catalysts

MDPI

Supplementary Material

Catalytic fast pyrolysis of lignin isolated by hybrid organosolv – steam explosion pretreatment of hardwood and softwood biomass for the production of phenolics and aromatics

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Results

Physicochemical characteristics ZSM-5 catalysts

a) TEM images of commercial, conventional microporous ZSM-5 zeolites

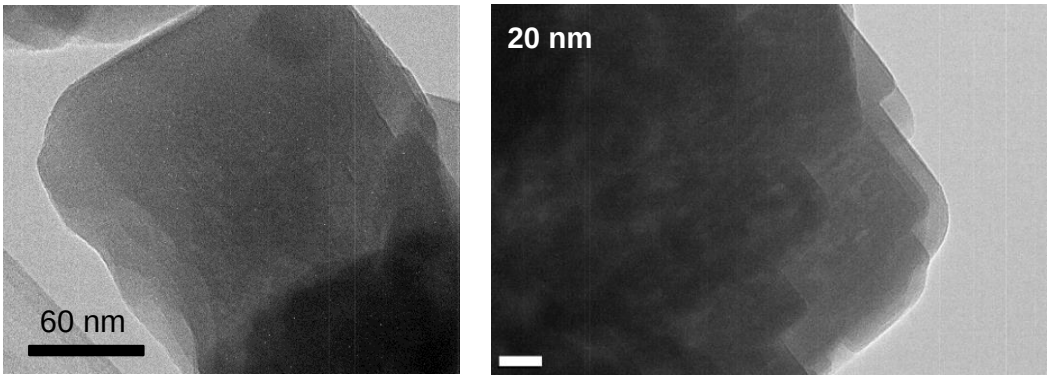


Figure S1. Representative TEM images of the commercial microporous zeolite ZSM-5 (40).

Py/GC-MS lignin pyrolysis results

Table S1. Composition of bio-oil derived from non-catalytic and catalytic fast pyrolysis of Spruce lignin in the Py/GC-MS system (GC-MS peak area, %). The catalytic results refer to experiments at 600°C with catalyst to lignin (C/L) ratio of 4.

Compounds	Silica Sand (Thermal)	ZSM-5 (11.5)	ZSM-5 (40)	Nano-ZSM-5	Meso-ZSM-5 (45nm)	Meso-ZSM-5 (9nm)
Aromatics (AR)						
Bis(2-ethylhexyl) phthalate	0.33	-	-	-	-	-

Benzene	-	4.02	1.32	1.95	5.68	2.06
Toluene	-	7.46	7.20	9.56	12.26	7.89
Ethylbenzene	-	0.36	0.82	1.83	1.49	1.44
Benzene, 1,3-dimethyl-	-	4.98	9.91	14.83	3.82	10.60
Benzene, 1-ethyl-3-methyl-	-	0.52	1.06	2.09	3.09	3.74
Benzene, 1,2,3-trimethyl-	-	0.79	5.80	0.53	8.33	9.68
Indane	-	0.27	0.70	0.66	0.77	0.69
Indene	-	1.20	1.67	0.65	0.71	0.59
1H-Indene, 2,3-dihydro-5-methyl-	-	0.17	0.67	0.66	0.67	0.80
Benzene, (1-methyl-2-cyclopropen-1-yl)-	-	0.55	1.27	1.55	1.27	1.34
2-Methylindene	-	0.35	0.62	0.29	0.31	0.32
Naphthalene, 1,2,3,4-tetrahydro-1,1,6-trimethyl-	-	0.06	0.23	-	-	-
Biphenyl	-	0.11	-	-	-	-
1H-Indene, 2,3-dihydro-4-methyl-	-	0.12	-	-	-	-
1H-Indene, 1,3-dimethyl-	-	0.14	0.56	-	0.17	0.19
Benzene, propyl-	-	0.04	-	0.24	-	0.09
Mesitylene	-	1.98	3.75	8.71	-	-
1H-Indene, 1-methyl-	-	0.80	-	-	-	-
4-Phenylbut-3-ene-1-yne	-	5.68	-	-	-	-
(1-Methylenebut-2-enyl)benzene	-	0.18	-	-	-	-
Benzene, pentamethyl-	-	0.05	-	-	-	-
Benzene, 1-ethyl-2-methyl-	-	-	1.13	1.70	-	-
Benzene, 1,2,4,5-tetramethyl-	-	-	0.23	0.35	0.48	0.80
1H-Indene, 3-ethenyl-2,3-dihydro-1,1-dimethyl-	-	-	0.48	-	-	-
Benzene, 2-butenyl-	-	-	0.27	-	-	-
Benzene, 1,4-diethyl-	-	-	-	0.18	-	0.10
Benzene, 1-methyl-4-propyl-	-	-	-	0.21	-	0.18
Benzene, 1,2-diethyl-	-	-	-	0.39	-	0.27
Benzene, 1,2,3,4-tetramethyl-	-	-	-	0.16	0.22	-
p-Xylene	-	-	-	-	11.34	-
o-Xylene	-	-	-	-	3.91	3.67
Benzene, 1,3-diethyl-	-	-	-	-	0.11	-
Benzene, 1-ethyl-3,5-dimethyl-	-	-	-	-	0.23	2.39
Benzene, 2-ethyl-1,4-dimethyl-	-	-	-	-	0.22	0.18
1H-Indene, 3-methyl-	-	-	-	-	1.18	-
Benzene, 1-methyl-4-(1-methyl-2-propenyl)-	-	-	-	-	0.17	0.28
Benzene, 1-ethyl-2,3-dimethyl-	-	-	-	-	0.10	0.17
Benzene, cyclopropyl-	-	-	-			0.74
Benzene, 1-propynyl-	-	-	-	-	-	0.78
Benzene, 1-methyl-3-(1-methyl-2-propenyl)-	-	-	-	-	-	0.22
Benzene, 2-ethenyl-1,3,5-trimethyl-	-	-	-	-	-	0.33
Benzene, 1-methyl-2-(2-propenyl)-	-	-	-	-	-	0.46
Aliphatics (ALI)						
Azulene	-	7.29	-	-	6.31	3.65
Stigmastan-3,5-diene	-	0.08	-	-	-	-
1,5-Hexadiyne	-	3.63	-	-	-	-
1,5-Hexadien-3-yne, 2-methyl-	-	3.08	-	-	-	-
3,5-Octadiyne	-	4.65	-	-	-	-
Bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene	-	6.66	-	-	-	-

Cyclopropyl methyl carbinol	-	-	0.77	-	-	-
Cyclopropane, 1,2,3-trimethyl-	-	-	-	0.92	-	-
Cyclopentene, 4-methyl-	-	-	-	0.12	0.05	-
Cyclopentene, 3-methyl-	-	-	-	-	0.05	-
Cyclobutane, (1-methylethylidene)-	-	-	-	-	0.29	0.24
Hexane, 2,2,3-trimethyl-	-	-	-	-	-	0.09
n-Hexane	-	-	-	-	-	0.08
Cyclopentane, methyl-	-	-	-	-	-	0.20
Cyclopentene, 1-methyl-	-	-	-	-	-	0.15
Heptane	-	-	-	-	-	0.14
Cyclopentene, 4,4-dimethyl-	-	-	-	-	-	0.13
Dodecane	-	-	-	-	-	1.56
Tetradecane	-	-	-	-	-	2.15
Heneicosane	-	-	-	-	-	0.56
2-Pentene, 3-methyl-	-	-	-	-	-	0.43
2-Pentene, 3-methyl-, (Z)-	-	-	-	-	-	0.49
Heptane, 2,4-dimethyl-	-	-	-	-	-	0.12
Decane	-	-	-	-	-	0.15
Hexadecane	-	-	-	-	-	0.44
2-Pentene, 2-methyl-	-	-	-	-	-	0.26
Cyclopentene, 1,5-dimethyl-	-	-	-	-	-	0.15
1,3-Dimethyl-1-cyclohexene	-	-	-	-	-	0.15
Octane, 3-methyl-	-	-	-	-	-	0.13
Tridecane, 5-methyl-	-	-	-	-	-	0.21
Octadecane	-	-	-	-	-	0.11
Phenols (PH) and substituted phenols						
Phenol	0.94	1.43	2.54	-	-	-
Phenol, 2-methyl-	1.03	0.64	2.30	4.50	2.00	2.65
p-Cresol	1.43	-	-	-	-	-
Phenol, 2,4-dimethyl-	1.54	0.38	1.47	-	0.70	1.08
Catechol	2.35	1.19	0.64	0.61	-	0.37
Phenol, 2-ethyl-4-methyl-	0.14	-	-	-	-	-
Phenol, 2-ethyl-5-methyl-	0.25	0.38	-	0.63	-	0.19
1,4-Benzenediol, 2,5-dimethyl-	0.46	-	-	-	-	-
1,2-Benzenediol, 4-methyl-	2.78	2.51	0.79	0.38	-	-
1,4-Benzenediol, 2,6-dimethyl-	-	0.35	1.47	-	-	-
1,2-Benzenediol, 3-methyl-	-	-	0.91	-	-	-
Methyleugenol	0.17	-	-	-	-	-
Phenol, 3-methyl-	1.76	0.96	3.49	7.33	3.79	2.64
Phenol, 2,6-dimethyl-	0.13	1.08	0.21	0.93	0.96	0.44
Phenol, 3,5-dimethyl-	0.15	0.07	-	2.34	0.94	-
Phenol, 2,3,5-trimethyl-	0.15	0.13	0.32	0.85	0.27	0.43
Phenol, 3-ethyl-5-methyl-	0.22	-	0.21	-	-	-
Phenol, 4-ethyl-2-methyl-	-	0.08	0.25	0.78	0.26	0.26
Benzaldehyde, 2-hydroxy-6-methyl-	0.39	-	-	-	-	-
2,3-Dihydroxybenzaldehyde	0.25	-	-	-	-	-
4-Hydroxy-3-methylacetophenone	-	0.51	-	-	-	-
1-(4-Hydroxybenzylidene)acetone	-	-	0.37	-	-	0.16
Phenol, 2,3-dimethyl-	-	0.25	0.29	2.49	1.02	0.92

