Electronic Supplementary Information

Solvent Consumption in Non-Catalytic Alcohol Solvolysis of Biorefinery Lignin

J. B. Nielsen, A. Jensen, C. B. Schandel, C. Felby and A. D. Jensen

S. 1. Lignin rich feedstock composition

The lignin rich solid residual was obtained from enzymatic hydrolysed wheat straw that had been pretreated at 190°C for 10 min. The compositional analysis shown below was conducted using the NREL protocol[1].

Table S. 1 Compositional data of lignin rich residual

	Glucan	Xylan	Mannan	Arabinan	Galactan	Acid insoluble lignin	Ash	Total
Wt%	12.43	3.04	3.05	1.39	1.55	65.39	14.65	101.51
SD	0.28	0.14	0.083	0.045	0.050	0.53	0.066	

S. 2. Elemental Analysis Data (O/C and H/C)

Elemental analysis of the oil and residual solid fraction was conducted as described in the main text. Full elemental analysis data represented as the molar O/C and H/C for oils and solids as a function of reaction temperature is shown in Fig. S. 1.

A comparison between the effects of the different alcohols solvents shows that the obtained oil product and residual solids have similar molar O/C. This highlights similar effects of the solvent on the lignin depolymerisation. The molar O/C of the oil is reduced to a minimum of around 0.15 to 0.20 at 350˚C to 400˚C. The molar O/C of the residual solid fraction drops almost linearly as a function of reaction temperature with similar values as the oil product at 300˚C and 350˚C but at 400˚C the O/C achieves values of 0.1 or lower which is lower than for the oil product.

Despite similarities in molar O/C for oils and solids the molar H/C of the solids is much lower and for all temperatures less than 1.0. The molar H/C for the solids drops as the reaction temperature is increased which shows increased aromaticity and possibly due to presence of poly aromatic hydrocarbons (PAH). The molar H/C of the oils is nearly unchanged as a function of reaction temperature with values between 1.4 and 1.7. It is clearly seen that the molar H/C of the oil product at all reaction temperatures is increased as the chain length of the alcohol solvent used is increased. This may be due to the alcohol solvent alkylating the depolymerised lignin as described in the main text.

