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Supporting Information for

Hydrothermal Depolymerization of Biorefinery Lignin-rich Streams: Influence of Reaction Conditions and Catalytic Additives on the Organic Monomers Yields in Biocrude and Aqueous Phase

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1. Analytical Methods

All solvents and reagents required for this work were purchased from Carlo Erba and Sigma Aldrich: they were used as received without any further purification. All chemicals were ACS reagent grade. Water for HPLC was HPLC grade. Ultrapure water (0.055 μS cm^{-1}) for HTL experiments was collected from TKA Microlab ultrapure water system. Analytical standards for GC and HPLC were ≥ 98% purity. Chemical standards for instrument calibrations were purchased from Leco for CHNS analysis. All gases were purchased from Rivoira. Argon, air, nitrogen and CO_2 were provided with a 99.999 % purity, helium with a 99.9995 % purity.

Error! Reference source not found. shows the calibration compounds selected for the qualitative and quantitative analysis of BC1 and AP in GC-MS and HPLC.

Table S1. Compounds calibrated in GC-MS and HPLC.

Compound class	GC-MS	HPLC
Sugars		D-cellobiose D(+)glucose D(+)xylose D(+)galactose L(+)arabinose D(+)mannose Xylitol
Acids	Acetic acid Propionic acid Benzoic acid	Acetic acid Propionic acid Benzoic acid Succinic acid Lactic acid Glutaric acid Glycolic acid
Alcohols		Methanol Ethanol

		Glycerol
Alkylphenols	m-Cresol p-Cresol o-Cresol	
Aromatics/HC	Toluene	
Catechols	1,2-Benzenediol 1,4-Benzenediol	1,2-Benzenediol
Dimethoxyphenols	Phenol, 2,6-dimethoxy-	Phenol, 2,6-dimethoxy-
Furanics	HMF 2-Acetylfuran	HMF
Ketones	Cyclopentanone 2-Cyclopenten-1-one 2-Cyclopenten-1-one, 2,3-dimethyl- 2-Cyclopenten-1-one, 3-methyl- 1,2-Cyclopentanedione, 3-methyl-	1,2-Cyclopentanedione, 3-methyl-
Methoxycatechols	1,4-Benzenediol, 3-methoxy-	1,4-Benzenediol, 3-methoxy-
Methoxyphenols	Phenol, 2-methoxy- Phenol, 2-methoxy-4-propyl- Phenol, 2-methoxy-4-methyl- Phenol, 2-methoxy-4-propenyl- Phenol, 2,6-dimethoxy-4-(2-propenyl)- Phenol, 4-ethyl-2-methoxy-	Phenol, 2-methoxy-
Phenolic Aldehydes	Benzaldehyde, 4-hydroxy-3-methoxy- Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	
Phenolic Ketones	Ethanone, 1-(3-hydroxy-4-methoxyphenyl)- Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	
Phenol	Phenol	Phenol

2. Slurry feedstock analysis

The aqueous fraction of LRS slurry sample, prepared at 10 wt.% B/W, was filter and analyzed in HPLC. Figure S1 depicts the water-solubles compounds in the LRS slurry before the depolymerization reactions, highlighting the presence of sugars and carboxylic acids trapped in the stream after the ethanol fermentation step in the industrial plant.