1-Phenyl-1-butene	-	0.10	0.27	0.32	0.39	0.35
Phenol, 4-ethyl-	-	0.10	-	0.29	0.10	0.17
Phenol, 3,4-dimethyl-	-	0.16	0.62	0.90	0.37	1.21
Phenol, 2-(1-methylpropyl)-	-	0.09	-	-	-	-
Phenol, 2-methyl-6-(2-propenyl)-	-	0.33	-	-	-	-
Phenol, 2,5-dimethyl-	-	-	2.30	3.71	0.93	2.23
1H-Inden-5-ol, 2,3-dihydro-	-	-	0.42	0.55	0.31	0.40
Phenol, 3,4,5-trimethyl-, methylcarbamate	-	-	-	0.22	0.20	0.13
Phenol, 2,3,6-trimethyl-	-	-	-	0.64	-	-
Phenol, 2,4,5-trimethyl-	-	-	-	0.46	-	0.18
Phenol, 3,4,5-trimethyl-	-	-	-	0.18	-	-
Phenol, 2,3,5,6-tetramethyl-	-	-	-	0.70	-	-
Phenol, 4-(2-propenyl)-	-	-	-	-	-	0.19
Furans (FUR)						
6-Methoxy-3-methylbenzofuran	0.79	0.36	0.65	-	-	-
Furan, 2-(2-furanylmethyl)-5-methyl-	0.49	-	-	-	-	-
Benzofuran	-	0.14	0.48	0.44	0.39	0.51
Benzofuran, 2-methyl-	-	0.08	0.44	0.73	0.38	0.57
Benzofuran, 7-methoxy-	-	0.10	0.40	-	-	-
Dibenzofuran	-	0.18	0.30	-	0.29	-
5-Isopropyl-3,3-dimethyl-2-methylene-2,3-dihydrofuran	-	0.03	-	-	-	-
Benzofuran, 4,7-dimethyl-	-	-	0.46	0.86	-	0.13
Benzofuran, 7-methyl-	-	-	0.30	-	-	-
Acids (AC)						
Oxalic acid	0.78	-	0.95	-	-	-
Acetic acid	0.45	-	0.22	-	-	-
Benzoic acid, 3,5-dimethyl-	0.31	-	-	-	-	-
n-Hexadecanoic acid	0.23	0.22	-	-	-	-
Dehydroabietic acid	2.62	0.37	0.16	-	-	-
Esters (EST)						
1-Phenanthrenecarboxylic acid, 7-ethenyl-	0.55	-	-	-	-	-
Alcohols (AL)						
2-Hexanol, 5-methyl-	0.61	-	-	-	-	-
Campesterol	0.32	-	-	-	-	-
7-Octen-2-ol	0.48	-	-	-	-	-
1H-Indenol	-	0.11	-	-	-	0.43
1-Pentanol, 4-methyl-	-	-	-	-	0.08	-
1-Pentanol, 2-methyl-	-	-	-	-	-	0.33
Ethers (ETH)						
2,5-Dimethylanisole	0.15	0.07	-	-	-	-
Methyl-(2-hydoxy-3-ethoxy-benzyl)ether	1.40	-	-	-	-	-
(3-Nitrophenyl) methanol, isopropyl ether	0.42	-	-	-	-	-
Aldehydes (ALD)						
Benzaldehyde, 4-(1-methylethyl)-	-	0.11	-	-	-	-
2-Isopropylbenzaldehyde	-	-	-	-	0.20	-
Benzaldehyde, 4-ethyl-	-	-	-	-	0.15	-
Ketones (KET)						
Dibenz[d,f]cycloheptanone, 2,3,9-trimethoxy-	0.73	0.37	0.54	-	-	-
6-Methoxy-1-indanone	0.52	0.27	0.36	0.31	0.15	-

7-(3,4-Methylenedioxy)-tetrahydrobenzofuranone	5.91	-	1.35	-	-	-
2(3H)-Furanone, dihydro-3,4-bis[(4-hydroxy-3-	0.34	-	-	-	-	-
2H-Inden-2-one, 1,3-dihydro-	-	0.09	-	-	0.16	-
Ethanone, 1-(4,5-diethyl-2-methyl-1-cyclopenten-1-yl)-	-	0.25	-	-	-	-
2(3H)-Furanone, dihydro-5-methyl-5-phenyl-	-	1.56	-	-	-	-
5',6',7',8'-Tetrahydro-2'-acetonaphthone	-	-	0.16	-	-	-
Polycyclic aromatic hydrocarbons (PAH)						
2-Naphthalenol, 3-methoxy-	0.27	0.14	0.22	-	-	-
Naphthalene, 1-methyl-	-	7.13	0.34	5.70	6.64	3.84
Naphthalene, 2-methyl-	-	0.73	7.30	-	2.62	3.98
Naphthalene, 1-ethyl-	-	0.32	0.53	0.31	0.17	0.46
Naphthalene, 2,6-dimethyl-	-	2.17	0.28	0.51	2.58	1.71
Naphthalene, 2,3-dimethyl-	-	0.33	0.28	0.94	1.60	1.02
Naphthalene, 2-ethenyl-	-	0.09	-	-	-	-
Naphthalene, 1,4,6-trimethyl-	-	0.06	-	-	-	-
1-Naphthalenol	-	0.28	0.92	0.95	0.60	0.98
Fluorene	-	0.37	0.16	0.26	0.23	0.17
Anthracene	-	1.06	0.46	0.47	0.89	0.65
Phenanthrene, 3-methyl-	-	0.68	0.40	0.26	0.47	0.25
Anthracene, 9-methyl-	-	0.51	0.39	-	0.09	0.20
Phenanthrene, 1,7-dimethyl-	-	0.16	-	-	-	-
Naphthalene, 2-(1-methylethyl)-	-	0.14	0.35	0.19	0.38	0.39
Naphthalene, 1,2-dihydro-6-methyl-	-	0.19	-	-	-	-
Naphthalene, 1,2-dihydro-3-methyl-	-	0.12	-	-	-	-
Naphthalene, 1,5-dimethyl-	-	3.01	-	-	-	-
Naphthalene, 1,2-dimethyl-	-	0.09	-	0.17	0.60	0.41
Naphthalene, 1,6,7-trimethyl-	-	0.07	0.19	-	0.25	0.18
1-Naphthalenol, 2-methyl-	-	0.35	0.61	0.71	0.49	0.76
Phenanthrene, 2,7-dimethyl-	-	0.14	-	-	-	-
Retene	-	0.11	-	-	-	-
Naphthalene	-	-	6.47	3.95	-	3.63
Naphthalene, 2-ethyl-	-	-	0.56	-	0.70	0.48
Naphthalene, 1,7-dimethyl-	-	-	3.60	1.42	1.78	1.25
Naphthalene, 1,3-dimethyl-	-	-	0.15	0.27	0.58	0.31
Naphthalene, 2,3,6-trimethyl-	-	-	0.21	0.20	0.67	0.56
Phenanthrene	-	-	0.59	0.39	-	0.58
Anthracene, 2-methyl-	-	-	-	-	0.19	-
Nitrogen Compounds (NIT)						
.alpha.-Amino-3'-hydroxy-4'-methoxyacetophenone	0.78	0.07	-	-	-	-
Acenaphtho[1,2-b]quinoxaline, 9-methoxy-	0.45	0.21	0.31	-	-	-
N-[4-(Acridin-9-yl)-2-methylphenyl]-N-ethylamine	0.20	-	-	-	-	-
(+-)-2-Phenethanamine, 1-methyl-N-vanillyl-	0.47	-	-	-	-	-
Vanilic acid hydrazide	1.18	0.10	-	-	-	-
1,2-Benzenediol,4-(2-aminopropyl)-	-	0.35	-	-	-	-
2-Butanamine, 2-methyl-	-	-	0.80	-	-	-
1H-Benzimidazole, 5,6-dimethyl-	-	-	-	-	-	0.18
Oxy-Aromatics (OxyAR)						
4-Methoxycinnamaldehyde	0.25	-	-	-	-	-
2-Allyl-1,4-dimethoxybenzene	0.27	-	-	-	-	-

