Evaluation of high loaded Ni-based catalysts for upgrading of fast pyrolysis bio-oil

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Supplementary Material

1. Upgraded beech wood fast pyrolysis bio-oil with Ni/SiO_2 catalyst

The autoclave picture can be seen below (Fig. S.1).The upgrading was conducted at 325 ℃ and 80 bars for 120 minutes, including the heating ramp. Due to the low amount of upgraded oil produced in each experiment, it was necessary to repeat this procedure for at least four times. Hence, a significant amount of sample was produced, enough for characterization and further upgrading reactions. Some of the characterization results of upgraded light phases and upgraded oils are presented in Table S.1. The Ni/SiO_2 catalysts used for these reactions, synthesized by wet impregnation technique was composed by 7.9 wt.% of nickel. More information can be found elsewhere [1].

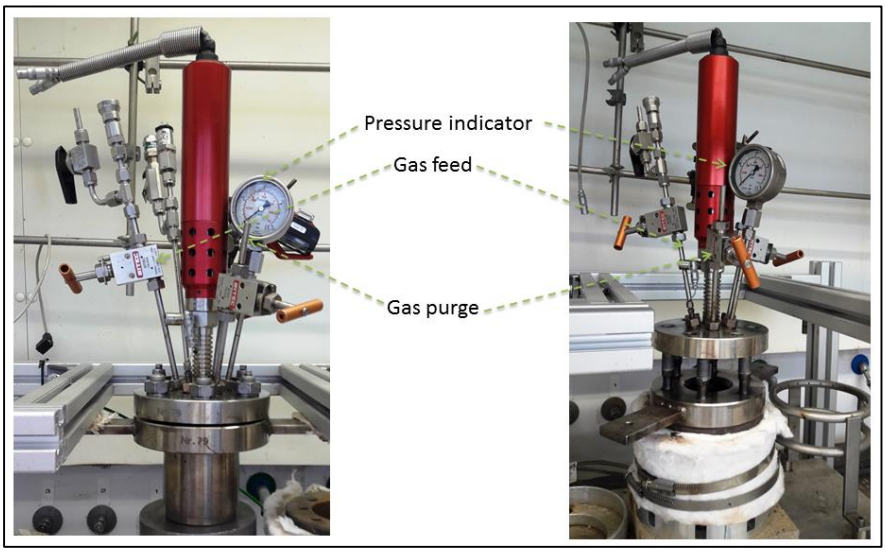

Fig S.1 Autoclave used during the experiments.

Table S.1. Characterization of upgraded beech wood fast pyrolysis bio-oils obtained with Ni/SiO_2.

Parameter	Reaction 1 (wet basis)	Reaction 2 (wet basis)	Reaction 3 (wet basis)	Reaction 4 (wet basis)	Average (wet basis)	Average (dry basis)	Standard Deviation (wet basis)
H_2 consumption (mol/Kg BWBO)	7.0	8.0	7.7	7.7	7.6	-	0.35
UPGRADED OIL							
Carbon (wt.%)	68.4	69.6	69.6	69.0	69.1	72.9	0.57
Hydrogen (wt.%)	8.2	8.6	8.5	8.7	8.5	8.4	0.21
Oxygen (wt.%)	22.8	21.3	21.4	21.8	21.82	18.18	0.68
Nitrogen (wt.%)	0.3	0.3	0.3	0.3	0.3	0.3	-
Sulfur (wt.%)	0.3	0.2	0.2	0.2	0.22	0.26	0.05
H_2O (wt.%)	5.6	4.9	4.8	5.2	5.1	-	0.36
HHV (MJ/Kg)	30.5	31.1	31.2	30.9	30.9	33.4	0.33
pH value	2.5	3.8	3.3	2.5	3.0	-	0.64
Density (g/cm^3)	1.12	-	1.11	-	1.11	-	0.005
Degree of deoxygenation (calculated in dry basis)	42.79	46.00	45.45	45.09	-	44.83	1.2
UPGRADED LIGHT PHASE							
Carbon (wt.%)	**-**	11.7	11.5	**-**	11.6	43.72	0.14
Hydrogen (wt.%)	**-**	11.5	11.4	**-**	11.45	12.39	0.071
Oxygen (wt.%)	**-**	73.8	74.0	**-**	73.9	42.19	0.141
Nitrogen (wt.%)	**-**	0.3	0.3	**-**	0.3	1.13	-
Sulfur (wt.%)	**-**	0.1	0.2	**-**	0.15	0.56	0.071
H_2O (wt.%)	**-**	74.5	74.2	71.7	73.47	-	1.537
pH value	**-**	3.1	3.1	2.9	3.03	-	0.115
Density (g/cm^3)	**-**	1.03	1.03	1.03	1.03	-	0.001

2. Upgraded products

The figure S.2 shows the detailed upgraded products after the centrifugation step. The UAP is concentrated on the top, upgraded oil in the bottom while the spent catalyst is concentrated in the tube's wall as well as in the bottom.

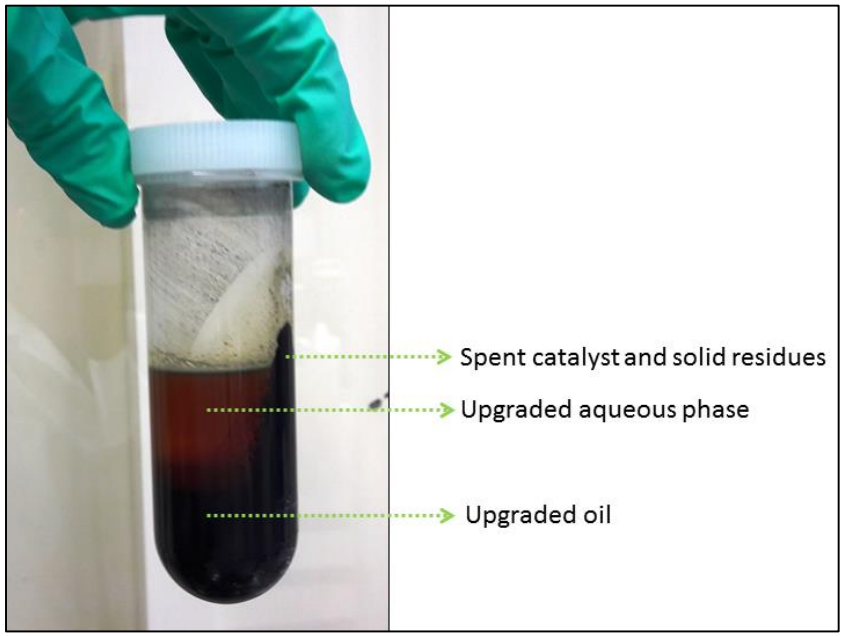

Fig S.2. detailed of the upgraded products after the centrifugation step.

After the separation, the products are divided in tubes and later characterized. The Figure S.3 shows the typical upgraded products obtained after the upgrading of beech wood fast pyrolysis bio-oil with Ru/C, Ni catalyst and Ni-Cr catalyst.

Fig S.3. Upgraded products separated after centrifugation. From the left to the right: spent catalyst after filtration; upgraded aqueous phase and the two last samples in the right side are the upgraded oil.

The upgraded products obtained for the two steps upgrading reaction are presented in Fig. S.4. A colorless upgraded aqueous phase was obtained in this case.

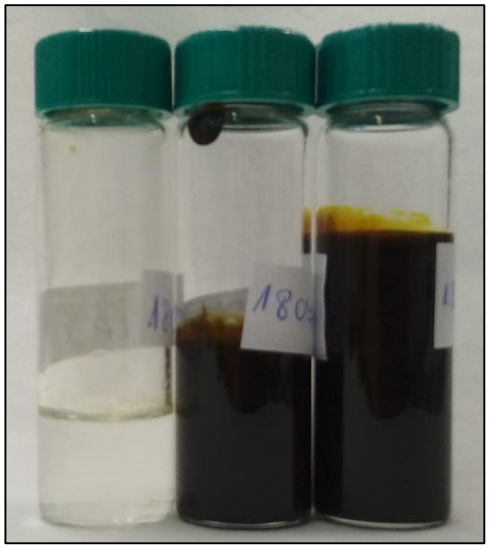

Fig S.4. Products obtained after the second upgrading performed with UBWBO. From the left: upgraded aqueous phase and two bottles containing the upgraded oil.