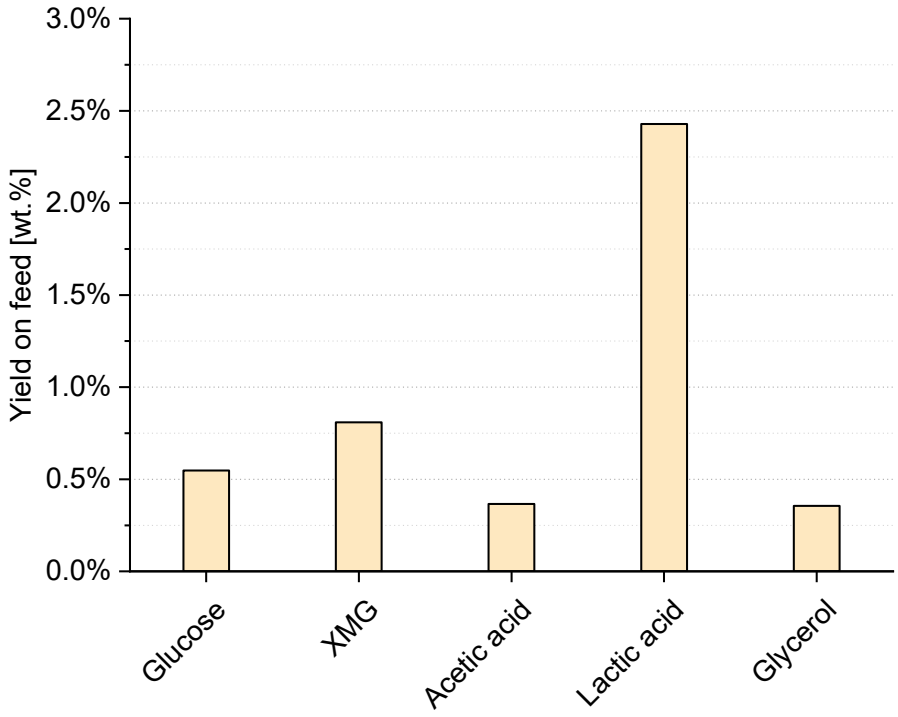

Figure S1: Water-soluble compounds in LRS liquid fraction of the slurry: yield on feed at 10 wt.% and 20 wt.% of B/W.

3. HTL overall products mass yields

The whole yield dataset obtained after LRS HTL is reported in **Error! Reference source not found.**, including the standard deviation measured for each collected product during the test replications.

Table S2. Yields of the HTL products from all investigated reaction conditions. Absolute standard deviation is reported in brackets.

Exp. Conditions	Catalyst	BC1	BC2	SR	Gas	WSO + loss*
300°C 5 min 10 wt.% B/W	-	9.8% (1.6%)	38.8% (11.5%)	16.5% (3.0%)	2.4% (0.7%)	32.6% (10.5%)
300°C 10 min 10 wt.% B/W	-	11.0% (0.3%)	33.0% (7.7%)	19.5% (2.0%)	1.5% (1.9%)	34.9% (9.8%)
350°C 5 min 10 wt.% B/W	-	27.0% (6.7%)	32.0% (6.4%)	11.4% (0.9%)	4.5% (0.8%)	23.8% (5.4%)

350°C 10 min 10 wt.% B/W	-	29.3% (0.0%)	22.5% (6.4%)	11.8% (0.2%)	5.5% (1.4%)	30.9% (7.0%)
370°C 5 min 10 wt.% B/W	-	36.8% (1.7%)	15.8% (3.1%)	13.0% (0.9%)	4.0% (0.1%)	30.3% (2.3%)
300°C 5min 10 wt.% B/W	2 wt.% KOH	18.8% (0.7%)	36.5% (2.6%)	13.5% (0.7%)	2.2% (n.d.)	29.0% (2.6%)
350°C 5 min 10 wt.% B/W	2 wt.% KOH	37.0% (1.4%)	17.0% (0.5%)	10.2% (0.7%)	4.4% (0.6%)	31.3% (1.1%)
370°C 5 min 10 wt.% B/W	2 wt.% KOH	39.2% (0.5%)	9.7% (1.9%)	12.3% (0.0%)	4.3% (0.1%)	34.5% (2.0%)
350°C 5 min 10 wt.% B/W	4 wt.% KOH	35.5% (2.1%)	17.7% (1.4%)	9.3% (0.5%)	2.2% (0.3%)	35.4% (0.6%)
300°C 5 min 10 wt.% B/W	sCO2	15.5% (5.0%)	38.1% (8.2%)	16.2% (0.7%)	3.3% (n.d.)	26.9% (2.56%)

* calculated by difference, n.d.: not determined

4. Qualitative BC1 analysis

An example of a complete BC1 GC-MS qualitative analysis with absolute and relative peaks area is reported in Table S3. The identified compounds are divided in classes to facilitate the data reading.

Table S3: Qualitative analysis of a light biocrude sample produced at 350 °C, 10 min, 10 wt.% (procedure 1).