1,2-Dimethoxy-4-(1-methoxy-1-propenyl)benzene	1.91	-	-	-	-	-
Cholesta-4,6-dien-3-ol, (3.beta.)-	0.17	-	-	-	-	-
Benzene, 1-ethyl-4-methoxy-	0.31	0.43	-	-	-	-
1,2-Dimethoxy-4-n-propylbenzene	1.42	-	-	-	-	-
3,4-Dimethoxytoluene	-	-	0.64	-	-	-
Dibenz[a,c]cycloheptane, 2,3,7-trimethoxy-	-	-	0.34	-	-	-
2,4-Dimethylanisole	-	-	-	0.21	-	-
Oxy-Phenols (OxyPH) and substituted oxy-phenols						
Phenol, 2-methoxy-	5.45	0.99	1.45	1.23	0.38	0.21
Phenol, 2-methoxy-3-methyl-	0.32	-	-	-	-	-
Creosol	11.52	2.28	2.54	1.53	0.40	0.21
1,2-Benzenediol, 3-methoxy-	0.28	-	-	-	-	-
Phenol, 4-ethyl-2-methoxy-	2.84	0.73	0.74	0.28	-	-
2,4'-Dihydroxy-3'-methoxyacetophenone	-	0.11	-	-	-	-
2-Methoxy-4-vinylphenol	6.55	0.99	1.02	0.52	0.21	-
3-Methoxy-5-methylphenol	0.31	0.16	0.26	-	-	-
Eugenol	2.39	0.39	-	-	-	-
Phenol, 2-methoxy-4-propyl-	1.06	0.15	0.16	0.17	-	-
4-Ethylcatechol	0.80	0.82	-	-	-	-
Vanillin	5.22	0.61	-	-	-	-
Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-	4.31	1.44	1.44	0.57	-	-
trans-Isoeugenol	8.33	-	-	-	-	-
Apocynin	1.30	0.31	-	-	-	-
2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	0.53	0.09	-	-	-	-
4-((1E)-3-Hydroxy-1-propenyl)-2-methoxyphenol	2.61	-	0.32	-	-	-
2-Propenal, 3-(4-hydroxy-3-methoxyphenyl)-	3.72	0.21	0.17	-	-	-
[1,1'-Biphenyl]-4,4'-diol, 3,3'-dimethoxy-	0.17	-	-	-	-	-
Carinol	1.00	0.38	0.37	-	-	-
(-)-Nortrachelogenin	1.06	0.56	0.66	-	-	-
Phenol, 2-methoxy-4-methyl-6-[propenyl]-	0.20	-	-	-	-	-
2-Methoxy-5-methylphenol	-	0.12	0.22	-	-	-
3-Allyl-6-methoxyphenol	-	-	0.40	-	-	-
Phenol, 2-methoxy-4-(1-propenyl)-	-	-	-	-	0.16	-

Table S2. Composition of bio-oil derived from non-catalytic and catalytic fast pyrolysis of Birch lignin in the Py/GC-MS system (GC-MS peak area, %). The catalytic results refer to experiments at 600°C with catalyst to lignin (C/L) ratio of 4.

Compounds	**Silica Sand (Thermal)**	**ZSM-5 (11.5)**	**ZSM-5 (40)**	**Nano-ZSM-5**	**Meso-ZSM-5 (45nm)**	**Meso-ZSM-5 (9nm)**
Aromatics (AR)						
Toluene	0.41	7.71	6.09	8.36	7.89	6.54
Benzene, pentamethyl-	0.16	-	-	-	-	-
Benzene, 3-ethyl-1,2,4,5-tetramethyl-	0.31	-	-	-	-	-
Benzene	-	2.85	1.05	2.06	3.20	1.69
Ethylbenzene	-	0.56	1.14	2.28	1.39	2.03
Benzene, 1,3-dimethyl-	-	6.50	11.13	16.62	11.26	4.45
Styrene	-	0.09	-	-	-	-

Benzene, 1-ethyl-3-methyl-	-	0.65	2.10	4.86	2.24	1.05
Benzene, 1,2,3-trimethyl-	-	1.43	5.81	0.36	4.62	14.89
Indane	-	0.25	0.65	0.56	0.58	0.78
1H-Indene, 1-chloro-2,3-dihydro-	-	0.61	-	0.45	-	-
1H-Indene, 2,3-dihydro-5-methyl-	-	0.19	0.74	0.57	0.64	1.21
Benzene, (1-methyl-2-cyclopropen-1-yl)-	-	0.38	0.85	1.24	0.86	1.23
2-Methylindene	-	0.15	0.39	0.30	0.25	0.29
o-Xylene	-	0.73	2.04	-	-	-
Indene	-	0.50	0.77	-	0.46	0.50
1H-Indene, 2,3-dihydro-4-methyl-	-	0.18	0.65	-	0.66	-
Benzene, 1,2,4-trimethyl-	-	3.79	-	0.54	-	5.10
Benzene, 1,2,3,4-tetramethyl-	-	0.11	0.35	-	0.59	0.18
Benzene, 1-ethyl-4-methyl-	-	-	1.15	-	-	-
Benzene, 1-ethenyl-3-ethyl-	-	-	0.29	-	-	-
Benzene, 1,2,4,5-tetramethyl-	-	-	0.34	0.98	1.17	2.70
1H-Indene, 1,3-dimethyl-	-	-	0.42	0.58	0.42	0.57
Benzene, propyl-	-	-	0.17	0.33	0.11	0.22
Benzene, 1,2-diethyl-	-	-	0.35	0.62	0.22	0.61
1H-Indene, 5,6-dimethoxy-	-	-	0.12	-	-	-
Mesitylene	-	-	-	8.81	4.99	-
Benzene, 1-ethenyl-2-methyl-	-	-	-	0.24	-	-
Benzene, 1-methyl-3-propyl-	-	-	-	0.19	-	-
Benzene, 1,4-diethyl-	-	-	-	-	0.21	0.37
Benzene, 1-methyl-4-propyl-	-	-	-	-	0.13	0.31
Benzene, 1-ethyl-3,5-dimethyl-	-	-	-	-	0.23	0.26
Benzene, 2-ethyl-1,4-dimethyl-	-	-	-	-	0.19	0.33
Benzene, 1-methyl-2-(2-propenyl)-	-	-	-	-	0.44	0.70
1H-Indene, 2,3-dihydro-1,6-dimethyl-	-	-	-	-	0.27	0.24
1H-Indene, 2,3-dihydro-4,7-dimethyl-	-	-	-	-	0.25	0.20
Benzene, 4-ethyl-1,2-dimethyl-	-	-	-	-	0.20	-
Benzene, 2-butenyl-	-	-	-	-	0.32	-
4-Phenylbut-3-ene-1-yne	-	-	-	-	3.57	-
Benzene, 1-methyl-4-(1-methyl-2-propenyl)-	-	-	-	-	0.13	-
1,4-Methanonaphthalene, 1,4-dihydro-	-	-	-	-	4.62	-
Benzene, 1-ethyl-2,3-dimethyl-	-	-	-	-	-	0.13
1H-Indene, 2,3-dihydro-1,3-dimethyl-	-	-	-	-	-	0.24
p-Xylene	-	-	-	-	-	4.73
Aliphatics (ALI)						
1-Heptene	0.09	-	-	-	-	-
1-Undecene	0.11	-	-	-	-	-
Azulene	-	4.94	-	-	3.82	-
3-Methylenecyclopentene	-	0.20	-	-	-	-
1-Propene, 2-methyl-	-	-	0.32	-	-	-
Cyclobutane, methoxy-	-	-	0.85	-	-	-
2-Butene, 2-methyl-	-	-	0.79	-	-	-
Cyclopropane, 1,1,2-trimethyl-	-	-	0.16	-	-	-
3-Hexene, (Z)-	-	-	0.14	-	-	-
Cyclopropane, 1-ethyl-1-methyl-	-	-	-	0.77	0.27	-
2-Pentene, 3-methyl-	-	-	-	0.95	-	-