3. Evaluation of different reaction times

The comparison of different reaction times was conducted at 4 h and 2 h, respectively. The results obtained are demonstrated in Table S.2. Despite the higher H_2 consumption for the reaction conducted for 4 hours, the other parameters are comparable.

Table S.2 Comparison of reactions conducted with Ni catalyst at 225 ℃ for 2 h and 4 h, wet basis.

	Ni, 225 ℃, 4 hours of reaction[1]	**Ni, 225 ℃, 2 hours of reaction**
Upgraded oil composition		
C (wt.%)	58.3	58.2
H (wt.%)	8.0	8.5
O (wt.%)	33.1	33.0
pH value	4.1	3.9
H_2O (wt.%)	10.5	11.6
HHV (MJ/Kg)	26.3	26.1
Mass Balance		
Gas production (wt.%)	1.31	1.37
Upgraded aqueous phase (wt.%)	46.9	50.7
Upgraded oil (wt.%)	43.2	40.9
Solids (wt.%)	0.4	0.5
Loss (wt.%)	8.2	6.5
Gas composition		
CO_2 (mol/Kg PO)	0.29	0.30
CH_4 (mol/Kg PO)	0.03	0.03
H_2 consumption (mol/Kg PO)	11.62	9.48

[1]Already presented in the manuscript, but in order to facilitate the comparison to the reader, the result is presented again in the Supplementary Material.

4. Elemental analysis and physicochemical characterization of the upgraded aqueous phases with Ni, Ni-Cr and Ru/C catalysts

Table S.3 Elemental analysis and physicochemical properties of upgraded aqueous phase upgraded with Ni, Ni-Cr and Ru/C catalysts

	Ni, 175 °C 1-step UR	**Ni, 225 °C 1-step UR**	**Ni-Cr, 175 °C 1-step UR**	**Ni-Cr, 225 °C 1-step UR**	**Ru/C, 175 °C 1-step UR**	**Ru/C, 225 °C 1-step UR**	**Ni-Cr, 325 °C 2-step UR[1]**
C (wt.%)	28.5	26.5	28.0	25.5	27.8	23.8	1.6
H (wt.%)	9.7	9.9	9.5	9.4	9.2	9.7	14.5
O (wt.%)	61.7	63.5	62.3	64.9	62.9	66.3	82.1
N (wt.%)	<1.0	<1.0	<1.0	<1.0	<0.2	<0.2	<1.0
S (wt.%)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
pH value	3.5	3.5	3.5	3.6	3.0	3.1	3.7
H_2O (wt.%)	42.6	46.6	43.3	48.7	44.0	52.0	97.0
HHV (MJ/Kg)	12.8	12.2	12.6	11.8	12.4	[2]	[2]

[1] UR: upgrading reactions; [2]Not determined – high water concentration

5. NH_3-TPD

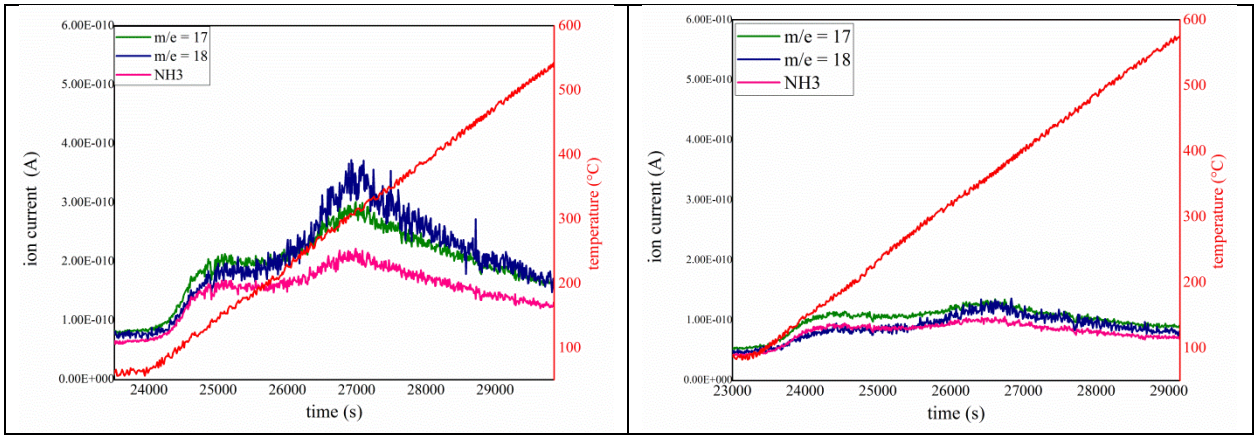

Fig S.5 NH_3-TPD of fresh nickel-based catalysts. Left: Ni catalyst; Right: Ni-Cr catalyst

For a quantitative analysis of the desorbed ammonia it is considered that the ammonia desorption is always accompanied by water desorption of in varying amounts. m/e = 17 is a trace of ammonia but inflected by the fragmentation of water in the ion source of the QMS detector. The general fragmentation pattern of water (library data) tells that the relative abundance of m/e =17 is 23% of the abundance of m/e = 18 for water.

Therefore a pure "NH_3" trace is created by assuming that (m/e = 17) – (0,23 * (m/e = 18)) is the ammonia amount of m/e =17 without the water inflection. This NH_3-trace is used for the quantitative calculations. The molar amount of desorbed ammonia is derived from a comparative measurement with a substance with a known amount of NH_3 desorption. This is a H-ZSM5 sample (the high temperature peak is used).

6. Detailed chemical composition received from GC-MS/FID measurements

Table S.4 Single compounds identified by GC-MS/FID in the upgraded oils and feedstocks.

Compound *(wet basis; dry basis)*	**BWBO (wt.%)**		**UBWBO (wt.%)**	**Ni, 225 °C 1-step UR (wt.%)**		**Ni-Cr, 225 °C 1-step UR (wt.%)**		**Ni-Cr, 325 °C 2-step UR** (wt.%)**	
	LP	**HP**		**UAP**	**UO**	**UAP**	**UO**	**UAP**	**UO**
Nonaromatic Compounds	**19.81; 30.72**	**14.18; 16.54**	**13.69; 14.61**	**28.70; 55.68**	**15.0; 16.91**	**20.72; 41.57**	**13.15; 14.64**	**2.96; 80.99**	**5.13; 5.28**
Acids	**6.18; 9.59**	**4.643; 5.42**	**9.709; 10.37**	**10.025; 19.45**	**8.637; 9.73**	**4.554; 9.14**	**7.96; 8.86**	**2.735; 74.72**	**-**
Formic acid	n.q.	-	-	-	-	**-**	-	-	-
Acetic Acid[c]	4.732; 7.338	3.183; 3.714	4.388; 4.685	5.195; 10.08	3.693; 4.162	4.554; 9.138	3.232; 3.598	1.118; 30.53	-
Propionic Acid[c]	1.117; 1.732	1.062; 1.240	5.322; 5.682	4.776; 9.267	4.786; 5.395	-	4.625; 5.148	1.463; 39.96	-
Butyric Acid[c]	0.120; 0.187	0.151; 0.176	-	0.053; 0.103	0.158; 0.178	-	0.099; 0.111	0.125; 3.41	-
3-butenoic acid	0.025; 0.038			-		-		-	
(Z)-(cis)-2-butenoic Acid[#]	0.076; 0.117	0.093; 0.109	-	-	-	-	-	-	-
Pentanoic Acid[#]	0.021; 0.033	0.036; 0.042	-	-	-	-	-	-	-
4-pentenoic acid	0.038; 0.060			-		-		-	
Hexanoic Acid[#]	0.052; 0.081	0.118; 0.138	-	-	-	-	-	-	-
2-methyl-propanoic acid	-	-	-	-	-	-	-	0.030; 0.815	
Nonaromatic Esters	**0.388; 0.60**	**0.256; 0.30**	**0.079; 0.08**	**0.788; 1.53**	**0.589; 0.66**	**0.578; 1.16**	**0.275; 0.31**	**-**	**-**
Propanoic acid, methyl ester[#]	0.012; 0.019	0.021; 0.024	0.079; 0.084	-	-	-	-	-	-
Acetic acid 2-hydroxyethyl ester[c]	0.185; 0.287	0.103; 0.120	-	0.671; 1.303	0.517; 0.583	0.471; 0.944	0.209; 0.233	-	-
poss: Oxopropanoic acid methylester, 2-	0.091; 0.140			-	-	-		-	
Butenoic acid, dimethyl ester or isomer	0.014; 0.022			-	-	-		-	

