Supplementary Material

Pyrolysis of Woody Biomass Loaded with Phytic Acid in a Fluidized-Bed Reactor for Producing Levoglucosenone

Tsinjo Nirina Rafenomananjara[a], *Shinji Kudo*[a,b]*, *Chihiro Asano*[a], *Ren Akai*[a], *Yasuyo Hachiyama*[b], *and Jun-ichiro Hayashi*[a,b]

[a] Interdisciplinary Graduate School of Engineering Sciences and [b] Institute for Materials Chemistry and Engineering, Kyushu University, 6-1 Kasuga Koen, Kasuga, 816-8580, Japan

* Email: kudo.shinji.641@m.kyushu-u.ac.jp

Table of Contents

Table S1 Compounds detected in GC-MS analysis for representative bio-oils

Retention time (min)	Compounds	Group	*Yj* (–)[1)]					
			Run 1	Run 9	Run 10	Run 11	Run 12	Run 14
8.45	2-Butanone	L		0.019	0.038			
8.82	Methyl 2-hydroxy-2-methoxyacetate	L			0.106			
8.83	1,2-Ethanediol	L	0.101	0.019				
9.19	Benzene	A	0.060	0.035		0.440		
9.85	Hydroxy-acetaldehyde	L	0.023	0.030	0.038	0.742	0.037	0.078
11.30	Acetic acid	L	0.963	0.758	0.930	0.535	0.658	0.757
12.76	1-hHydroxy-2-propanone	L		0.000		0.667	0.076	
15.66	4-Methyl-3-penten-2-one	L		0.013				
16.68	Acetic acid, methyl ester	L				0.324		
17.77	Ethyl pipecolinate	O		0.033	0.047		0.031	
17.77	3-Aminoisoxazole	O	0.014	0.021	0.000		0.147	0.225
17.80	1H-pyrazol-4-ol	O				0.119		0.021
18.34	Propanoic acid, 2-oxo-, methyl ester	L				0.297		0.000
18.92	Furfural	F	1.24	1.22	1.27	0.463	0.926	0.714
19.34	4-Hydroxy-4-methyl-2-pentanone	L	0.393	0.580	0.146	0.778		
19.42	2-Propylfuran	F						0.055
20.46	5-Methyl-2(3H)-furanone	L	0.049	0.027	0.039			
21.46	1-(2-Furanyl)ethanone	F	0.019	0.019	0.032			
22.08	4-Cyclopentene-1,3-dione	L	0.046					
22.82	1,2-Cyclopentanedione	L				0.246		
23.70	5-Methyl-2-furancarboxaldehyde	F	0.064	0.080	0.104	0.236	0.108	0.071
23.76	4-Methyl-3-(methylamino)pentan-2-one	O		0.013	0.060		0.145	0.095
23.78	4-Acetylmorpholine	O				0.164		
24.77	2(5H)-Furanone	L				0.131		
25.20	2,4-Diaminopyrimidine	O		0.064	0.107	0.126		
25.21	4-Methyl-2-oxo-(1H)-pyrimidine	O					0.033	
25.22	6-Methyl-4(1H)-pyrimidinone	O		0.030			0.074	0.062
25.22	5-Methyl-2(5H)-furanone	L	0.071					
25.37	[(2-Amino-3-hydroxypropanoyl)amino]acetic acid	O		0.036	0.051	0.565	0.254	0.288
26.04	3-Methyl-1,2-cyclopentanedione	L				0.231	0.034	
26.86	Phenol	A	0.082			0.132		
27.54	Guaiacol	A	0.177	0.113	0.128	0.703	0.160	
27.57	1-(1-Cyclohexen-1-yl)-ethanone	O						0.099
27.57	2,5-Dimethylfuran-3,4(2H,5H)-dione	F						0.039
28.51	Furyl hydroxymethyl ketone	F	0.236	0.242	0.332		0.320	0.275
29.23	2-Methyl-1,3-cyclohexanedione	L		0.029	0.137		0.051	0.044
29.26	2,3-Dimethylfumaric acid	L					0.069	0.000
29.28	3-Ethyl-3-heptanol	L						
29.29	1-Butoxypropan-2-yl pentanoate	L						0.027
29.41	5-Hexen-1-ol	L			0.027			
29.42	Hexahydrofuro[2,3-b]furan-3-ol	S						0.061
29.46	2-Butene-1,4-diol, diformate	L				0.119	0.092	
30.55	**Levoglucosenone (LGO)**	S	0.344	6.27	5.22	0.04	4.17	5.41
30.58	Creosol	A				1.925		
30.71	2,5-Dimethylphenol	A				0.225		
30.73	d-Lyxo-d-manno-nononic-1,4-lactone	L		0.017	0.031			
30.74	4-Isopropyl-7-methyl-3,8-dioxatricyclo[5.1.0.02,4]octane	L					0.062	0.042
30.74	3,4-Anhydro-d-galactosan	S					0.049	0.030
32.91	4-Ethyl-2-methoxyphenol	A				0.369		
33.10	4-Methyl-2-oxopentanenitrile	O	0.057	0.081	0.088	1.47	0.192	0.273
33.48	Nanofin	O						0.054
33.48	Piracetam	O					0.043	0.075