1,3-Cyclohexadiene	-	-	-	0.62	-	-
Cyclopentene, 1,5-dimethyl-	-	-	-	0.14	-	0.10
Cyclopentane, methyl-	-	-	-	-	0.09	0.12
Cyclopentene, 4-methyl-	-	-	-	-	0.05	0.13
1,4-Cyclohexadiene, 3-ethenyl-1,2-dimethyl-	-	-	-	-	2.16	3.40
Dodecane	-	-	-	-	0.06	2.50
Chamazulene	-	-	-	-	0.10	-
3,5-Octadiyne	-	-	-	-	9.93	-
1-Pentene, 2-methyl-	-	-	-	-	-	0.16
Hexane, 3-methyl-	-	-	-	-	-	0.12
Heptane	-	-	-	-	-	0.11
Cyclopentene, 4,4-dimethyl-	-	-	-	-	-	0.28
1,3-Dimethyl-1-cyclohexene	-	-	-	-	-	0.16
Nonane	-	-	-	-	-	0.13
Decane	-	-	-	-	-	0.22
Undecane, 3-methyl-	-	-	-	-	-	0.13
Tetradecane, 5-methyl-	-	-	-	-	-	0.32
Tetradecane	-	-	-	-	-	3.57
Hexadecane	-	-	-	-	-	1.45
Octadecane	-	-	-	-	-	0.31
Cyclopentene, 1-methyl-	-	-	-	-	-	0.11
Heptadecane	-	-	-	-	-	0.71
Heneicosane	-	-	-	-	-	0.16
Phenols (PH) and substituted phenols						
Phenol, 2-methyl-	0.47	0.23	0.74	2.28	1.04	1.45
p-Cresol	0.60	-	-	-	-	-
Phenol, 2,4-dimethyl-	0.91	0.23	0.62	-	0.58	0.97
Catechol	0.60	-	-	-	-	-
Phenol	0.69	-	-	-	3.25	-
Phenol, 2,6-dimethyl-	0.24	0.10	0.11	0.51	0.55	0.35
Phenol, 2,3,5-trimethyl-	0.40	0.34	-	0.47	0.27	0.25
Phenol, 2-ethyl-5-methyl-	0.83	-	-	0.16	-	-
2-Allylphenol	0.40	-	-	-	-	-
1,4-Benzenediol, 2,5-dimethyl-	0.90	-	-	-	-	-
1,2-Benzenediol, 4-methyl-	1.86	-	0.52	-	-	-
1,4-Benzenediol, 2,6-dimethyl-	-	0.17	1.17	0.71	-	-
1,2-Benzenediol, 3-methyl-	0.44	-	-	-	-	-
Phenol, 2-methyl-6-(2-propenyl)-	0.34	-	-	-	-	-
Phenol, 2-(2-penten-4-yl)-4-methyl-	0.16	-	-	-	-	-
Phenol, 3-methyl-	0.92	0.39	1.24	3.75	-	-
Phenol, 2-(2-methyl-2-propenyl)-	0.16	-	-	-	-	-
1-Phenyl-1-butene	-	0.09	0.32	0.38	0.38	-
1,4-Benzenediol, 2,3,5-trimethyl-	-	0.58	0.52	-	0.14	-
4-Hydroxy-3-methylacetophenone	-	0.18	-	-	-	-
1-(4-Hydroxybenzylidene)acetone	0.17	-	-	-	-	-
Phenol, 2,3-dimethyl-	-	0.08	0.58	1.02	0.33	-
Phenol, 3-(1-methylethyl)-	-	0.12	-	-	-	-
Phenol, 3-methyl-6-propyl-	-	0.28	-	0.61	0.17	-
3-Methyl-4-isopropylphenol	-	0.23	-	-	-	-

Methyleugenol	-	0.12	0.23	-	-	-
Phenol, 3,5-dimethyl-	-	-	0.46	-	0.28	0.68
Phenol, 2,5-dimethyl-	-	-	0.43	4.32	0.76	1.20
Phenol, 3,4-dimethyl-	-	-	0.19	0.57	0.51	0.50
2-Ethoxy-4-methylphenol	-	-	0.73	2.26	-	-
Phenol, 3-ethyl-5-methyl-	-	-	-	0.48	-	-
Phenol, 2,3,6-trimethyl-	-	-	-	0.31	0.17	0.34
1H-Inden-5-ol, 2,3-dihydro-	-	-	-	0.21	-	0.21
Phenol, 2,4,5-trimethyl-	-	-	-	-	0.26	0.19
Phenol, 4-ethyl-2-methyl-	-	-	-	-	0.14	0.21
Phenol, 3,4,5-trimethyl-, methylcarbamate	-	-	-	-	-	0.13
Furans (FUR)						
6-Methoxy-3-methylbenzofuran	0.18	0.18	-	-	-	-
Furane-3-carboxylic acid, 5-tert-butyl-2-(4-tert-	-	0.26	-	-	-	-
Benzofuran	-	-	0.13	-	0.13	0.19
Benzofuran, 2-methyl-	-	-	0.14	0.15	0.11	0.22
Acids (AC)						
Acetic acid	0.35	-	0.37	0.39	0.12	-
2,5-Dimethylterephthalicdihydroxamic acid	0.64	-	-	-	-	-
3,5-Dimethoxy-4-hydroxyphenylacetic acid	0.83	1.35	0.62	0.49	-	-
Benzenepropanoic acid, 2,5-dimethoxy-	6.33	-	-	-	-	-
Mandelic acid, 3,4-dimethoxy-, methyl ester	0.21	0.27	0.50	-	-	-
Benzoic acid, 4-(1-methylethyl)-	1.49	-	-	-	-	-
n-Hexadecanoic acid	0.25	-	-	-	0.25	-
Octadecanoic acid	0.20	-	-	-	-	-
Benzoic acid, 4-hydroxy-3,5-dimethoxy-	-	0.24	-	-	-	-
Oxalic acid	-	-	1.10	-	-	-
Formic acid	-	-	1.02	-	-	-
Esters (EST)						
2,4-Hexadienedioic acid, 3,4-diethyl-, dimethyl ester,	-	0.77	0.61	-	-	-
2,4-Hexadienedioic acid, 3,4-diethyl-, dimethyl ester,	-	0.25	-	0.40	-	-
Benzoic acid, 2-methyl-3-nitro-, methyl ester	-	-	0.26	-	-	-
Oxalic acid, 6-ethyloct-3-yl isobutyl ester	-	-	-	-	-	0.15
Alcohols (AL)						
1-Pentanol, 5-methoxy-	0.30	-	-	-	-	-
3-Hexen-1-ol, (E)-	-	0.09	-	-	-	-
Benzeneethanol, .alpha.,.beta.-dimethyl-	-	12.04	-	-	-	11.81
Benzenemethanol, 4-ethyl-	-	0.26	-	-	-	-
2-Phenyl-4-penten-2-ol	-	-	0.16	-	-	0.20
dl-Erythro-1-phenyl-1,2-propanediol	-	-	1.24	-	2.18	-
1-(2,4-Dimethylphenyl)ethanol	-	-	-	0.18	-	-
Benzenemethanol, .alpha.-methyl-.alpha.-propyl-	-	-	-	-	0.09	-
1-Pentanol, 4-methyl-	-	-	-	-	0.09	-
2,5-Dimethoxybenzyl alcohol	-	-	-	-	0.50	-
Ethers (ETH)						
Benzene, 1,4-dimethoxy-2,3,5,6-tetramethyl-	-	0.10	-	-	-	-
Aldehydes (ALD)						
Furfural	0.38	-	-	-	-	-