Unknown aliphatic ester	0.059; 0.092			-	-	0.019; 0.037		-	
Poss: ethenyl ester propanoic acid[#]	0.021; 0.033	0.045; 0.053	-	-	-	-	-	-	-
Unknown aliphatic ester[#]	-	0.055; 0.064	-	-	-	-	-	-	-
7-oxodehydroabietic acid, methyl ester[#]	0.005; 0.008	0.032; 0.037	-	-	-	-	-	-	-
2-hydroxyethyl ester propanoic acid	-	-	-	0.030; 0.059	0.072; 0.081	0.017; 0.034	0.008; 0.008	-	-
Poss: butanoic acid, propyl ester	-	-	-	0.012; 0.023	-	-	0.025; 0.028	-	-
Similar to furancarboxylic acid, tetrahydro-3-methyl-5-oxo-,methyl ester	-	-	-	0.035; 0.068	-	0.071; 0.144	0.032; 0.036	-	-
Poss: furancarboxylic acid, tetrahydro-3-methyl-5-oxo-, methyl ester	-	-	-	0.039; 0.076	-	-	-	-	-
Nonaromatic Alcohols	**2.679; 4.15**	**0.926; 1.08**	**0.176; 0.19**	**17.507; 33.97**	**4.164; 4.69**	**15.537; 31.17**	**4.343; 4.83**	**0.114; 3.12**	**0.455; 0.47**
1-propanol	-	-	-	0.113; 0.220	0.134; 0.152	0.125; 0.251	0.132; 0.147	-	-
cyclohexanol[#]	-	-	-	0.011; 0.021	-	0.047; 0.093	0.215; 0.239	0.044; 1.190	0.455; 0.469
Ethylene glycol[c]	2.614; 4.053	0.88; 1.027	-	13.592; 26.371	2.382; 2.685	11.378; 22.829	1.729; 1.925	-	-
2-propen-1-ol[#]	0.021; 0.033	0.019; 0.022			-	-		-	-
Poss: 2-methyl-2-propanol[#]	0.013; 0.020				-	-		-	-
1,2-ethanediol, monoformate[#]	0.031; 0.048	0.027; 0.032			-	-		-	-
cyclopentanol[c]	-	-	-	0.048; 0.092	0.117; 0.132	0.060; 0.121	0.165; 0.184	0.011; 0.292	-
(n)-2-butanol[#]	-	-	-	0.008; 0.016	0.018; 0.020	0.031; 0.062	0.060;0.067	0.060; 1.632	-
2-methyl-1-butanol[#]	-	-	-	0.010; 0.020	-	-	-	-	-
Poss: 2-methyl-1-butanol[#]	-	-	-	0.008; 0.016	0.031; 0.035	-	0.026; 0.029	-	-
Unknown aliphatic alcohol[#]	-	-	-	0.028; 0.054	0.028; 0.032	-	-	-	-
Propylene glycol[#]	-	-	-	2.326; 4.513	0.756; 0.852	2.034; 4.080	0.623; 0.694	-	-
2-methyl-cyclopentanol[#]	-	-	-	0.026; 0.051	0.105; 0.118	0.054; 0.108	0.217; 0.241	-	-
3-methyl-cyclopentanol[#]	-	-	-	0.011; 0.022	0.050; 0.056	0.014; 0.027	0.067; 0.074	-	-
2-methyl-trans-cyclopentanol[#]	-	-	-	0.012; 0.024	0.052; 0.058	0.042; 0.084	0.194; 0.216	-	-
Poss: 2,3-butanediol[#]	-	-	-	0.116; 0.224	0.053; 0.060	0.146; 0.292	0.051; 0.056	-	-
Poss: [R-(R*, R*)]-2,3-butanediol[#]	-	-	-	0.163; 0.317	0.069; 0.078	0.202; 0.405	0.095; 0.106	-	-

1,2-butanediol,(ñ) [#]	-	-	-	0.330; 0.641	0.165; 0.186	0.338; 0.677	0.143; 0.160	-	-
Poss: 1-methoxy-2-butanol[#]	-	-	-		0.056; 0.063	0.089; 0.179	0.101; 0.112	-	-
Isomer of 1-methoxy-2 butanol	-	-	-	-	-	0.166; 0.332	-	-	-
Unknown not identifiable aliphatic alcohol[#]	-	-	-	0.232; 0.456	0.107; 0.121	-	-	-	-
1,4-butanediol[#]	-	-	-	0.160; 0.311	0.042; 0.047	0.140; 0.282	0.025; 0.028	-	-
1,4-pentanediol[#]	-	-	-	0.020; 0.038	-	0.041; 0.083		-	-
Poss: Isomer of cyclopentane-1,2-diol	-	-	-	0.029; 0.057		0.047; 0.094		-	-
Unknown aliphatic alcohol[#]	-	-	0.078; 0.083	-	-	0.067; 0.134	-	-	-
2,4-dimethyl-cyclopentanol [#]	-	-	0.098; 0.105	-	-	-	-	-	-
(R)-(-)-2-pentanol	-	-	-	-	-	-	0.045; 0.050	-	-
Isomer of 1-methoxy-2-butanol	-	-	-	-	-	-	0.092; 0.102	-	-
Unknown aliphatic alcohol	-	-	-	-	-	0.040; 0.081	0.061; 0.067	-	-
Isomer of 3-methyl-1,2-cyclopentanediol	-	-	-	0.031; 0.059	-	0.024; 0.048	0.024; 0.027	-	-
glycerin	-	-	-	0.087; 0.168	-	0.063; 0.126	-	-	-
Isomer of 1,2,3-butanetriol	-	-	-	0.010; 0.019	-	-	-	-	-
Trans-1,2cyclohexanediol	-	-	-	-	-	0.227; 0.455	0.278; 0.309	-	-
1,2,4-butanetriol or Isomer	-	-	-	-	-	0.025; 0.050	-	-	-
Poss: trans-1,2-cyclohexanediol	-	-	-	-	-	0.074; 0.149	-	-	-
Unknown aliphatic alcohol[#]	-	-	-	0.133; 0.259		0.045; 0.091	-	-	-
Unknown not identiable aliphatic alcohol	-	-	-	-	-	0.020; 0.039	-	-	-
Nonaromatic Aldehydes	**4.133; 6.41**	**2.759; 3.22**	**-**	**-**	**-**	**-**	**-**	**-**	**-**
hydroxyacetaldehyde[c]	3.883; 6.021	2.428; 2.832	-	-	-	-	-	-	-
3-hydroxypropionaldehyde[#]	0.134; 0.207	0.115; 0.134	-	-	-	-	-	-	-
Butanal[#]	-	0.014; 0.016	-	-	-	-	-	-	-
2-butenal[#]	0.014; 0.022	0.024; 0.027	-	-	-	-	-	-	-
2-methyl-2-butenal[#]	-	0.029; 0.034	-	-	-	-	-	-	-