Table S1 Continued

Retention time (min)	Compounds	Group	*Yj* (–)[1)]					
			Run 1	Run 9	Run 10	Run 11	Run 12	Run 14
33.60	2,3-Anhydro-d-mannosan	S					0.026	0.021
33.71	2-Pentanol, propanoate	L					0.079	0.068
33.91	1,4:3,6-Dianhydro-α-d-glucopyranose (DGP)	S	0.373	0.580	0.573	0.135	0.858	0.858
34.09	Ethanol, 2-(2-butoxyethoxy)-, acetate	L	0.015	0.014				0.033
34.44	2-Methyl-9-β-d-ribofuranosylhypoxanthine	O			0.040			
34.45	4-Trimethyl-benzenemethanol	A		0.039				
34.46	1-(2-Hydroxy-5-methylphenyl)ethanone	A						0.090
34.46	3-Methoxyacetophenone	A	0.016	0.015		1.07	0.214	0.091
34.53	1,3-Di-O-acetyl-α-β-d-ribopyranose	S	0.015	0.027		0.125	0.000	0.000
35.07	5-Acetoxymethyl-2-furaldehyde	F	0.067	0.080	0.084		0.106	0.085
35.08	3-Allyl-6-methoxyphenol	A				0.507		0.062
35.15	2-Methoxy-5-propylphenol	A				0.137		0.000
35.40	5-Hydroxymethylfurfural	F	0.067	0.099	0.154	0.579	0.416	0.400
35.50	3-Methoxycyclohex-2-en-1-one	L			0.029		0.095	0.131
35.53	3-Ethoxy-5-methyl-1H-pyrazole	O		0.012				
36.19	3,4-Dimethyl-1-pentyn-3-ol	L	0.040	0.056	0.028			
36.64	cis-1,2-Cyclohexanediol	L	0.016	0.089	0.095		0.239	0.167
36.65	2-Butene-1,4-diol	L		0.013				
37.04	2-Hydroxyoctanoic acid, acetate	L						0.021
37.32	3-Heptanol	L	0.062	0.085	0.121	0.492	0.464	0.491
37.75	2,3,4,5-Tetraacetyl-1-O-methyl-d-xylitol	L	0.013				0.026	
37.82	2-Methoxy-4-(1-propenyl)phenol	A				2.22	0.174	0.064
37.94	1,4-Anhydro-d-mannitol	S	0.042	0.016	0.026			
38.03	Silacyclohexane	O	0.296	0.325	0.310		0.192	0.192
38.11	2-Amino-N-(2,3-dihydro-1H-inden-2-yl)acetamide	O					0.000	0.135
38.33	Hydroquinone	A					0.036	
38.42	Xanthosine	O	0.053	0.058	0.051	0.584	0.089	0.024
38.51	Vanillin	A	0.040	0.039	0.075	0.415	0.102	0.091
38.63	cis-2-Butenylene diacetate	L			0.025		0.036	
38.64	2-Butene-1,4-diol, diacetate	L		0.013			0.044	0.065
38.67	1,5-Diacetoxypentane	L	0.013					
38.76	3,4-Epoxytetrahydrothiophene-1,1-dioxide	O						0.020
39.68	2,2-Diethyl-1,3-propanediol	L						0.021
39.69	Carbazic acid, 3-pentylidene-, methyl ester	O					0.065	
39.90	2-Methoxy-4-propylphenol	A	0.799	0.801	0.728	0.488	0.000	0.834
39.92	2-Methoxy-5-propylphenol	A				0.000	0.816	
40.48	Apocynin	A				0.276	0.029	
40.67	1,6-Anhydro-β-d-talopyranose	S				0.133		
40.71	1,2-Dimethoxy-4-n-propylbenzene	A	0.018	0.011			0.026	
40.83	Tetradecahydro-phenanthrene	L	0.048	0.000			0.000	
41.60	1-(4-Hydroxy-3-methoxyphenyl)-2-propanone	A	0.149	0.149	0.169	0.270	0.239	0.212
42.00	2-Methoxy-α,5-dimethyl-benzeneacetaldehyde,	A	0.031	0.044	0.027	0.000		0.019
42.65	4-(1-Hydroxyallyl)-2-methoxyphenol	A	0.013	0.016	0.030	0.276	0.031	0.056
42.83	Butyrovanillone	A	0.024	0.041	0.076		0.025	0.019
43.03	2-oxo-2H-1-Benzopyran-3-carboxaldehyde	S	0.187					
43.49	Isopentyloxyethyl acetate	L				0.139		
43.53	1,3-Di-O-acetyl-α-β-d-ribopyranose	S			0.030	0.140	0.092	0.142
43.78	9-Oxabicyclo[6.1.0]non-6-en-2-one	L	0.418					
43.78	1-(1-Butyny)cyclopentanol	L	0.490					
43.78	1,6-Anhydro-β-D-glucopyranose (LGA)	S		0.314	0.330	11.0	2.048	2.157
44.04	1,1,1,5,5,5-Hexamethyl-3,3-bis[(trimethylsilyl)oxy]-trisiloxane	O	0.014	0.014				0.040
44.33	4-Hydroxy-3-methoxy-benzenepropanol	A		0.022	0.048	0.396	0.288	0.172