Compounds	Ret. Time	Peak Area	Peak Area %
Acids		**2151718**	**2.51**
Acetic acid	1.5	813323	0.95
Benzoic acid	18.8	605610	0.71
Benzoic acid, 4-hydroxy-,	22.2	46651	0.05
Benzoic acid, methyl ester	17.2	32652	0.04
Butanoic acid	3.9	60503	0.07
Butanoic acid, 2-methyl-	6.3	89297	0.1
Butanoic acid, 3-methyl-	5.9	125501	0.15
p-Coumaric acid	26.0	49121	0.06
Propanoic acid	2.3	249107	0.29
Propanoic acid, 2-methyl-	3.1	79953	0.09
Alcohols		**161551**	**0.19**
4-Hydroxy-3-methoxyphenylethyl alcohol	25.3	161551	0.19
Alkylphenols		**1194483**	**1.39**

Phenol, 2,4-dimethyl-	18.5	28564	0.03
Phenol, 2-methyl-	16.1	337350	0.39
Phenol, 3-ethyl-	18.2	175917	0.21
Phenol, 4-ethyl-	18.9	166345	0.19
Phenol, 4-methyl-	16.7	486307	0.57
Aromatics/HC		**714058**	**0.83**
Benzene, (1,2-dimethyl-1-propenyl)-	19.7	42199	0.05
Benzene, 1,2,4-tripropyl-	28.8	346325	0.4
Naphthalene, 2,3-dimethoxy-	28.9	176218	0.21
Naphthalene, 2,6-dimethoxy-	28.9	149316	0.17
Catechols		**5477458**	**6.37**
1,2,3-Benzenetriol, 5-methyl-	24.3	187823	0.22
1,2-Benzenediol, 4-ethyl	22.9	371959	0.43
1,2-Benzenediol, 4-methyl-	21.2	625851	0.73
1,3-Benzenediol, 4-propyl-	24.4	371289	0.43
1,4-Benzenediol	21.0	422458	0.49
1,4-Benzenediol, 2,5-dimethyl-	46.9	142710	0.16
1,4-Benzenediol, 2-methyl-	22.3	574502	0.67
1,2-Benzenediol	19.4	2780866	3.24
Dimethoxyphenols		**13437988**	**15.67**
2,3-Dimethoxyphenol	20.4	129738	0.15
3,4-Dimethoxyphenol, 2-methylpropyl ether	22.2	110302	0.13
4-(3-hydroxypropyl)-2,6-dimethoxyphenol	30.4	197007	0.23
4-(4-Hydroxy-3-methoxystyryl)-2,6-dimethoxyphenol	49.4	76189	0.09
Phenol, 2,6-dimethoxy-	22.4	9784411	11.41
Phenol, 2,6-dimethoxy-4-(1E)-1-propen-1-yl-	27.4	1165517	1.36
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	26.4	346115	0.4
Phenol, 2,6-dimethoxy-4-methyl-	22.8	47078	0.05
Phenol, 3,4-dimethoxy-	21.9	108115	0.13
Phenol, 3,4-dimethoxy-, acetate	22.5	1473516	1.72
Furanics		**192004**	**0.22**
3,4-dimethylfuran	20.5	45455	0.05
Benzofuran, 2-methyl-	17.5	146549	0.17
Ketones		**1675868**	**1.95**
1,3-Cyclopentanedione, 2-ethyl-2-methyl-	18.4	37007	0.04
2-Cyclohexen-1-one, 6-methyl-3-(1-methylethyl)-	21.9	136547	0.16
2-Cyclopenten-1-one, 2,3-dimethyl-	29.9	450594	0.52
2-Cyclopenten-1-one, 2-methyl-	9.6	544991	0.64
2-Cyclopenten-1-one, 3,4-dimethyl-	29.4	136475	0.16
2-Ethyl-3-methylcyclopent-2-en-1-one	18.0	71029	0.08
Cyclohexanone, 2-isopropyl-2,5-dimethyl-	16.1	79909	0.09