Poss: hexanal[#]	-	0.014; 0.016	-	-	-	-	-	-	-
Butanedial or propanal[#]	-	0.136; 0.158	-	-	-	-	-	-	-
Poss: 3-hydroxy-butanal	0.017; 0.027	-	-	-	-	-	-	-	-
Butanedial or Propanal	0.085; 0.132	-	-	-	-	-	-	-	-
Nonaromatic Ketones	**6.428; 9.97**	**5.594; 6.53**	**3.723; 3.98**	**0.378; 0.73**	**1.567; 1.77**	**0.051; 0.10**	**0.580; 0.65**	**0.115; 3.15**	**1.837; 1.89**
Acetol (hydroxypropanone)[c]	4.732; 7.338	3.171; 3.70	-	-	-	-	-	-	-
Acetonylacetone (2,5-hexandione) [c]	0.006; 0.009	0.035; 0.041	-	-	0.027; 0.031	-	-	-	-
2-butanone[c]	0.051; 0.079	0.082; 0.096	0.229; 0.245	0.022; 0.044	0.080; 0.090	-	-	-	0.387; 0.398
1-hydroxy-2-butanone[c]	0.412; 0.639	0.305; 0.356	-	-	-	-	-	-	-
2,3-butandione (diacetyl)[c]	0.127; 0.198	0.102; 0.119	-	-	-	-	-	-	-
3-hydroxy-2-butanone[c]	0.056; 0.086	0.053; 0.061	0,118; 0,126	0.101; 0.196	-	-	-	-	-
1-acetyloxy-propan-2-one[c]	0.071; 0.110	0.093; 0.109	-	-	-	-	-	-	-
cyclopentanone[c]	-	0.107; 0.125	0,283; 0,303	-	0.239; 0.269	-	0.183; 0.203	0.028; 0.766	-
2-cyclopenten-1-one[c]	0.132; 0.205	0.202; 0.236	-	-	-	-	-	-	-
2,3-dimethyl-2-cyclopenten-1-one[c]	0.062; 0.095	0.091; 0.106	0.149; 0.159	-	-	-	-	-	-
2-methyl-2-cyclopenten-1-one[c]	0.034; 0.053	0.09; 0.105	-	-	-	-	-	-	-
3-methyl-2-cyclopenten-1-one[c]	0.057; 0.089	0.097; 0.114	-	-	-	-	-	-	-
2-hydroxy-2-cyclopenten-1-one[#]	0.030; 0.046	0.023; 0.027	-	-	-	-	-	-	-
2-hydroxy-1-methyl-1-cyclopenten-3-one[c]	0.408; 0.632	0.578; 0.675	-	-	-	-	-	-	-
3-ethyl-2-hydroxy-2-cyclopenten-1-one[c]	0.054; 0.084	0.091; 0.106	-	-	-	-	-	-	-
2-cyclohexen-1-one[c]	0.004; 0.007	0.009; 0.011	-	-	-	-	-	-	-
Poss: 3-buten-2-one = 2-butenone[#]	0.008; 0.013	0.009; 0.011	-	-	-	-	-	-	-
Poss: 3-methyl-2-butanone[#]	-	0.020; 0.023	0.082; 0.088	0.008; 0.015	0.034; 0.038	-	-	-	-
3-methyl-3-buten-2-one[#]	0.016; 0.025	0.038; 0.044	-	-	-	-	-	-	-
2-pentanone[#]	-	0.024; 0.028	0.205; 0.219	-	0.119; 0.134	-	-	0.016; 0.447	0.152; 0.156
3-pentanone[#]	-	0.012; 0.014	0.160; 0.171	-	-	-	-	0.023; 0.620	0.131; 0.135
Poss: 2,3-pentanedione[#]	0.021; 0.033	0.027; 0.031	-	-	-	-	-	-	-

3-penten-2-one[#]	0.007; 0.011	0.011; 0.013	-	-	-	-	-	-	-
Poss: 4-hydroxy-2-pentanone	0.017; 0.026		-	0.036; 0.071	-	-		-	
2-methyl-cyclopentanone[#]	-	0.025; 0.029	-	-	-	-	0.223; 0.248	0.025; 0.695	-
Isomer of 3-methyl-2-cyclopenten-1-one[#]	0.006; 0.009	0.012; 0.015	-	-	-	-	-	-	-
1-hydroxy-3-methyl-2-butanone[#]	0.016;0.024	0.022; 0.026	-	-	-	-	-	-	-
Isomer of 3,4-dimethyl-cyclopentenone[#]	0.010; 0.015	0.026; 0.030	-	-	-	-	-	-	-
Poss: 1-(acetyloxy)-butan-2-one[#]	0.029; 0.044	0.067; 0.078	-	-	-	-	-	-	-
Ethyl-vinyl-cyclopentanone[#]	-	0.024; 0.028	-	-	-	-	-	-	-
Isomer of 3-ethyl-2-hydroxy-cyclopenten-1-one[#]	0.025; 0.038	0.042; 0.050	-	-	-	-	-	-	-
Poss: 2-cyclohexene-1,4-dione[#]	0.011; 0.017	0.021; 0.024	-	-	-	-	-	-	-
Poss: 2,4-dimethyl-1,3-cyclopentanedione[#]	0.015; 0.023	0.024; 0.028	-	-	-	-	-	-	-
3-ethyl-2-cyclopenten-1-one	-	0.036; 0.042	-	-	-	-	-		-
2-methyl-3-pentanone[#]	-	-	0.066; 0.070	-	-	-	-	-	-
3-hexanone[#]	-	-	0.018; 0.019	-	-	-	-	-	-
2-hexanone[#]	-	-	0.042; 0.045	-	-	-	-	-	-
4-methyl-3-hexanone[#]	-	-	0.026; 0.027	-	-	-	-	-	-
Dimethyl-cyclopentanone	-	-	-	0.008; 0.015	-	-	0.040; 0.045	-	-
2-hydroxy-3-pentanone[#]	-	-	0.069; 0.074	0.062; 0.121	-	-	-	-	-
2-methyl-cyclopentanone[#]	-	-	1.147; 1.225	0.140; 0.271	0.670; 0.755	0.051; 0.101	-	-	0.416; 0.429
3-methyl-cyclopentanone[#]	-	-	0.336; 0.359	-	-	-	-	-	0.158; 0.162
2,5-dimethyl-cyclopentanone[#]	-	-	0.043; 0.046	-	0.043; 0.049	-	0.013; 0.015	-	-
3,4-dimethyl-trans-cyclopentanone[#]	-	-	0.080; 0.085	-	-	-	-	-	-
Cyclohexanone[#]	-	-	0.075; 0.080	-	-	-	-	0.023; 0.624	0.243; 0.250
2-ethyl-cyclopentanone[#]	-	-	0.258; 0.276	-	0.106; 0.120	-	0.030; 0.033	-	-
2-methyl-cyclohexanone[#]	-	-	0.096; 0.103	-	-	-	-	-	-