Table S1 Continued

Retention time (min)	Compounds	Group	Yj (–)[1]					
			Run 1	Run 9	Run 10	Run 11	Run 12	Run 14
44.73	4-Hydroxy-3-methoxy-phenylacetylformic acid	A					0.033	
44.97	2-Methoxy-4-vinylphenol	A	0.013	0.018	0.037		0.062	0.023
45.20	3,5,5-Trimethyl-cyclohexene	L	0.130					
46.75	Tetradecamethyl-hexasiloxane	O	0.013	0.031				0.030
46.80	(5α,9α,10β)-Kaur-15-ene	L	0.033	0.044	0.027		0.088	0.034
47.03	1,6-Anhydro-β-D-glucofuranose	S		0.018	0.030	0.384	0.136	0.195
47.21	Coniferyl aldehyde	A				0.295		0.028
48.33	1-(1-Butyny)cyclopentanol	L	0.671	0.076	0.036			
48.33	Octahydro-cyclobuta[1,2:3,4]dicyclopentene-1,6-dione	L	0.069		0.043			
49.13	3-(2E)-2-Dodecenyldihydro-2,5-furandione	F					0.079	0.034
49.40	Hexadecamethyl-heptasiloxane	O	0.029	0.021				0.098
52.73	Bicyclo[3.3.1]nona-3,7-diene-2,9-dione	L	0.116	0.033				
55.29	Isopimarol	L			0.074			
56.52	(4.α)-Kaur-16-en-18-ol	L	0.103	0.018				
57.72	5-[(E)-5-Hydroxy-3-methylpent-3-enyl]-1,4a-dimethyl-6-methylidene-3,4,5,7,8,8a-hexahydro-2H-naphthalene-1-carbaldeh	L		0.186	0.119	0.582	0.383	0.337
59.43	5-(5-Formyl-5,8a-dimethyl-2-methylenedecahydronaphthalen-1-yl)-3-methylpent-2-en-1-yl acetate	L		0.012				
60.13	2-(3-Hydroxy-propyl)-cyclohexanol	L	0.019					
60.68	Ferruginol	L	0.283	0.318	0.317	0.554	0.398	0.404
61.35	6,7-Dehydro-ferruginol	L	0.027	0.044	0.041		0.031	0.029

[1] Y_j (–) = Y_{LGO} (Peak area of compound j) / (Peak area of LGO); Y_{LGO} = yield of LGO (wt%)

* The list includes compounds with low similarity index.