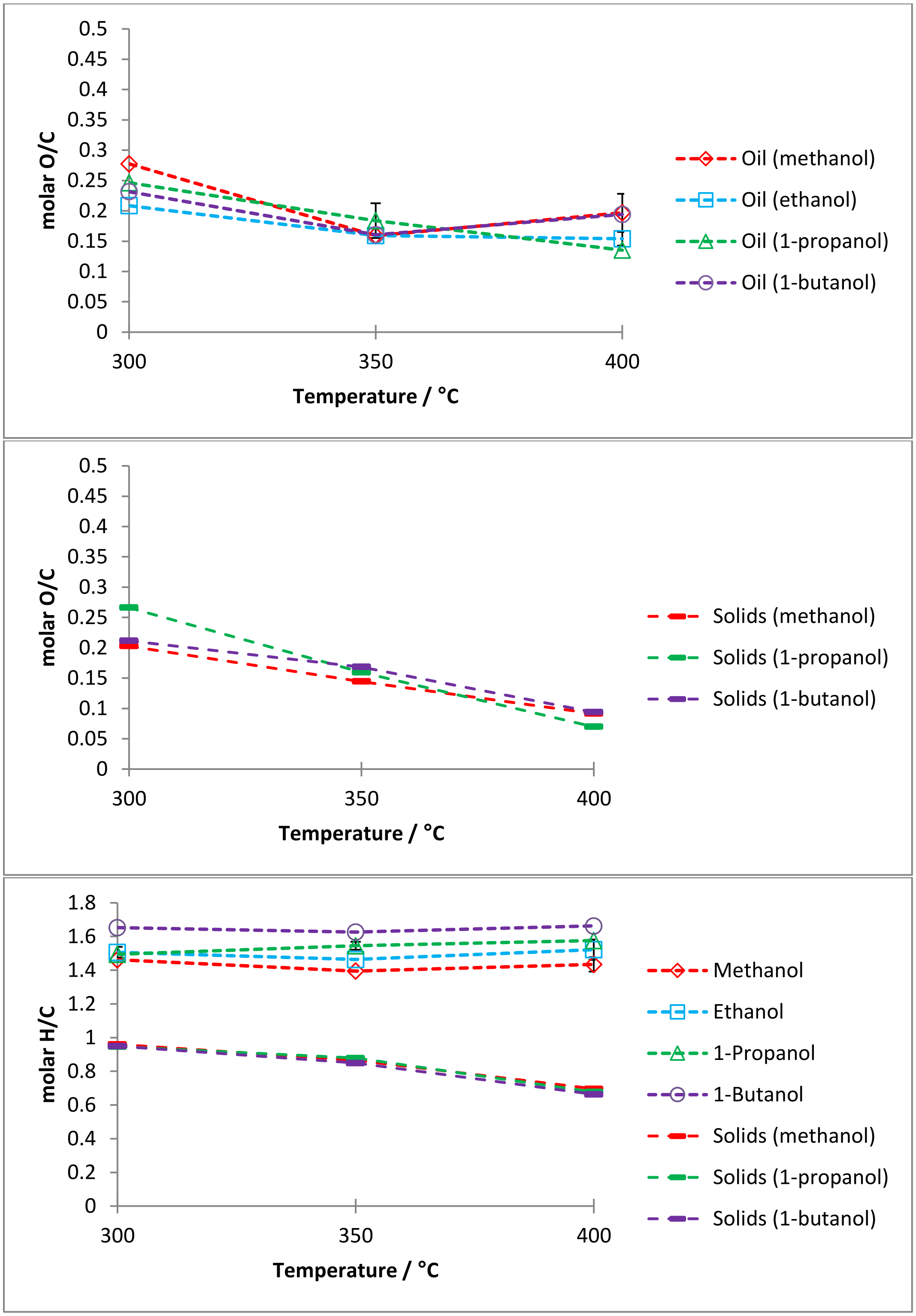


Fig. S. 1 molar O/C and H/C of isolated oil and dried solids shown as a function of reaction temperature and different alcohol solvent. The lignin feedstock has a molar H/C of 1.2 and molar O/C of 0.5. Top: molar O/C of oils; middle: molar O/C of solids; bottom: molar H/C of oils and solids. Reaction conditions: 10 g lignin in 100 ml alcohol was treated for 4 h.

S. 3. Full Solvent Consumption Data

Solvent consumption was determined as described in the main text. Yield of water was determined by Karl Fischer titration as described in the main text. Yield of light organics (other than the solvent alcohol) was determined by GC-FID as described in the main text. Full solvent consumption data obtained is shown in Fig. S. 2.

When the reaction temperature is increased the solvent consumption increases for all solvents used.