Poss: 3-methyl-cyclohexanone	-	-	-	-	-	-	-	-	0.164; 0.169
2-ethyl-cyclohexanone[#]	-	-	0.032; 0.034	-	-	-	-	-	-
2,3,4-trimethyl-2-cyclopenten-1-one[#]	0.013; 0.020	0.022; 0.025	0.128; 0.137	-	-	-	-	-	-
Trimethyl-2-cyclopenten-1-one[#]	-	-	0.078; 0.083	-	-	-	-	-	-
Poss: dimethyl-cyclopentanone	-	-	-	-	0.124; 0.140	-	0.020; 0.022	-	-
Poss: trimethyl-cyclopentanone	-	-	-	-	0.037; 0.041	-	-	-	-
4-hydroxy-3-hexanone	-	-	-	-	0.088; 0.099	-	-	-	-
4-methyl-cyclohexanone	-	-	-	-	-	-	-	-	0.186; 0.192
Poss: 5-methyl-4-hexen-3-one	-	-	-	-	-	-	0.045; 0.050	-	-
Overlapping ethyl-cyclohexanone	-	-	-	-	-	-	0.027; 0.030	-	-
4-ethyl-cyclohexanone	-	-	-	-	-	-	-	-	0.079; 0.082
Hydrocarbons	-	**-**	**-**	**-**	**0.043; 0.05**	-	-	-	**2.836; 2.92**
n-pentadecane	-	-	-		-	-	-	-	0.031; 0.032
n-heptadecane	-	-	-	-	-	-	-	-	0.104; 0.108
cyclohexane	-	-	-	-	-	-	-	-	0.529; 0.544
Methyl-cyclohexane	-	-	-	-	-	-	-	-	0.608; 0.625
Poss: ethyl-cyclopentane	-	-	-	-	-	-	-	-	0.353; 0.363
1,3-dimethyl-cis-cyclohexane	-	-	-	-	-	-	-	-	0.096; 0.099
1-ethyl-3-methyl-trans-cyclopentane	-	-	-	-	-	-	-	-	0.088; 0.091
Poss: propyl-cyclopentane	-	-	-	-	-	-	-	-	0.270; 0.278
Ethyl-cyclohexane	-	-	-	-	-	-	-	-	0.355; 0.365
1-methyl-2-propyl-cyclopentane	-	-	-	-	-	-	-	-	0.063; 0.065
Propyl-cyclohexane	-	-	-	-	-	-	-	-	0.259; 0.267
Heterocyclic compounds	**2.33; 3.62**	**2.52; 2.94**	**0.70; 0.75**	**1.88; 3.66**	**2.41; 2.73**	**1.85; 3.71**	**2.52; 2.80**	**0.16; 4.44**	**0.34; 0.35**
Furans	**2.162; 3.35**	**2.29; 2.67**	**0.70; 0.75**	**1.761; 3.42**	**2.23; 2.51**	**1.702; 3.41**	**2.269; 2.53**	**0.163; 4.44**	**0.344; 0.35**
2(3H)-furanone[#]	0.083; 0.129	0.078; 0.091	-	-	-	-	-	-	-
2(5H)-furanone[c]	0.351; 0.545	0.406; 0.474	-	-	-	-	-	-	-
2-furaldehyde[c]	0.281; 0.436	0.491; 0.573	-	-	-	-	-	-	-
3-furaldehyde[c]	0.014; 0.022	0.021; 0.025	-	-	-	-	-	-	-

5-methyl-2-furaldehyde[c]	0.042; 0.065	0.081; 0.095	-	-	-	-	-	-	-
5-(hydroxymethyl)-2-furaldehyde[c]	0.441; 0.684	0.484; 0.565	-	-	-	-	-	-	-
1-(2-furanyl)-ethanone[c]	0.025; 0.039	0.041; 0.048	-	-	-	-	-	-	-
3-methyl-(5H)-furan-2-one[c]	0.088; 0.136	0.111; 0.129	-	-	-	-	-	-	-
x,x-dihydro-x-methyl-furan-x-on	0.075; 0.116	-	-	-	-	-	-	-	-
tetrahydro-2-methoxy-furan	0.004; 0.006	-	-	-	-	-	-	-	-
Poss: dihydro-4-hydroxy-2(3H)-furanone[#]	0.018; 0.029	0.013; 0.016	-	-	0.135; 0.152	-	-	-	-
Poss: 5-methyl-2(5H)-furanone[#]	0.043; 0.066	0.059; 0.069	-	-	-	-	-	-	-
3-methyl-furandione-2,5-[#]	0.034; 0.052	0.035; 0.041	-	-	-	-	-	-	-
4-methyl-(5H)-furan-2-one[#]	0.142; 0.219	0.138; 0.161	-	-	-	-	-	-	-
Lactone derivative poss: (S)-(+)-2′,3′-dideoxyribonolactone[#]	0.076; 0.118	0.061; 0.071	-	-	-	-	-	-	-
Isomer of 2,5-dihydro-3,5-dimethyl-2-furanone[#]	0.037; 0.057	0.056; 0.065	-	-	-	-	-	-	-
Lactone derivative = furanone derivative[#]	0.022; 0.035	0.027; 0.032	-	0.30; 0.583	0.019; 0.021	-	0.129; 0.143	-	-
Lactone derivative[#]	0.072; 0.111	0.050; 0.058	-	-	0.150; 0.169	0.274; 0.549	-	-	-
γ-valerolactone	-	-	0.077; 0.083	-	-	-	-	0.022; 0.602	-
γ-butyrolactone[c]	0.135; 0.210	0.137; 0.160	0.475; 0.507	0.360; 0.699	0.450; 0.507	0.339; 0.680	0.416; 0.463	-	-
2-hydroxy- γ-butyrolactone[c]	0.178; 0.277	-	-	0.082; 0.158	-	0.049; 0.099	-	-	-
α-methyl-butyrolactone	-	-	0.036; 0.039	0.078; 0.151	0.129; 0.145	0.088; 0.176	0.142; 0.158	-	-
Tetrahydrofuran	-	-	0.038; 0.041	0.109; 0.211	0.313; 0.353	0.102; 0.205	0.308; 0.343	0.14; 3.838	0.133; 0.137
Tetrahydro-2-methyl-furan	-	-	-	-	-	0.064; 0.128	0.272; 0.303	-	0.088; 0.090
Tetrahydro-2,5-dimethyl-furan	-	-	-	-	-	-	0.071; 0.079	-	0.124; 0.127
Poss: tetrahydro-2-methyl-furan	-	-	-	0.031; 0.060	0.134; 0.151	0.322; 0.646	-	-	-
Tetrahydro-dimethyl-furan	-	-	-	-	0.026; 0.030	-	-	-	-
Unknown furan derivative	-	-	-	-	0.022; 0.025	-	0.050; 0.056	-	-
Poss: tetrahydro-2-methyl-2-furanol	-	-	-	0.391; 0.759	0.361; 0.407	-	0.320; 0.357	-	-

Poss: tetrahydro-2-furanmethanol	-	-	-	0.063; 0.122	0.085; 0.096	0.187; 0.376	0.221; 0.245	-	-
Poss: tetrahydro-derivative furan	-	-	-	-	0.027; 0.030	-	-	-	-
Unknown furanone derivative MW= 112	-	-	-	-	0.013; 0.015	-	-	-	-
Dihydro-5-methyl-2(3H)-furanone	-	-	-	0.053; 0.103	0.099; 0.111	0.079; 0.159	0.146; 0.163	-	-
Dihydro-3,5-dimethyl-2(3H)-furanone	-	-	-	0.021; 0.041	0.049; 0.056	-	0.035; 0.039	-	-
Poss: 5-ethyldihydro-2(3H)-furanone	-	-	-	-	0.218; 0.246	-	-	-	-
Dihydro-4-methyl-2(3H)-furanone	-	-	0.074; 0.079	0.103; 0.199	-	0.096; 0.192	0.141; 0.157	-	-
Tetrahydro-3-furanol	-	-	-	0.027; 0.053	0.018; 0.020	0.025; 0.050	-	-	-
Poss: Isomer of 3,4-furandiol, trans-	-	-	-	0.034; 0.066	-	-	-	-	-
Unknown furanol compound	-	-	-	0.109; 0.212	-	0.077; 0.154	-	-	-
Pyrans	**0.170; 0.26**	**0.230; 0.27**	**-**	**0.124; 0.24**	**-**	**0.147; 0.29**	**0.247; 0.27**	**-**	**-**
Poss: tetrahydro-2-[(tetrahydro-2-furanyl)methoxy]-2H-Pyran	-	-	-	0.089; 0.173	0.138; 0.156	0.147; 0.294	0.247; 0.27	-	-
Poss: tetrahydro-2H-pyran-2-methanol	-	-	-	0.035; 0.068	-	-	-	-	-
C5H8O2: poss. Tetrahydro-2H-pyran-2-one or dihydro-4-methyl-2(3H)-furanone	-	-	-	-	0.041; 0.046	-	-	-	-
2H-pyran-2-one[#]	-	0.023; 0.027	-	-	-	-	-	-	-
Maltol (3-hydroxy-2-methyl-4H-pyran-4-one)[c]	0.108; 0.168	0.146; 0.171	-	-	-	-	-	-	-
3-hydroxy-5,6-dihydro-(4H)-pyran-4-one[#]	0.062; 0.096	0.060; 0.070	-	-	-	-	-	-	-
Aromatic Compounds	**2.67; 4.14**	**7.07; 8.25**	**4.47; 4.77**	**1.54; 2.98**	**7.27; 8.2**	**0.93; 1.87**	**6.25; 6.95**	**0.00; 0.09**	**1.94; 1.99**
Benzenes	**0.006; 0.01**	**0.101; 0.12**	**0.075; 0.08**	**-**	**0.057; 0.06**	**-**	**0.099; 0.11**	**0.003; 0.09**	**0.599; 0.62**
toluene[c]	-	0.016; 0.019	-	-	0.024; 0.027	-	0.032; 0.036	-	0.077; 0.079
ethylbenzene[c]	-	-	-	-	-	-	0.022; 0.024	-	
Propyl-benzene	-	-	-	-	-	-	-	-	0.059; 0.060
1-methyl-naphtalene	-	-	-	-	-	-	-	-	0.177; 0.182