Benzaldehyde, 2,3-dimethoxy-	0.52	-	0.52	-	-	-
1,1'-Biphenyl-3,4,4'-trimethoxy-6'-formyl-	-	0.30	-	-	-	-
Ketones (KET)						
3',5'-Dimethoxyacetophenone	2.69	1.33	1.89	0.51	0.15	-
Ethanone, 1-(4,5-diethyl-2-methyl-1-cyclopenten-1-yl)-	0.32	-	-	-	-	-
7-(3,4-Methylenedioxy)-tetrahydrobenzofuranone	0.66	-	-	-	-	-
2,4,6-Cycloheptatrien-1-one, 2-hydroxy-5-(1-methylethyl)-	0.26	-	-	-	-	-
1,2,3,4,5,6,7,8-Octahydrophthalen-2-one, 4,4,5,6,7,8-	-	0.11	-	-	-	-
tert-Butyl-p-benzoquinone	-	0.13	-	-	-	-
2',4'-Dimethoxyacetophenone	-	0.28	-	-	-	-
Polycyclic aromatic hydrocarbons (PAH)						
Naphthalene, 2-methyl-	-	3.71	3.53	0.59	1.57	4.14
Naphthalene, 1-ethyl-	-	0.18	0.28	0.22	0.47	0.39
Naphthalene, 1,7-dimethyl-	-	2.57	2.91	1.61	3.24	-
Naphthalene, 2,3-dimethyl-	-	0.33	0.23	1.10	-	0.87
Naphthalene, 1,4,6-trimethyl-	-	0.21	0.50	-	-	-
Fluorene	-	0.10	-	-	0.09	-
Anthracene, 2-methyl-	-	0.35	-	-	-	-
Naphthalene, 2-ethyl-	-	0.28	0.25	-	0.12	-
Naphthalene, 1,5-dimethyl-	-	0.10	-	-	-	-
1-Naphthalenol	-	0.18	0.25	-	0.47	0.52
Anthracene, 9-methyl-	-	0.53	0.30	-	-	-
Naphthalene, 1-methyl-	-	8.19	4.46	3.01	4.31	-
Naphthalene, 2,6-dimethyl-	-	0.50	0.22	-	2.60	3.23
Naphthalene, 2-(1-methylethyl)-	-	0.25	-	0.28	0.36	0.56
Naphthalene, 1,6,7-trimethyl-	-	0.07	-	-	0.33	0.38
1-Naphthalenol, 2-methyl-	-	0.13	-	-	0.52	0.55
Anthracene	-	0.72	0.33	-	0.43	0.14
Phenanthrene, 3-methyl-	-	0.43	0.19	-	0.23	-
Naphthalene	-	-	3.60	2.40	-	2.82
Naphthalene, 2,3,6-trimethyl-	-	-	0.20	0.18	0.78	0.58
Naphthalene, 1,6-dimethyl-	-	-	2.78	-	-	-
Naphthalene, 1,2-dimethyl-	-	-	-	-	0.31	0.30
Naphthalene, 1,3-dimethyl-	-	-	-	-	0.16	-
Phenanthrene, 2-methyl-	-	-	-	-	0.18	-
Phenanthrene	-	-	-	-	0.17	-
Naphthalene, 1,2-dihydro-3-methyl-	-	-	-	-	-	0.16
Nitrogen Compounds (NIT)						
4-(3-Aminobutyl)-2-methoxyphenol	0.73	-	-	-	-	-
Phenylamine, N,4,5-trimethyl-2-nitro-	1.10	0.36	0.31	-	-	-
3-methoxy-4-hydroxy-methyl-nitrostyrene	0.16	-	-	-	-	-
3,4-Dimethoxy-6-amino toluene	1.96	1.23	-	-	-	-
Benzeneethanamine, 3,4,5-trimethoxy-	0.42	-	-	-	-	-
3,5-Dimethoxy-4-hydroxyphenethylamine	0.58	-	-	-	-	-
5-Methylmercapto-6-methoxy-8-aminoquinoline	0.09	-	-	-	-	-
4-(4-Biphenylyl)-5-phenyl-2-thiazolamine	0.13	-	-	-	-	-
Benzamide, 2-methoxy-4-methylthio-N-(3-pyridyl)-	0.33	-	-	-	-	-
2,4-Diamino-5-benzyl-6-phenylthieno[2,3-d]pyrimidine	1.02	-	-	-	-	-
2,3-Dimethoxyphenethylamine	1.16	-	-	-	-	-

3-Ethoxy-4-methoxyphenethylamine	0.36	0.21	-	0.24	-	-
2,4,6(1H,3H,5H)-Pyrimidinetrione, 5-ethyl-5-(2-	0.53	-	-	-	-	-
2,6-Dimethoxyamphetamine	0.38	-	-	-	-	-
1-Cyclohexyl-3-isopropylcarbodiimide	0.19	-	-	-	-	-
Phenethylamine, 2,4,5-trimethoxy-.alpha.-methyl-	-	0.29	-	-	-	-
Pyrazol-5-ol, 3-(3,4-dimethoxyphenyl)-	-	0.07	-	-	-	-
1H-Benzimidazole, 5,6-dimethyl-	-	-				0.13
Oxy-Aromatics (OxyAR)						
3,4-Dimethoxytoluene	0.66	0.75	-	1.11	-	-
Benzene, 1,2,3-trimethoxy-5-methyl-	1.08	1.24	1.74	0.91	0.22	0.16
1,2-Dimethoxy-4-(1,2-dimethoxyethyl)benzene	0.10	0.20	-	-	-	-
1,2-Dimethoxy-4-(1-methoxy-1-propenyl)benzene	1.37	-	-	-	-	-
Benzene, 1,2,3-trimethoxy-5-(2-propenyl)-	0.20	0.15	-	-	-	-
1,2-Dimethoxy-4-(2,3-dimethoxy-1-propenyl)benzene	3.19	-	-	-	-	-
2,6-Dimethoxytoluene	0.46	0.26	-	-	-	-
1,2,4-Trimethoxybenzene	6.77	4.84	6.58	3.03	0.66	0.29
3,5-Dimethoxytoluene	-	0.34	0.46	-	0.14	-
2,3-Dimethoxytoluene	-	0.49	-	-	-	-
Asarone	-	0.37	0.39	-	-	-
Benzene, 1-methoxy-4-methyl-2-(1-methylethyl)-	-	0.06	-	-	-	-
Oxy-Phenols (OxyPH) and substituted oxy-phenols						
Phenol, 2-methoxy-	1.03	0.23	0.24	0.64	-	-
Phenol, 2-methoxy-3-methyl-	0.29	-	-	-		-
Creosol	1.79	0.61	0.41	1.08	0.14	-
1,2-Benzenediol, 3-methoxy-	1.87	0.40	0.52	1.36	0.09	-
Phenol, 4-ethyl-2-methoxy-	0.47	-	-	-	-	-
2-Methoxy-4-vinylphenol	1.28	0.30	0.17	0.39	-	-
3-Methoxy-5-methylphenol	0.34	0.18	0.19	0.54	-	-
Phenol, 2,6-dimethoxy-	4.09	1.36	1.88	1.95	0.33	-
Eugenol	0.50	-	-	-	-	-
Phenol, 2-methoxy-4-propyl-	0.45	-	-	-	-	-
Vanillin	1.13	0.15	-	-	-	-
Phenol, 2-methoxy-4-(1-propenyl)-	0.27	0.13	-	-	-	-
Phenol, 4-methoxy-3-(methoxymethyl)-	6.60	-	-	-	-	-
Apocynin	0.47	-	-	-	-	-
Phenol, 3-methoxy-2,5,6-trimethyl-	0.16	0.18	0.17	-	-	-
4-((1E)-3-Hydroxy-1-propenyl)-2-methoxyphenol	0.61	-	-	-	-	-
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	7.91	3.98	4.00	1.24	0.23	-
Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	5.67	3.25	2.61	1.41	0.27	-
3-(2-Methoxy-5-methylphenyl)acrylic acid	0.30	1.84	2.51	-	-	-
Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	4.22	2.15	0.93	1.02	-	-
3,5-Dimethoxy-4-hydroxycinnamaldehyde	2.84	1.04	0.29	-	-	-
Phenol, 4,4'-methylenebis[2,6-dimethoxy-	0.16	0.10	-	-	-	-
2-Methoxy-5-methylphenol	0.48	-	-	-	-	-
Phenol, 3-methoxy-2,4,5-trimethyl-	0.23	-	-	0.53	-	-
Phenol, 3,4-dimethoxy-	2.40	1.28	1.27	2.54	0.51	-
Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-	0.54	-	-	-	-	-
Phenol, 2-methoxy-4-methyl-6-[propenyl]-	0.97	0.18	-	-	-	-
Ethanone, 1-(2-hydroxy-5-methoxyphenyl)-	1.82	-	-	-	-	-

6-Methoxycoumaran-7-ol-3-one	1.12	-	-	-	-	-
Desaspidinol	0.26	-	-	-	-	-
Phenol, 4-methoxy-2,3,6-trimethyl-	-	0.08	-	-	-	-