Table S2 List of symbols and acronyms

AAEMs	Alkali and alkaline earth metallic species
CD	Cedar (softwood)
DAEM	Distributed activation energy model
DGP	1,4:3,6-dianhydro-α-D-glucopyranose
E	Activation energy
GC	Gas chromatography
GC-FID	Gas chromatography – Flame Ionization Detector
GC-MS	Gas chromatography – Mass Spectrometry
k_0	Frequency factor
LGA	Levoglucosan
LGO	Levoglucosenone
PA	Phytic acid
TGA	Thermogravimetric analysis
SATP	Standard Ambient Temperature and Pressure
T_1–T_5	Temperature inside the reactor, monitored at different positions
$T_{1,ave}$	Average T_1 during the pyrolysis run
U_{mf}	Minimum fluidization velocity
X	Mass-based conversion
Y_i	Semi-quantitative yields for each compound group
Y_{LGO}	Yield of LGO on a CD-mass basis, quantified using a calibration curve

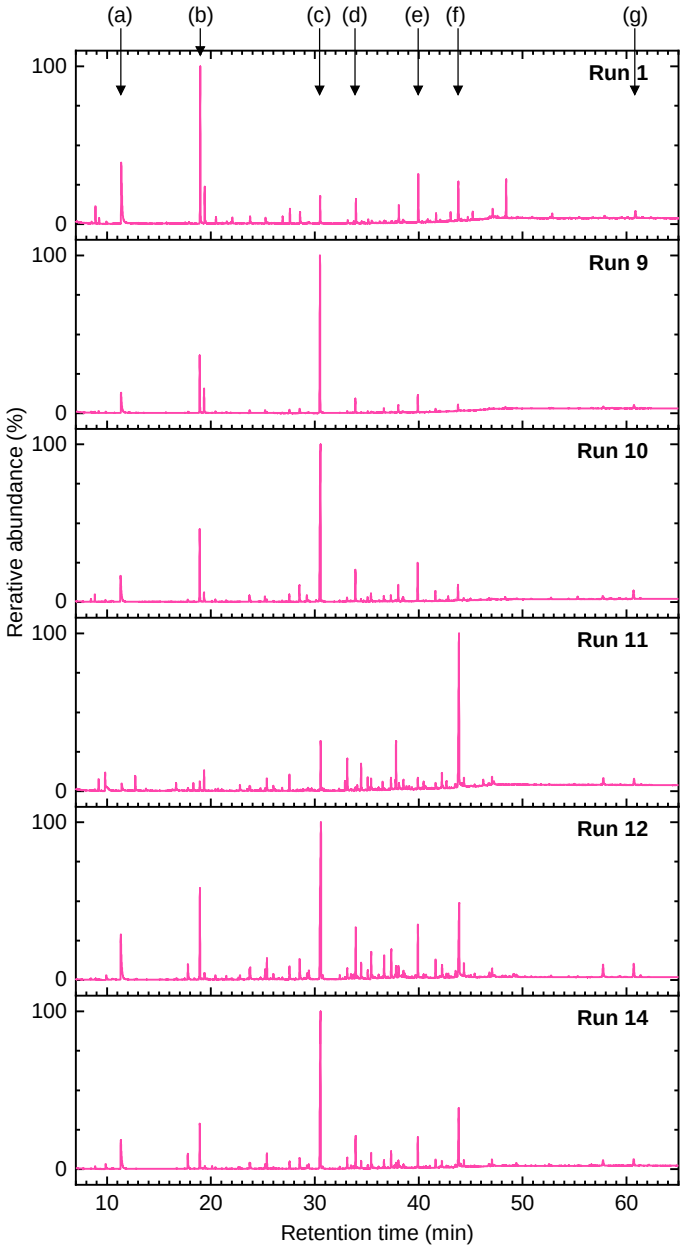

Figure S1. GC-MS chromatograms of bio-oils. Runs 1, 9, 12, and 14 are bio-oils recovered at the cold trap. The bio-oil at the cold trap contained more L, compared to that recovered at the filter trap. The latter was more abundant in LGO due to its tendency to form aerosols. Runs 10 and 11 are mixture of bio-oils recovered at the two traps. Main components: (a) acetic acid, (b) furfural, (c) LGO, (d) DGP, (e) 4-propyl guaiacol, (f) LGA, and (g) ferruginol.