3,4-dimethoxy-toluene[c]	-	-	0.016; 0.017	-	-	-	-	-	-
2,3-dimethoxy-toluene[c]	-	0.018; 0.021	-	-	-	-	-	-	-
1-meythoxy-4-methyl-benzene[#]	-	0.023; 0.027	-	-	-	-	-	-	-
2,3-dihydro-1H-inden-1-one[c]	0.006; 0.009	0.014; 0.016	-	-	-	-	-	-	-
1-methoxy-2,3-dimethyl-benzene[#]	-	0.010; 0.012	-	-	-	-	-	-	-
Poss: dimethoxy-propyl-benzene	-	0.020; 0.023	-	-	-	-	0.027; 0.031	-	-
Benzene[#]	-	-	0.020; 0.021	-	-	-	-	0.003; 0.092	0.083; 0.085
1,2-dimethoxy-4-propyl-benzene[#]	-	-	0.015; 0.016	-	-	-	-	-	-
C18H22:Biphenyl, diisopropyl-[#]	-	-	0.023; 0.025	-	-	-	0.017; 0.019	-	-
C9H10: 2-propenyl-benzene or 2,3-dihydro-1H-indene[#]	-	-	-	-	0.033; 0.038	-	-	-	-
Octahydro-cis-1H-Indene	-	-	-	-	-	-	-	-	0.091; 0.094
1,2,3,4-tetrahydro-naphtalene	-	-	-	-	-	-	-	-	0.053; 0.054
1,2,3,4-tetrahydro-6-methyl-naphtalene	-	-	-	-	-	-	-	-	0.059; 0.061
Catechols	**n.q.**	**n.q.**	**-**	**n.q.**	**n.q.**	**n.q.**	**-**	**-**	**-**
catechol	Available n.q.	Available n.q.	-	-	-	-	-	-	-
3-methyl-catechol	-	Available n.q.	-	Available n.q.	-	-	-	-	-
hydroquinone	Available n.q.	Available n.q.	-	-	-	-	-	-	-
Methyl-benzenediol	Available n.q.	Available n.q.	-	-	n.q.	-	-	-	-
Aromatic Alcohols	-	-	-	**0.055; 0.11**	-	-	-	-	-
Poss: O-hexanoyl-1,2-benzendiol	-	-	-	0.055; 0.106	-	-	-	-	-
Aromatic Aldehydes	**0.022; 0.03**	**0.044; 0.05**	-	-	-	-	-	-	-
Benzaldehyde[c]	0.003; 0.005	0.013; 0.015	-	-	-	-	-	-	-
3-hydroxy-benzaldehyde[#]	0.019; 0.029	0.031; 0.036	-	-	-	-	-	-	-
Aromatic Ketones	**0.003; 0.005**	**0.008; 0.009**	**-**	-	-	-	-	-	-
acetophenone[c]	0.003; 0.005	0.008; 0.009	-	-	-	-	-	-	-
Aromatic Esters	-	**-**	**-**	0.050; 0.10	-	-	0.083; 0.09	-	-

Poss: homovanillic acid methyl ester	-	-	-	0.050; 0.096	-	-	0.083; 0.092	-	-
Lignin Derived Phenols	**0.269; 0.42**	**0.844; 0.98**	**0.856; 0.91**	**0.056; 0.11**	**0.70; 0.79**	**0.035; 0.07**	**0.707; 0.79**	**-**	**0.679; 0.70**
Phenol[c]	0.064; 0.099	0.114; 0.132	0.158; 0.168	0.025; 0.048	0.101; 0.114	-	0.020; 0.022	-	-
o-cresol[c]	0.040; 0.061	0.099; 0.115	0.076; 0.081	-	-	-	0.103; 0.114	-	-
p-cresol[c]	0.038; 0.059	0.097; 0.113	0.097; 0.104	0.017; 0.033	0.086; 0.097	0.017; 0.034	0.074; 0.083	-	0.077; 0.079
m-cresol[c]	0.026; 0.041	0.063; 0.073	0.076; 0.082	0.014; 0.026	0.060; 0.067	0.018; 0.036	0.070; 0.078	-	0.080; 0.083
2,5-dimethyl-phenol[c]	0.024; 0.038	0.040; 0.046	0.171; 0.182	-	-	-	-	-	0.141; 0.145
2,4-dimethyl-phenol[c]	0.016; 0.025	0.058; 0.068	-	-	0.089; 0.10	-	0.089; 0.099	-	-
2,6-dimethyl-phenol[c]	-	0.016; 0.019	-	-	-	-	-	-	-
2,3-dimethyl-phenol[c]	-	0.013; 0.015	-	-	-	-	-	-	-
3,5-dimethyl-phenol[c]	-	0.009; 0.010	-	-	-	-	-	-	-
3-ethyl-phenol[c]	-	0.033; 0.039	-	-	0.102; 0.115	-	0.109; 0.121	-	-
4-ethyl-phenol[c]	-	0.023; 0.027	0.031; 0.033	-	0.025; 0.029	-	0.026; 0.029	-	-
4-propyl-phenol[c]	-	0.041; 0.048	0.220; 0.235	-	0.181; 0.204	-	0.176; 0.196	-	0.317; 0.326
4-propenyl-trans-phenol[#]	-	0.023; 0.027	-	-	-	-	-	-	-
4-hydroxy-benzaldehyde[c]	0.009; 0.014	0.016; 0.019	-	-	-	-	-	-	-
Ethyl-methyl-phenol[#]	-	0.025; 0.030	-	-	0.031; 0.034	-	-	-	-
Poss: methoxy-trimethyl-phenol[#]	-	0.014; 0.017	-	-	-	-	-	-	-
Poss: allyl- or propenyl-phenol[#]	0.005; 0.007	0.022; 0.025	-	-	-	-	-	-	-
Phenolic dimere[#]	0.024; 0.037	0.041; 0.048	-	-	-	-	-	-	-
Unknown phenolic dimere compound[#]	0.023; 0.035	0.097; 0.113	-	-	-	-	-	-	-
Poss: x-methyl-x-propyl-phenol[#]	-	-	0.027; 0.029	-	0.026; 0.029	-	0.039; 0.044	-	-
C4-phenol	-	-	-	-	-	-	-	-	0.064; 0.066
Guaiacols (methoxy phenols)	**2.272; 3.52**	**5.788; 6.75**	**3.54; 3.78**	**1.375; 2.67**	**5.528; 6.23**	**0.898; 1.80**	**5.209; 5.80**	**-**	**0.660; 0.68**
Guaiacol[c]	0.330; 0.511	0.669; 0.780	0.797; 0.851	0.169; 0.328	0.648; 0.731	0.140; 0.282	0.704; 0.783	-	-
3-methyl-guaiacol[#]	0.014; 0.022	0.035; 0.040	-		0.049; 0.055	-	0.047; 0.052	-	-
4-methyl-guaiacol[c]	0.306; 0.475	0.842; 0.983	0.884; 0.944	0.169; 0.329	1.112; 1.253	0.137; 0.276	1.137; 1.266	-	0.178; 0.183
4-ethyl-guaiacol[c]	0.086; 0.134	0.299; 0.348	0.470; 0.502	0.052; 0.102	0.486; 0.548	0.065; 0.129	0.686; 0.764	-	0.174; 0.179
4-vinyl-guaiacol[#]	0.038; 0.059	0.107; 0.125	-	-	-	-	-	-	0.309; 0.318