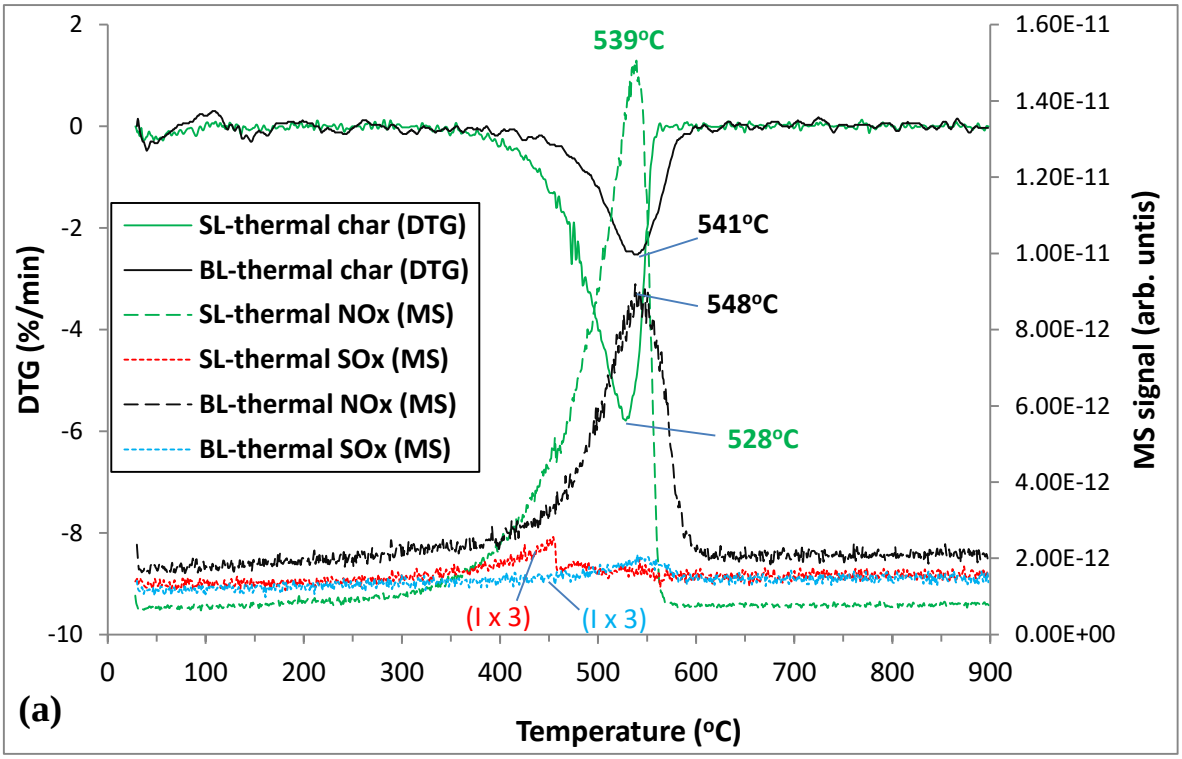
Downflow fixed-bed reactor pyrolysis results

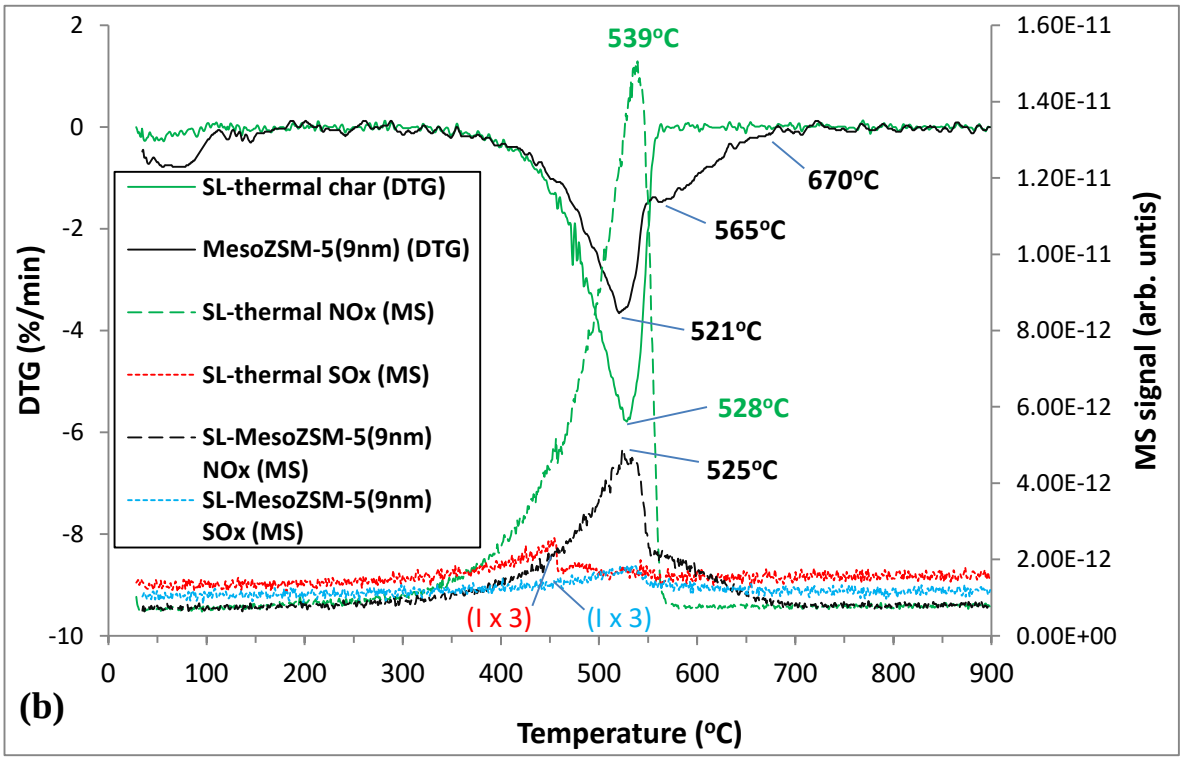
Table S3. Product yields (wt.% on lignin) and bio-oil composition for the thermal and catalytic pyrolysis of spruce lignin on the fixed-bed reactor at 600°C (Cat/Lignin = 1).

Spruce Lignin Pyrolysis	**Silica Sand**	**ZSM-5(40)**	**Meso-ZSM-5(9nm)**
Total Liquids (wt. %)	36.69	32.03	30.88
Organic Bio-oil (wt. %)	*31.30*	*19.73*	*15.40*
Water (wt. %)	*5.39*	*12.30*	*15.48*
Total Gases (wt. %)	15.60	18.95	21.81
Total Solids (char + coke on	42.17	46.66	44.27
Coke on catalyst (total solids minus the char from non-catalytic test) **(wt. %)**	-	4.49	2.10

Table S4. Product yields (wt.% on lignin) and bio-oil composition for the thermal and catalytic pyrolysis of birch lignin on fixed-bed reactor at 600°C (Cat/Lignin = 1).

Birch Lignin Pyrolysis	**Silica Sand**	**ZSM-5(40)**	**Meso-ZSM-5(9nm)**
Total Liquids (% wt.)	38.76	35.37	32.13
Organic Bio-oil (% wt.)	*32.80*	*22.60*	*19.33*
Water (% wt.)	*5.86*	*12.77*	*12.80*
Total Gases (% wt.)	13.06	16.14	19.29
Total Solids (char + coke on	42.73	45.55	46.88
Coke on catalyst (total solids minus the char from non-catalytic test) **(wt. %)**	-	2.82	4.15


539°C
541°C
548°C
528°C
SL-thermal char (DTG)
BL-thermal char (DTG)
SL-thermal NOx (MS)
SL-thermal SOx (MS)
BL-thermal NOx (MS)
BL-thermal SOx (MS)
(I x 3)
(I x 3)
DTG (%/min)
MS signal (arb. untis)
Temperature (°C)
(a)


539°C
670°C
565°C
521°C
528°C
525°C
SL-thermal char (DTG)
MesoZSM-5(9nm) (DTG)
SL-thermal NOx (MS)
SL-thermal SOx (MS)
SL-MesoZSM-5(9nm) NOx (MS)
SL-MesoZSM-5(9nm) SOx (MS)
(I x 3)
(I x 3)
DTG (%/min)
MS signal (arb. untis)
Temperature (°C)
(b)

