	5.74	5.44	5.43	5.11	5.73
Out	Gas (g)	0.7	1.2	0.9	0.9	0.7	1.3
	LtL-oil (g)	0.14	0.17	0.13	0.17	0.16	0.18
	Solids (g)	0.12	0.09	0.05	0.08	0.08	0.06
	Aqueous-phase (g)	3.61	3.66	3.70	3.54	3.86	3.83
	Total mass output (g)	4.57	5.12	4.78	4.68	4.80	5.37
Results	Gas (% of FA input)	114.8	98.4	97.8	97.8	114.8	106.6
	Aqueous-phase (% of solvent input)	89.7	91.0	92.0	88.3	96.4	95.6
	Solids (% of lignin input)	23.7	18.1	10.1	15.3	16.1	11.8
	LtL-oil yield (% of lignin input)	28.4	34.3	26.4	33.8	32.0	36.6
	Mass recovery (%)	89.0	89.2	87.9	86.3	93.9	93.8
Condi-tions	Experiment	EEHO--	EEHO+-	EEHO00I	EEHO00II	EEHO-+	EEHO++
	Feedstock	EEHO	EEHO	EEHO	EEHO	EEHO	EEHO
	Time (h)	2	2	2	2	2	2
	Temperature (°C)	320	320	340	340	360	360
In	**Lignin (g)**	0.50	0.50	0.50	0.50	0.50	0.50
	Formic Acid (g)	0.61	1.22	0.92	0.92	0.61	1.22
	Formic Acid (mL)	0.50	1.00	0.75	0.75	0.50	1.00
	Water (g)	4.01	4.00	4.01	4.01	4.02	4.02
	Lignin percentage of mass input (%)	9.8	8.7	9.2	9.2	9.7	8.7
	Total mass input (g)	5.12	5.72	5.42	5.44	5.14	5.74
Out	Gas (g)	0.6	1.2	0.9	0.9	0.6	1.2
	LtL-oil (g)	0.27	0.27	0.28	0.31	0.29	0.30
	Solids (g)	0.09	0.08	0.10	0.09	0.05	0.04
	Aqueous-phase (g)	3.79	3.72	3.84	3.85	3.92	3.85
	Total mass output (g)	4.75	5.27	5.12	5.15	4.86	5.40
Results	Gas (% of FA input)	98.4	98.4	97.8	97.8	98.4	98.4
	Aqueous-phase (% of solvent input)	94.5	93.1	95.8	96.0	97.6	95.8
	Solids (% of lignin input)	18.4	16.7	19.8	17.2	10.3	8.5
	LtL-oil yield (% of lignin input)	53.2	53.2	56.4	62.2	57.2	60.9
	Mass recovery (%)	92.8	92.2	94.3	94.8	94.8	94.0
Condi-tions	Experiment	BO--	BO+-	BO00I	BO00II	BO-+	BO++
	Feedstock	BO	BO	BO	BO	BO	BO
	Time (h)	2	2	2	2	2	2
	Temperature (°C)	320	320	340	340	360	360
In	**Lignin (g)**	0.50	0.50	0.50	0.50	0.50	0.50
	Formic Acid (g)	0.61	1.22	0.92	0.91	0.61	1.22
	Formic Acid (mL)	0.50	1.00	0.75	0.75	0.50	1.00
	Water (g)	4.01	4.03	4.14	4.00	4.01	4.01
	Lignin percentage of mass input (%)	9.8	8.7	9.0	9.2	9.8	8.7
	Total mass input (g)	5.12	5.75	5.56	5.41	5.12	5.74
Out	Gas (g)	0.6	1.1	0.8	0.8	0.6	1.2
	LtL-oil (g)	0.36	0.36	0.32	0.28	0.25	0.34
	Solids (g)	0.07	0.07	0.06	0.09	0.10	0.03
	Aqueous-phase (g)	3.81	3.85	3.95	3.77	3.85	3.98

	Total mass output (g)	4.84	5.38	5.13	4.95	4.80	5.55
Results	Gas (% of FA input)	98.4	90.2	87.0	87.9	98.4	98.4
	Aqueous-phase (% of solvent input)	95.1	95.5	95.4	94.3	96.0	99.3
	Solids (% of lignin input)	14.2	13.7	11.9	18.5	20.8	5.1
	LtL-oil yield (% of lignin input)	71.8	72.8	64.9	56.2	49.9	68.4
	Mass recovery (%)	94.6	93.6	92.3	91.4	93.8	96.9
Condi-tions	Experiment	WSO--	WSO+-	WSO00I	WSO00II	WSO-+	WSO++
	Feedstock	WSO	WSO	WSO	WSO	WSO	WSO
	Time (h)	2	2	2	2	2	2
	Temperature (°C)	320	320	340	340	360	360
In	**Lignin (g)**	0.50	0.50	0.50	0.50	0.50	0.50
	Formic Acid (g)	0.61	1.23	0.92	0.92	0.61	1.22
	Formic Acid (mL)	0.50	1.01	0.75	0.75	0.50	1.00
	Water (g)	4.01	4.02	4.03	4.00	4.02	4.01
	Lignin percentage of mass input (%)	9.8	8.7	9.2	9.2	9.7	8.7
	Total mass input (g)	5.12	5.75	5.45	5.42	5.13	5.73
Out	Gas (g)	0.6	1.2	0.9	0.9	0.6	1.2
	LtL-oil (g)	0.31	0.29	0.31	0.31	0.27	0.33
	Solids (g)	0.10	0.12	0.08	0.08	0.13	0.04
	Aqueous-phase (g)	3.78	3.78	3.94	3.88	3.68	3.95
	Total mass output (g)	4.79	5.39	5.23	5.17	4.68	5.52
Results	Gas (% of FA input)	98.4	97.6	97.8	97.8	98.4	98.4
	Aqueous-phase (% of solvent input)	94.3	94.0	97.8	96.9	91.6	98.6
	Solids (% of lignin input)	19.5	23.8	16.9	16.2	25.1	7.3
	LtL-oil yield (% of lignin input)	61.6	58.2	61.6	61.9	54.2	65.8
	Mass recovery (%)	93.5	93.7	96.0	95.3	91.2	96.3