4-propyl-guaiacol[c]	0.028; 0.044	0.140; 0.136	0.954; 1.019	0.071; 0.138	1.103; 1.243	0.069; 0.139	1.182; 1.316	-	-
eugenol[c]	0.080; 0.124	0.314; 0.366	-	-	-	-	-	-	-
Isoeugenol (4-propenyl-cis-guaiacol) [c]	0.110; 0.170	0.457; 0.533	-	-	-	-	-	-	-
Isoeugenol (4-propenyl-trans-guaiacol) [c]	-	0.594; 0.693	-	-	-	-	-	-	-
vanillin[c]	0.278; 0.431	0.461; 0.538	-	-	-	-	-	-	-
homovanillin[c]	0.049; 0.076	0.058; 0.068	-	-	-	-	-	-	-
Dihydroconiferyl alcohol[#]	0.187; 0.289	0.299; 0.349	-	0.492; 0.954	1.071; 1.207	0.413; 0.829	1.058; 1.178	-	-
Coniferyl alcohol (trans)[c]	0.116; 0.179	0.180; 0.210	-	-	-	-	-	-	-
Isomer of coniferyl alcohol[#]	0.130; 0.202	0.239; 0.279	-	-	-	0.038; 0.077	-	-	-
Acetoguajacone[#]	0.196; 0.304	0.344; 0.401	-	0.391; 0.758	0.485; 0.546	-	-	-	-
Propioguaiacone[#]	0.054; 0.084	0.068; 0.080	-	-	0.075; 0.085	-	-	-	-
coniferylaldehyde[c]	0.150; 0.233	0.353; 0.412	-	-	-	-	-	-	-
Guaiacol dimere[#]	0.004; 0.007	0.012; 0.014	-	-	-	-	-	-	-
Guaiacol dimere[#]	-	0.051; 0.059	-	-	-	-	-	-	-
Poss: Isomer of Propioguaiacone[#]	-	0.020; 0.023	-	-	-	-	-	-	-
Unknown guaiacol compound MW= 224[#]	0.013; 0.021	0.034; 0.040	-	-	0.088; 0.099	-	0.076; 0.085	-	-
Poss: dimere of guaiacyl compound MW= 274[#]	0.012; 0.018	0.036; 0.042	-	-	0.151; 0.170	-	0.156; 0.174	-	-
Guaiacyl acetone[c]	0.079; 0.122	0.131; 0.153	0.108; 0.116	-	0.070; 0.079	-	-	-	-
Poss:3-ethyl-guaiacol[#]	0.011; 0.018	0.046; 0.054	0.051; 0.055	-	0.043; 0.049	-	0.040; 0.045	-	-
Isomer of guaiacylacetone	-	-	-	-	0.046; 0.052	-	0.022; 0.024	-	-
Isomer of dihydroconiferyl alcohol	-	-	-	0.031; 0.059	0.063; 0.071	-	0.075; 0.083	-	-
Homovanillyl alcohol	-	-	-	-	0.038; 0.042	0.035; 0.071	0.025; 0.028	-	-
Syringols (dimethoxy phenols)	**0.099; 0.15**	**0.288; 0.34**	**-**	**-**	**0.988; 1.11**	**-**	**0.149; 0.17**	**-**	**-**
syringol	0.033; 0.052	0.066; 0.077	-	-	0.027; 0.030	-	-	-	-
4-methyl-syringol[c]	0.021; 0.033	0.043; 0.050	-	-	0.040; 0.045	-	0.049; 0.055	-	-
4-ethyl-syringol[c]	-	0.023; 0.027	-	-	0.020; 0.023	-	0.030; 0.034	-	-

4-allyl-syringol[c]	0.016; 0.025	0.032; 0.037	-	-	-	-	-	-	-
4-propyl-syringol[c]	-	0.016; 0.019	-	-	0.071; 0.080	-	0.069; 0.077	-	-
4-(1-propenyl)-cis-syringol[#]	-	0.023; 0.027	-	-	-	-	-	-	-
4-(1-propenyl)-trans-syringol[#]	-	0.040; 0.046	-	-	-	-	-	-	-
syringaldehyde[c]	0.028; 0.044	0.046; 0.054	-	-	-	-	-	-	-
Dihydrosinapyl alcohol	-	-	-	-	0.830; 0.936	-	-	-	-
Carbohydrates	**9.09; 14.09**	**3.72; 4.34**	**-**	**1.31; 2.54**	**-**	**0.19; 0.39**	**-**	**-**	**-**
Sugars	**9.088; 14.09**	**3.721; 4.34**	**-**	**1.311; 2.54**	**-**	**0.193; 0.39**	**-**	**-**	**-**
Levoglucosan[c]	5.591; 8.669	2.23; 2.60	-	-	-	-	-	-	-
1,6-anhydro-ß-D-glucofuranose,	0.064; 0.099	-		-	-	-		-	
1,6-anhydro-β-D-mannopyranose[c]	1.089; 1.689	0.311; 0.363	-	-	-	-	-	-	-
1,6-anhydro-ß-D-galactopyranose, (Levogalactosan)	0.173; 0.269	-		-	-	-	-	-	-
1,4:3,6-dianhydro-α-D-glucopyranose[#]	0.315; 0.488	0.160; 0.187	-	-	-	-	-	-	-
Anhydrosugar unknown[#]	0.614; 0.952	0.352; 0.410	-	0.236; 0.458	-	0.045; 0.089	-	-	-
Anhydrosugar unknown[#]	-	-		0.084; 0.162		0.092; 0.185	-	-	-
Poss; 1,4:3,6-dianhydro-D-glucitol	-	-	-	0.099; 0.193		0.057; 0.114	-	-	-
Poss: 2,3-anhydro-d-galactosan[#]	0.158; 0.245	0.093; 0.109	-	-	-	-	-	-	-
Poss: 2,3-anhydro-4-mannosan[#]	0.250; 0.388	0.162; 0.188	-	-	-	-	-	-	-
Unknown sugar derived compound[#]	0.046; 0.071	0.068; 0.079	-	0.101; 0.196	-	-	-	-	-
Unknown sugar derived compound[#]	0.049; 0.075	0.076; 0.089	-	0.132; 0.256	-	-	-	-	-
Anhydrosugar unknown[#]	0.469; 0.727	0.123; 0.143	-	0.659; 1.279	-	-	-	-	-
Anhydrosugar unknown[#]	0.073; 0.113	0.089; 0.104	-	-	-	-	-	-	-
Anhydrosugar unknown[#]	-	0.057; 0.067	-	-	-	-	-	-	-
Unknown sugar derived compound[#]	0.113; 0.176	-	-	-	-	-	-	-	-
-Other organic compounds	**0.71; 1.09**	**0.65; 0.76**	**0.07; 0.07**	**0.65; 1.26**	**0.45; 0.51**	**0.56; 1.11**	**0.20; 0.22**	**0.01; 0.16**	**0.20; 0.21**
N-compounds	**0.025; 0.04**	**0.016; 0.02**	-	**0.086; 0.17**	-	**0.115; 0.23**	-	-	-
Aliphatic Amide compound	-	-	-	0.086; 0.167	-	0.115; 0.23	-	-	-
Pyridine	0.025; 0.039	0.016; 0.019	-	-	-	-	-	-	-