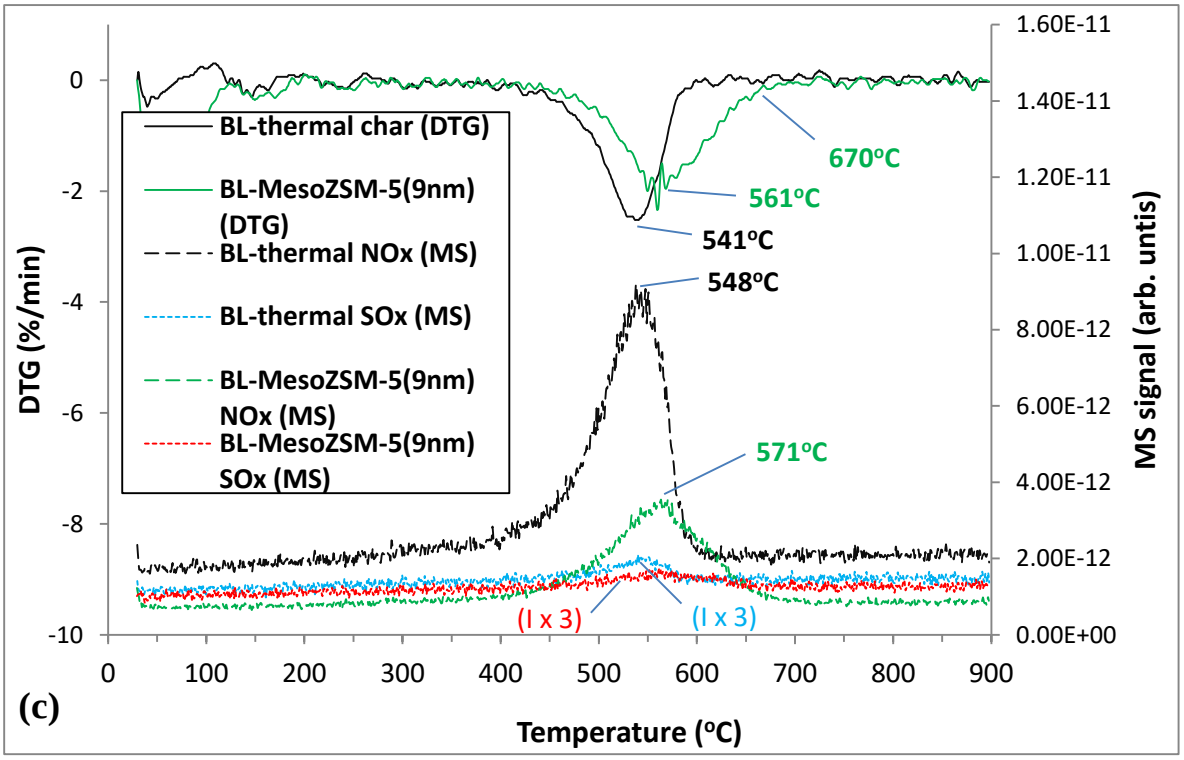


Figure S2. DTG curves (a) of char from spruce and birch lignin non-catalytic pyrolysis at 600°C, (b) of coked Meso-ZSM-5(9 nm) zeolite from catalytic fast pyrolysis of spruce lignin, and (c) , (b) of coked Meso-ZSM-5(9nm) zeolite from catalytic fast pyrolysis of birch lignin (the analysis of the coked catalysts from spruce and birch CFP with the conventional ZSM-5(40) zeolite provided similar graphs). The on-line MS signals of NOx (m/e 46) and SOx (m/e 64) are also shown in order to identify any S and N admixtures in char/coke; the thermal analyses were performed under oxidative (air) atmosphere.

Materials and Methods

Lignin characterization with 2D HSQC NMR measurements: Method for calculation of each type of aromatic unit and linkages

In the case of the birch derived lignin, the sum of the areas of the cross-peaks ($S_{2,6}$)/2 and G_2 was set as 100 Ar. In the case of spruce derived lignin the area of G2 cross-peak was used since there is not $S_{2,6}$ cross-peak. The relative abundance of each type of aromatic unit, linkage and end-group was calculated as

$$X\% = \frac{\int X}{100\ Ar}$$

In the case of linkages, the C_α-H_α correlation peak was used for the above calculation. In the case of $S_{2,6}$, $S'_{2,6}$ and $H_{2,6}$ type of aromatic units the half sum of the areas of C_2-H_2 and C_6-H_6 correlation peaks was used for the calculation of the abundances of each type of aromatic unit. The ratio of the S, G, H type of units was calculated using the respective relative abundances of the $S_{2,6}$+$S'_{2,6}$, G+G'_2, $H_{2,6}$ correlations. The abundance of FA structures was calculated as the mean value of FA_2 and FA_6 areas (in the case of the birch lignin there is only FA_2 peak). The abundance of J structure was calculated as the mean value of the areas of J_α and J_β cross peaks (in the case of the birch lignin there is only Jα peak).

Preparation of Meso-ZSM-5 zeolites with 9 nm and 45 nm mesopores

For the preparation of the mesoporous zeolite Meso-ZSM-5 (9 nm) the commercial NH_4-ZSM-5 zeolite (CBV 8014, Si/Al = 40) was initially calcined at 500 ºC for 3 h to obtain its proton form and was then subjected to mild alkaline treatment with a 0.2 M NaOH solution for 30 min at 65 ºC under stirring in a spherical flask which was then immersed into a cold bath to achieve instantaneous cooling, in order to control/stop the desilication of the zeolite. The suspension was filtered followed by washing of the zeolite with deionized water until pH~8 and drying overnight at 100°C. The desilicated zeolite sample was then treated with 0.1 N HCl aqueous solution for 6 hrs at 65 ºC to remove the generated extra-framework Al species as well as the sodium ions, thus producing again the proton form of the desilicated ZSM-5 zeolite. The zeolite was then recovered by filtration, washing with deionized water until pH~6 and drying overnight at 100°C. The mesoporous ZSM-5 sample Meso-ZSM-5 (45 nm), was prepared by the same method as for Meso-ZSM-5 (9 nm), except that the parent zeolite was the CBV 2314 (Si/Al = 11.5) and a 1 M NaOH aq. solution was used in this case.

Determination of the amount and relative strength of Brønsted and Lewis acid sites of ZSM-5 zeolites by FT-IR/pyridine sorption

The determination of the amount and relative strength of Brønsted and Lewis acid sites of the catalysts was performed by Fourier transform—infrared (FT-IR) spectroscopy combined with in situ adsorption of pyridine. The FT-IR spectra were recorded on a Nicolet 5700 FTIR spectrometer (resolution 4 cm−1) using the OMNIC software and a specially designed heated, high-vacuum IR cell with CaF2 windows. The samples were finely ground in a mortar and pressed in self-supported wafers (15 mg/cm^2) which were initially outgassed in situ at 450°C for 1 h under high vacuum (10–6 mbar), followed by recording of a background spectrum at 150°C. Adsorption/equilibration with pyridine vapors was then conducted at 150°C, by adding pulses of pyridine for 1 h at a total cell pressure of 1 mbar. Spectra were recorded at 150°C, after equilibration with pyridine at that temperature and after outgassing for 30 min at higher temperatures, i.e., 250, 350, and 450°C, in order to evaluate the strength of the acid sites. The bands at 1545 cm^{-1} (due to pyridinium ions) and 1450 cm^{-1} (due to coordinated pyridine) were used to identify and quantify the Brønsted and Lewis acid sites, respectively, by adopting the molar extinction coefficients provided by Emeis [Emeis, C. A., Determination of Integrated Molar Extinction Coefficients for Infrared Absorption Bands of Pyridine Adsorbed on Solid Acid Catalysts. Journal of Catalysis 1993, 141, 347-354].

Detailed description of fast pyrolysis reactors (Py-GC/MS & Downflow fixed bed reactor)

a) Pyrolysis tests using the Py/GC-MS system

The thermal (non-catalytic) and catalytic fast pyrolysis experiments of spruce and birch derived lignins were performed on a Multi-Shot Micro-Pyrolyzer (EGA/PY-3030D, Frontier Laboratories, Japan) connected to a gas chromatographer - mass spectrometer system (GCMS-QP2010, Shimadzu). The interface temperature between the micropyrolyzer and GC was set to 300°C and pyrolysis tests were conducted at 600 °C for 12 s. For the thermal fast pyrolysis experiments, a dried (80°C under vacuum for 6 h) mixture of approximately 1 mg lignin and 4 mg silica sand (used as inert heat carrier) was loaded in a stainless-steel cup which was automatically lowered into the preheated furnace. In the case of the catalytic fast pyrolysis (CFP) experiments, a dried mixture of 4 mg calcined catalyst with 1 mg lignin (catalyst to lignin ratio of 4) was loaded in the stainless steel cups for the respective pyrolysis experiments. The sample cups were weighed before and after pyrolysis by using a Mettler Toledo microbalance, with an accuracy of 0.00001 g, to determine the initial sample weight and the weight of the residual char or char/coke. Helium (99.999%) was employed as the carrier gas at a flow rate of 100 ml min^{-1} in the micropyrolyzer, with injector split ratio of 1:150 and 1 ml min^{-1} in the GC column. A capillary column was used (MEGA-5 HT) with stationary phase consisting of 5% diphenyl and 95% dimethylpolysiloxane (30 m × 0.25 mm and 0.25 μm film thickness). The GC oven was programmed for a 4 minute hold at 40°C followed by heating (5°C min^{-1}) up to 300°C, where it was held constant for 7 minutes. The injector and detector temperature was kept at 300°C. The mass

spectra were recorded in the range of m/z 45 to 500 with a scan speed of 5000 amu/s. Identification of mass spectra peaks was achieved by the use of the scientific library NIST11s. The derived compounds were classified and categorized in the following 16 groups-families: mono-aromatics (AR), aliphatics (ALI), phenols (PH), acids (AC), esters (EST), alcohols (AL), ethers (ETH), aldehydes (ALD), ketones (KET), polycyclic aromatic hydrocarbons (PAHs), sugars (SUG) nitrogen compounds (NIT), sulfur compounds (SUL), oxygenated aromatics (OxyAR), oxygenated phenols (OxyPH) and unidentified compounds (UN). To assess the reproducibility of the experimental data, three replicate runs were performed for each experiment. A schematic representation of the Py/GC-MS system is shown below in Figure S-3.