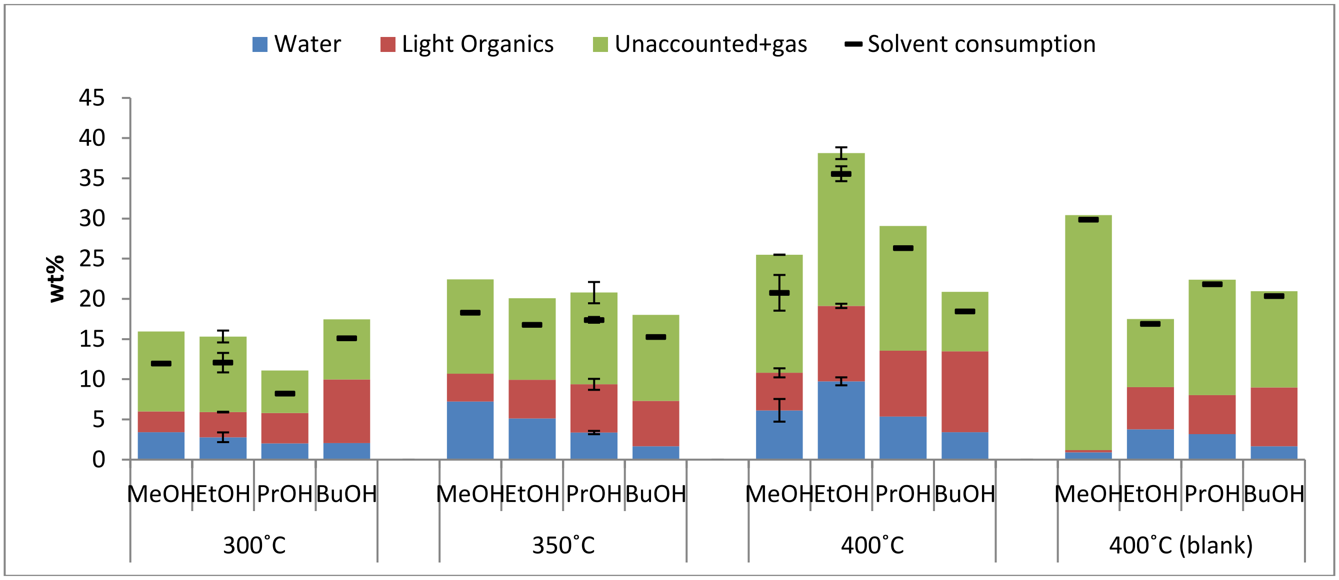


Fig. S. 2 solvent consumption and yields of water, light organics other than the solvent and unaccounted mass (gas) both in the presence of 10 g lignin and without for a 4 h reaction at different reaction temperatures using 100 ml alcohol solvent. Data is represented per mass of solvent added.

S. 4. Full GC-MS Data

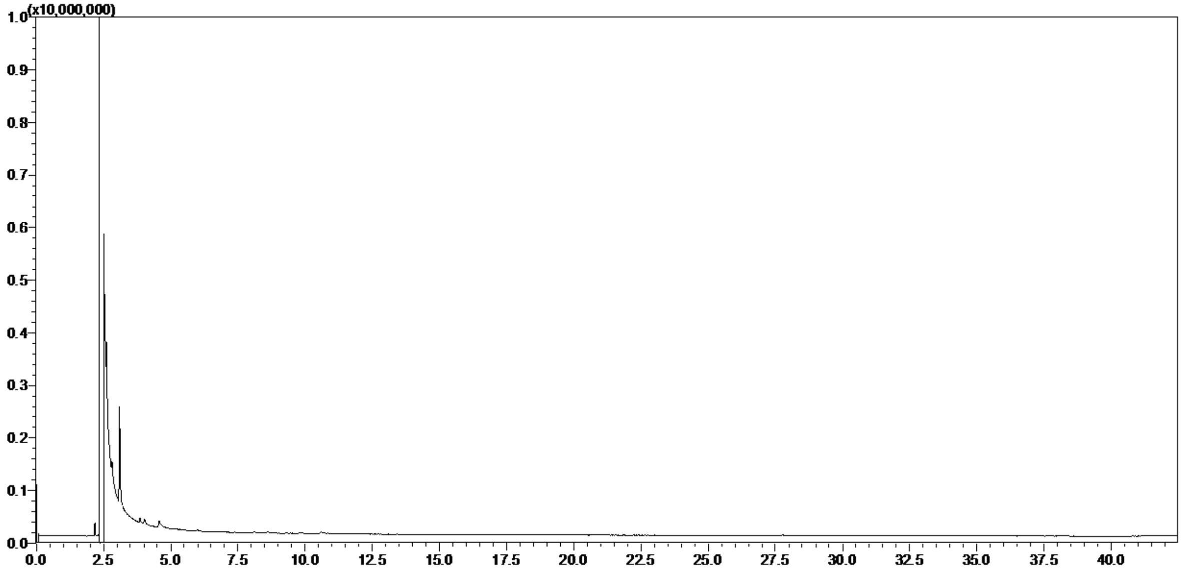
GC-MS was conducted on the light solvent fractions after reaction as described in the main text. GC-MS chromatograms obtained at all temperatures using the four different solvents are shown in Fig. S. 3 (methanol), Fig. S. 4 (ethanol), Fig. S. 5 (1-propanol) and Fig. S. 6 (1-butanol) and identified species are listed in Table S. 2 (methanol), Table S. 3 (ethanol), Table S. 4 (1-propanol) and Table S. 5 (1-butanol).

The GC-MS chromatograms for solvent phase products using the four different alcohols show that species formed at 300°C are equally formed at higher temperatures but as the temperature was increased more species are seen. The species formed in the solvent blanks resemble the ones formed with lignin present during solvolysis.