Acetates	**0.041; 0.06**	**0.016; 0.016**	**-**	**0.006; 0.01**	**0.019; 0.02**	**-**	**0.030; 0.03**	**-**	**-**
Poss: 1,2,3-propanetriol, monoacetate	0.041; 0.064	0.016; 0.019	-	-	0.019; 0.021	-	-	-	-
Tetrahydro-2-furanmethanol-acetate	-	-	-	0.006; 0.012	-	-	0.021; 0.023	-	
Cyclopentanol acetate	-	-	-	-	-	-	0.009; 0.010	-	-
Terpenes	-	**0.014; 0.02**	**0.04; 0.04**	-	**0.054; 0.06**	-	-	-	-
Dehydroabietic acid methyl ester	-	-	-	-	0.018; 0.021	-	-	-	-
7-oxodehydroabietic acid, methyl ester	-	-	-	-	0.036; 0.040	-	-	-	-
Poss: diterpene	-	0.014; 0.017	-	-	-	-	-	-	-
Dehydroabietic acid methyl ester	-	-	0.040; 0.043	-	-	-	-	-	0.143; 0.148
18-norabieta-8,11,13-triene	-	-	-	-	-	-	-	-	0.033; 0.034
Unknown compounds	**0.527; 0.82**	**0.494; 0.58**	**-**	**0.247; 0.48**	**0.223; 0.25**	**0.247; 0.50**	**0.105; 0.12**	**-**	**-**
Miscellaneous	**0.112; 0.17**	**0.108; 0.13**	**0.026; 0.030**	**0.312; 0.61**	**0.158; 0.18**	**0.194; 0.39**	-	**0.006; 0.016**	**0.028; 0.03**
Poss: 1,2-epoxy-3-propoxy-propane	-	-	-	0.072; 0.139	0.046; 0.052	-	-	-	-
Poss: acetaldehyde, diisobutylacetal	-	-	-	0.098; 0.189	0.036; 0.040	0.168; 0.337	0.042; 0.047	-	-
Poss: Isomer of acetaldehyde, diisobutyl acetal	-	-	-	0.108; 0.209	0.050; 0.057	-	-	-	-
2,2'-Bi-1,3-dioxolane	0.078; 0.120	0.040; 0.047	-	-	-	-	-	-	-
Poss: 1,4-dioxin, 2,3-dihydro-	0.008; 0.012	0.011; 0.013	-	-	-	-	-	-	-
2-methyl-1,3-dioxolane	0.010; 0.015	0.021; 0.024	-	-	-	-	-	-	-
Silanol, trimethyl-, formate	0.008; 0.012	-	-	-	-	-	-	-	-
1-phenyl-naphtalene (impurity in IS= fluoranthene)	0.010; 0.016	0.036; 0.042	0.026; 0.028	0.025; 0.049	0.025; 0.029	0.026; 0.052	0.024; 0.027	0.006; 0.164	0.028; 0.029
Unknown acid anhydrife or furan acid ester	-	-	-	0.010; 0.019	-	-	-	-	-
Area of identified peaks (%)	**98.1**	**93.9**	**69.8**	**91.2**	**78.8**	**88.0**	**76.0**	**72.2**	**49.4**
Area of unknown peaks (%)	**1.9**	**6.1**	**30.2**	**8.8**	**21.2**	**12.0**	**24.0**	**27.8**	**50.6**
TOTAL (wt.%)	**34.61; 53.66**	**28.14; 32.83**	**18.93; 20.21**	**34.08; 66.12**	**25.14; 28.33**	**24.25; 48.66**	**22.12; 24.62**	**3.14; 85.68**	**7.61; 7.84**

Possi= possible compound; c= calibrated; n.q.= not quantified; #=estimated response factor; IS= internal standard; MW= molecular weight.

7. Hydrogen consumption determination, amount of gas generated, mass balance and degree of deoxygenation

The hydrogen consumption was approximated by the ideal gas equation, considering the volume of the gas constant and yielding moles of hydrogen before and after the reaction (equation S.2).

$$H_{2\ consumed} = \frac{n_{H_2 i} - n_{H_2 f}}{m_{bio-oil}} \text{ (equation S.1)}$$

$$n_{H_{2i,f}} = \frac{y_{H_{2i,f}} \times p_{i,f} \times V_{cte}}{R \times T_{i,f}} \text{ (equation S.2)}$$

n_{H2i} is the initial number of mols of H_2; n_{H2f} is the number of mols of H_2 after reaction; m is the amount of fast pyrolysis bio-oil transferred to the autoclave (kg). The number of mols of H_2 used in equation S.1 is obtained by the equation S.2, where $n_{H2i,f}$ is the initial or final number of H_2 mols before or after reaction; $y_{H2i,f}$ is the initial or final H_2 fraction in the gas composition; $p_{i,f}$ is the pressure recorded before and after the upgraded reaction (atm); V_{cte} is the gas volume in the autoclave in L (considered constant); R is the ideal gas constant (0.082 L.atm.K^{-1}.mol^{-1}) and $T_{i,f}$ are the temperatures in Kelvin at which the pressure was registered before and after the upgrading reactions. The amount of gas generated and later used for mass balance calculation was obtained by equation S.3, considering the gas composition obtained by gas-chromatography (see section 3.3.2).

$$gas\ (g) = \sum x_j \times MW_j \times n_{t,f} \text{ (equation S.3)}$$

x_j is the mole fraction of gaseous compound j; MW_i is the molar mass of compound j (g.mol^{-1}) and $n_{t,f}$ is the total number of mols in the gas phase after the upgrading reaction. The remaining liquid mixture in the autoclave is composed by upgraded aqueous phase (UAP), upgraded oil (UOP), solid and spent catalyst. It was collected, weighted (in order to determine the recovery used in equation 4), and centrifuged (Thermo Fisher Heraeus Biofuge Stratos at 7000 rpm and 40 min). The liquid products obtained after centrifugation were separated and weighted for mass balance. The weight of UAP (g) was determined by weighting this phase, whereas the weight of UOP obtained was determined indirectly as follow:

$$UO(g) = LR - (UAP + cat + solids) \text{ (equation S.4)}$$

LR is the total liquid and solids mixture recovered (g) after the upgrading reaction, composed by UAP, UOP, solids and spent catalyst; UAP is the weight of upgraded light phase (g), obtained after centrifugation and separation; cat (g) is the amount of catalyst loaded to the reactor; and solids (g) is the amount of solids formed during the upgrading reaction (see equation S.5). Additionally both liquid phases and spent catalyst were further characterized and more details are given in section 3.3.2.

The solid residue collected in the reactor (residual amount) and the solid sample obtained after centrifugation (containing residues of UOP) were mixed, washed with acetone and vacuum-filtrated (quantitative ashless filter paper Whatman, 589/3 blue ribbon). The amount of solid is given by equation S.5.

$m_{solid}(g) = \frac{m_{cat} \times [C_{spcat}]}{100 - [C_{spcat}]}$ (equation S.5)

Where the m_{solid} is the mass of solid (g) in the spent catalyst; m_{cat} is the amount of catalyst (g) loaded to the reactor; [C_{spcat}] is the carbon concentration obtained by elemental analysis in the spent catalyst or by the difference in weight before and after reaction. The initial concentration of carbon in the fresh catalyst, if necessary, is discounted for solids calculation. The calculation for Ru/C considered the weight of catalyst added to the autoclave and the final weight recovered after the reaction. The difference is referred as the amount of solid deposited over the catalyst.

The degree of deoxygenation was obtained as follow:

$DOD = \left(1 - \frac{[O_{UO}]}{[O_{feed}]}\right) \times 100$ (equation S.6)

DOD is the degree of deoxygenation (% g/g); [O_{UOP}] is the concentration of oxygen in the upgraded oil (wt.%) and [O_{feed}] is the concentration of oxygen in the feed (wt.%). The pH value was determined using a pH-meter 691 and the water content by Karl Fischer Tritando 841. The calorific value was determined by calorimeter IKA C5000. Sulfur and metal content (leached after the reactions), were obtained by inductively coupled plasma optical emission spectrometer Agilent, 725. For this measurement the upgraded aqueous phase samples were filtrated using a 0.2 μm polytetrafluoroethylene filter.

Reference

1. Carriel Schmitt, C.; Gagliardi Reolon, M.; Zimmermann, M.; Raffelt, K.; Grunwaldt, J.-D.; Dahmen, N. Synthesis and Regeneration of Nickel-Based Catalysts for Hydrodeoxygenation of Beech Wood Fast Pyrolysis Bio-Oil. *Catalysts* **2018**, *8*, 449, doi:10.3390/catal8100449.