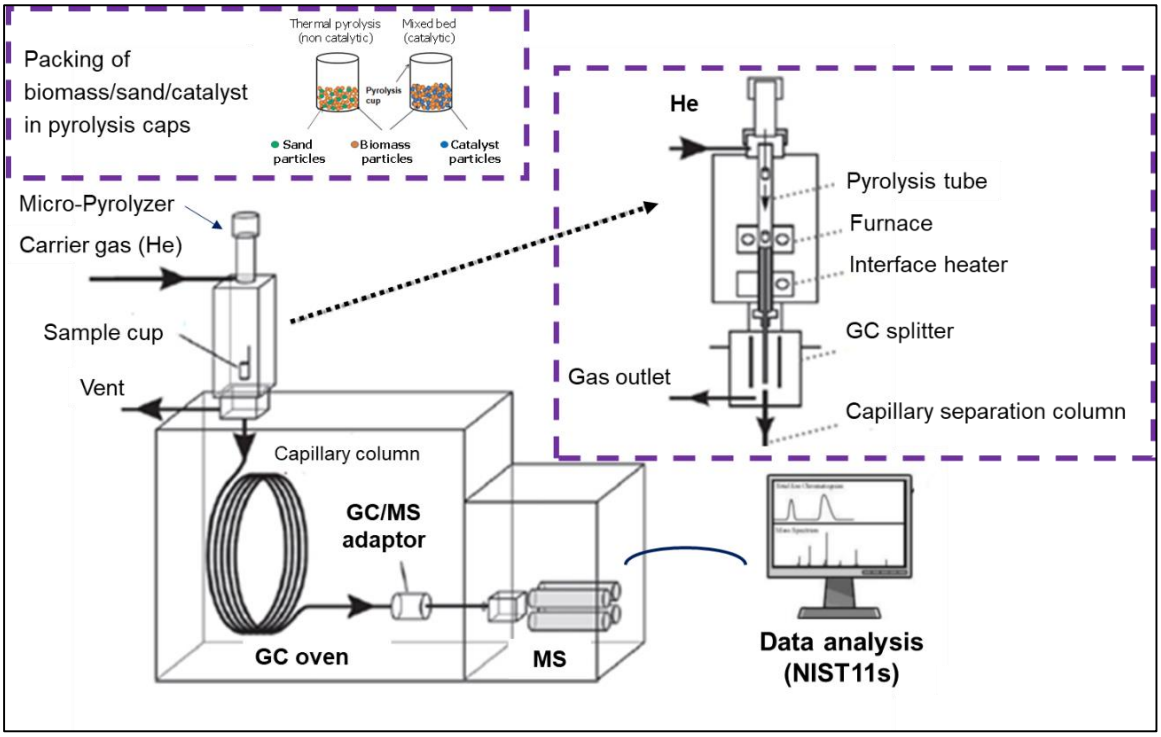


Figure S3. Schematic representation of Py/GC-MS system.

b) Fast pyrolysis tests on a downflow bench-scale fixed bed reactor

Thermal and catalytic fast pyrolysis experiments of the spruce and birch derived lignins were also performed on a bench-scale downflow fixed bed tubular reactor (ID 1.02 cm, height 35.5 cm), made of stainless steel 316 and heated by a 3-zone furnace. A specially designed piston system was used to introduce the solid lignin into the reactor. The amount of lignin (dried at 80^{o}C under vacuum for 6 h) used was typically 0.4 g and the amount of silica sand (in the non-catalytic, thermal pyrolysis experiments) or catalyst (in the catalytic experiments) was also 0.4 g. A constant stream of N_2 (100 cc/min) was fed from the top of the reactor during the pyrolysis experiments for the maintenance of the inert atmosphere during pyrolysis and the continuous withdrawal of the product vapors. In a typical experiment, lignin was inserted from the top of the reactor instantaneously with the aid of the piston in the preheated reactor zone and was initially pyrolyzed/vaporized at 600 ^{o}C on a hot quartz-wool layer placed on the top of the catalyst bed. The produced pyrolysis vapours were then driven downwards through the catalyst's bed with the aid of the constant N_2 flow (100 cm^3/min) for 20 min. The pyrolysis product vapors were then condensed in pre-weighted spiral glass receivers placed in a cooling bath (-20°C). The obtained bio-oil was collected and homogenized with 1 ml absolute ethanol before the analysis by GC–MS (GCMS-QP2010, Shimadzu). The NIST11s mass spectra library was used for the identification of the compounds in the bio-oil, which were categorized into 16 groups-families, as in the case of Py/GC-MS experiments. The water content of bio-oil was determined by Karl-Fischer titration (ASTM E203-08), while the elemental analysis (C/H/N/S) of the

organic fraction of the bio-oil was determined by a EuroEA 3000 C/H/N/S Analyzer (EuroVector); O was determined by difference. The non-condensable gases (NCG's) products were collected and analyzed in a HP 6890 GC, equipped with four columns (Precolumn: OV-101; Columns: Porapak N, Molecular Sieve 5A and Rt-Qplot (30m×0.53mm i.d.) and two detectors (TCD and FID). The amount of solids, which comprised of char and sand in the non-catalytic pyrolysis experiment, char plus coke-on-catalyst and catalyst in the catalytic pyrolysis experiments, as well as the quartz wool used to separate the two bed-zones, was determined by direct weighing. An indirect estimation of the coke formed on the catalyst, as wt.% on initial lignin, was performed by subtracting the measured char content of the non-catalytic experiment from the char+coke content of the catalytic experiments (char formation is not affected by the presence of the catalysts, as lignin and catalysts do not come in contact, see Fig. S-4 and related description above). Furthermore, the decomposition profile of the collected char and coke (on the spent catalysts) was studied by thermogravimetric analysis (TGA, NETZSCH STA 449 F5 Jupiter) using dry air as carrier gas, at a flow rate of 50 mL/min. The samples were heated from room temperature to 850 °C at heating rate of 10°C/min. A schematic representation of the bench-scale downflow fixed bed reactor for lignin fast pyrolysis is shown in Figure S-4.

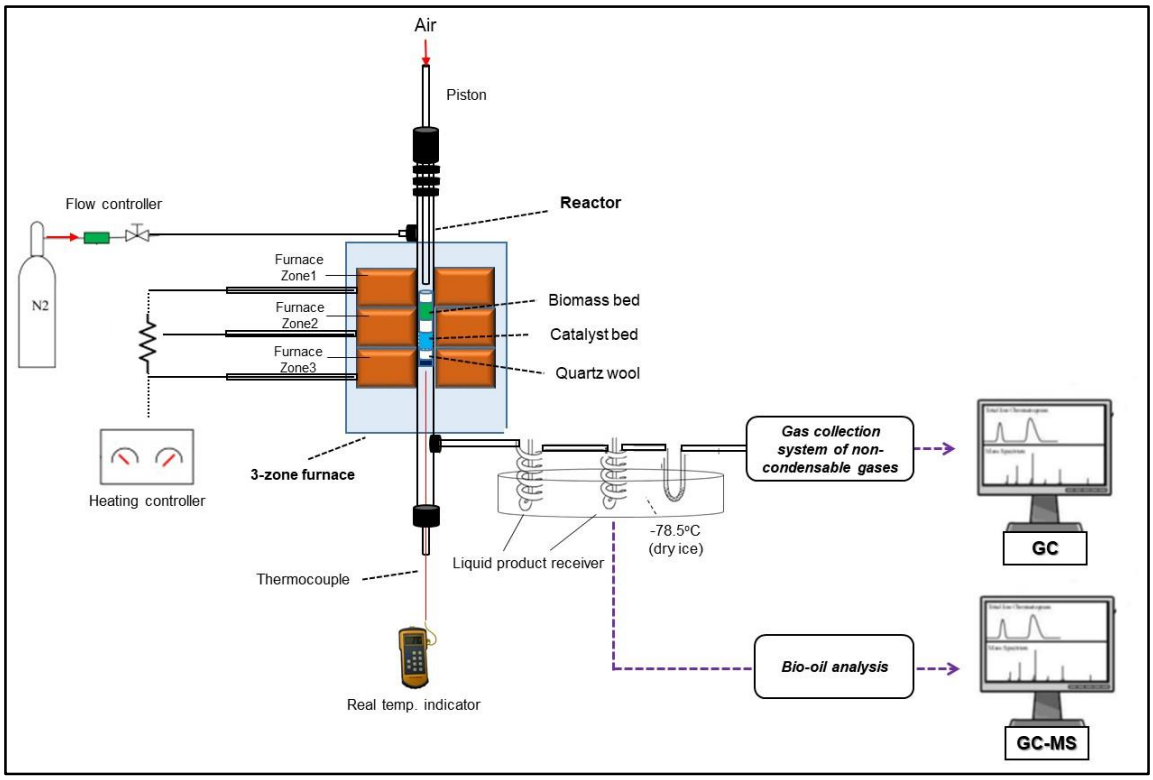


Figure S4. Schematic representation of bench-scale downflow fixed bed reactor for lignin fast pyrolysis.