Cyclopentanone	4.2	33382	0.04
Ethanone, 1-(2,3,4-trihydroxyphenyl)-	24.2	57754	0.07
p-Hydroxyphenylacetone	24.0	128180	0.15
Methoxyaromatics HC		**3548055**	**4.14**
1,5-Dimethoxy-4-methylnaphthalene	29.7	51569	0.06
Benzene, 1,2,3-trimethoxy-5-(1-propenyl)-, (E)-	29.0	171577	0.2
Benzene, 1,2,3-trimethoxy-5-methyl-	25.2	1773608	2.07
Benzene, 1,2-dimethoxy-	18.4	17150	0.02
Benzene, 1,3-dimethoxy-2-(2-propenyloxy)-	27.9	850040	0.99
Benzene, 1,3-dimethoxy-5-methyl-	20.9	88082	0.1
Benzene, 1,4-dimethoxy-2-methyl-	20.7	152616	0.18
Benzene, 4-butyl-1,2-dimethoxy-	25.6	66052	0.08
Benzene, methoxy-	10.3	46139	0.05
Benzenepropanol, 4-hydroxy-3-methoxy-	27.1	331222	0.39
Methoxycatechols		**7338192**	**8.56**
1,2-Benzenediol, 3-methoxy-5-(2-propen-1-yl)-	53.6	307819	0.36
1,2-Benzenediol, 3-methoxy-	20.8	143951	0.17
1,4-Benzenediol, 2-methoxy-	20.7	6886422	8.03
Methoxyphenols		**16898117**	**19.7**
Phenol, 4-butyl-2-methoxy-	25.3	923710	1.08
(4-Methoxyphenyl)(5-methyl-2-furyl)methane	30.9	59699	0.07
Phenol, 2,6-dimethoxy-4-methyl-	24.0	3283984	3.83
Phenol, 2-methoxy-	16.9	6154852	7.17
Phenol, 2-methoxy-3-methyl-	19.1	136254	0.16
Phenol, 2-methoxy-4-propenyl-	24.1	274826	0.32
Phenol, 2-methoxy-4-propyl-	22.7	1785865	2.08
Phenol, 2-methoxy-5-(2-propenyl)-	26.2	205889	0.24
Phenol, 4-ethyl-2-methoxy-	21.0	1860442	2.17
Phenol, 4-methoxy-3-methyl-	23.6	301356	0.35
Phenol, 2-methoxy-4-methyl-	19.4	1850915	2.16
Phenol, 3-methoxy-	20.1	60325	0.07
Phenolic Aldehydes		**2405789**	**2.81**
3,4-Dihydroxy-5-methoxybenzaldehyde	26.2	67849	0.08
Benzaldehyde, 3-hydroxy-	22.6	62335	0.07
Benzaldehyde, 3-hydroxy-4-methoxy-	23.2	254863	0.3
Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	27.2	193350	0.23
Homosyringaldehyde	26.5	1827392	2.13
Phenolic Ketones		**3335028**	**3.9**
1-(3-Methoxymethyl-2,4,5,6-tetramethylphenyl)ethanone	30.5	135034	0.16
1,2-Benzenediol, 4-(2-propen-1-yl)-	25.8	148716	0.17
1H-Inden-1-one, 2,3-dihydro-	21.2	111014	0.13

5-Sec-butylpyrogallol	25.4	810996	0.95
2-Butanone, 4-(4-hydroxy-3,5-dimethoxyphenyl)-	28.7	817407	0.95
2H-1-Benzopyran-2-one, 3,4-dihydro-6-methyl-	27.0	53659	0.06
4-Hydroxy-1-indanone	26.7	78536	0.09
Ethanone, 1-(2,5-dihydroxyphenyl)-	24.9	126032	0.15
Ethanone, 1-(2,6-dihydroxyphenyl)-	27.2	150364	0.18
Ethanone, 1-(2-hydroxy-6-methoxyphenyl)-	22.0	35491	0.04
Ethanone, 1-(3-hydroxy-4-methoxyphenyl)-	24.6	271930	0.32
Ethanone, 1-(3-hydroxyphenyl)-	23.2	256152	0.3
Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	28.2	339697	0.4
Ethanone,1-(2,3-dihydro-5-benzofuryl)-, o-(4-chlorobenzoyl)oxime	25.8	80110	0.09
Phenol		**9748189**	**11.36**
Phenol	13.8	9748189	11.36