Table S3 – Structure overview with corresponding compound nomenclature from semi-quantitative GC-MS analysis of bio-oils from experiments with minimum (--) and maximum (++) values for variables V1 and V2.

No.	Retention time (min)	Compound	EEH--	EEH++	EEHO--	EEHO++	BO--	BO++	WSO--	WSO++
			Area of total							
1	12.06	 Phenol								<2
2	13.62	 2.3-Dimethyl-2-cyclopenten-1-one		<2						
3	14.70	 4-Methyl phenol		<2		2-4				2-4
4	15.06	 2-Methoxy phenol (Guaiacol)	2-4	2-4	8-10	4-6	4-6	4-6	4-6	<2
5	17.08	 or 3-Ethyl phenol or 4-Ethyl phenol							4-6	6-8
6	17.75	 2-Methoxy-4-methyl phenol	<2	<2	2-4	<2		2-4	<2	<2
7	17.85	 1.2-Benzenediol (Catechol)		<2						<2
8	19.39	 3-Methoxy-1.2-benzenediol	<2					2-4	<2	
9	19.84	 4-Ethyl-2-methoxy phenol	<2	<2	4-6	2-4	<2	2-4	8-10	4-6
10	20.02	 4-Methyl-1.2-benzenediol		<2						
11	21.21	 2.3-Dihydro-1H-Inden-5-ol		2-4		<2				<2
12	21.48	 2.6-Dimethoxy phenol	2-4		6-8	2-4	>10	6-8	2-4	<2

13	21.85	 2-Methoxy-4-propyl phenol			2-4	<2		<2	<2	
14	22.13	 4-Ethylcatechol		2-4		<2			<2	2-4
15	23.55	 1.2.4-Trimethoxybenzene	<2		2-4		2-4	2-4		
16	24.07	 2-Methoxy-4-(1-propenyl) phenol				2-4				
17	25.19	 1.2.3-Trimethoxy-5-methyl benzene			2-4		2-4	<2		
18	25.29	 Homovanillyl alcohol	<2		<2			<2		
19	26.84	 3.4-Diethyl-2.4-hexadienedioic acid dimethyl ester	<2		2-4		2-4	2-4	<2	
20	28.00	 2.6-Dimethoxy-4-(2-propenyl) phenol					2-4			
21	28.34	 Dodecyl prop-2-enoate	8-10	2-4	4-6	<2	>10		2-4	
22	29.80	 Desaspinidol					2-4			

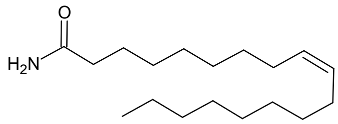
23	38.87	 9-Octadecanamide	6-8				8-10			

Table S4 – Distribution of hydroxyl group types as measured by ^{13}P-NMR. Values are represented as % of total –OH-content.

	Aliphatic OH (%)	**Acidic OH (%)**	**0 OMe-groups (%)**	**1 OMe-group (%)**	**2 OMe-groups (%)**
EEH --	7.2	6.2	44.9	13.1	28.6
EEH +-	7.4	6.6	46.9	12.2	26.9
EEH 00I	6.6	6.0	53.3	11.7	22.4
EEH 00II	5.7	6.8	54.8	11.3	21.4
EEH -+	3.2	7.0	62.1	9.2	18.5
EEH ++	6.5	6.8	59.2	9.0	18.6
EEHO --	5.4	4.3	42.7	14.8	32.8
EEHO +-	5.4	5.2	48.2	13.9	27.3
EEHO 00I	5.2	6.6	53.2	11.8	23.2
EEHO 00II	5.5	5.7	54.4	12.4	22.0
EEHO -+	7.7	6.9	55.7	11.2	18.5
EEHO ++	4.4	6.1	60.3	10.4	18.8
BO --	5.7	5.0	35.1	12.8	41.4
BO +-	4.3	4.3	35.3	13.2	42.8
BO 00I	3.5	4.6	44.6	12.1	35.2
BO 00II	3.2	4.7	49.1	12.1	30.8
BO -+	2.7	5.2	55.9	10.6	25.6
BO ++	2.9	4.9	55.6	10.6	26.0
WSO --	5.3	12.4	46.0	13.1	23.3
WSO +-	6.7	6.7	48.6	13.0	25.0
WSO 00I	6.1	10.7	52.0	10.3	20.9
WSO 00II	7.5	7.6	50.7	11.4	22.9
WSO -+	3.5	7.6	60.7	9.2	19.1
WSO ++	5.1	13.5	53.8	8.3	19.4