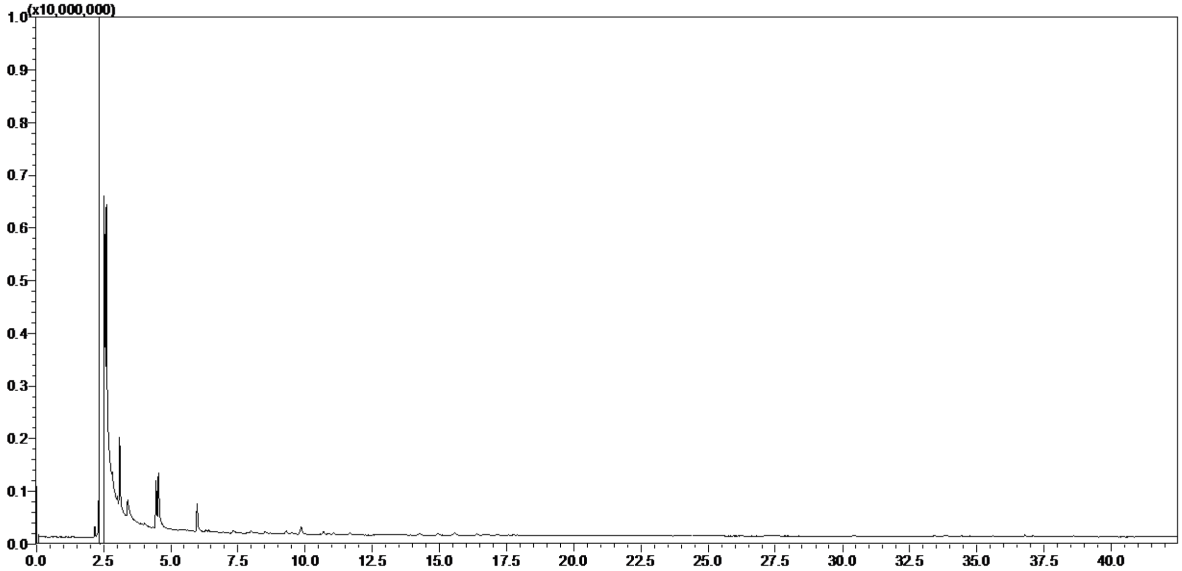
Methanol:

Fig. S. 3 GC-MS chromatograms of the light solvent fraction after reaction. Reaction conditions: 10 g lignin, 100 ml methanol and 4 h reaction at different reaction temperatures.

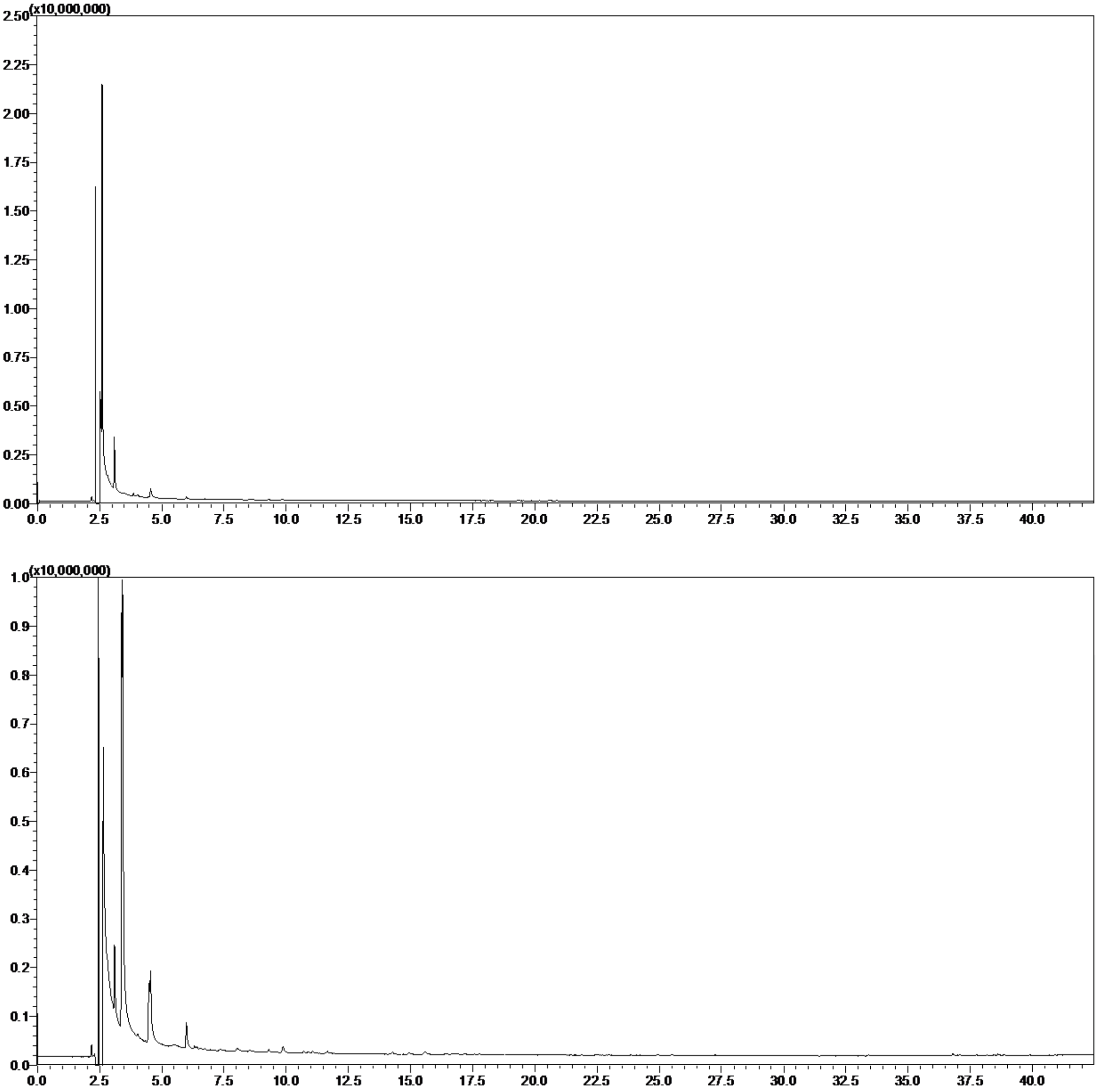
300˚C:



350˚C:



400˚C:


(x10,000,000)
2.50
2.25
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
40.0
(x10,000,000)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
40.0

400˚C (solvent blank):

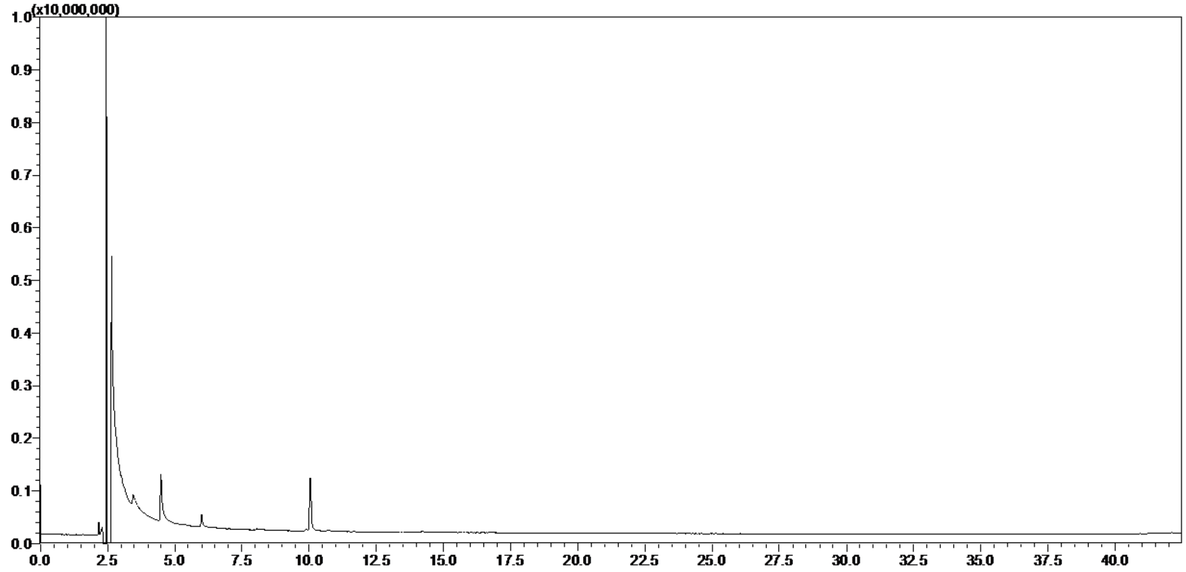
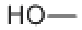
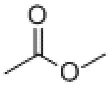
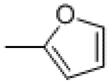
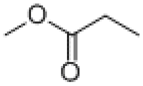
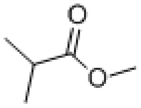
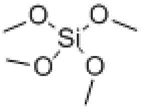


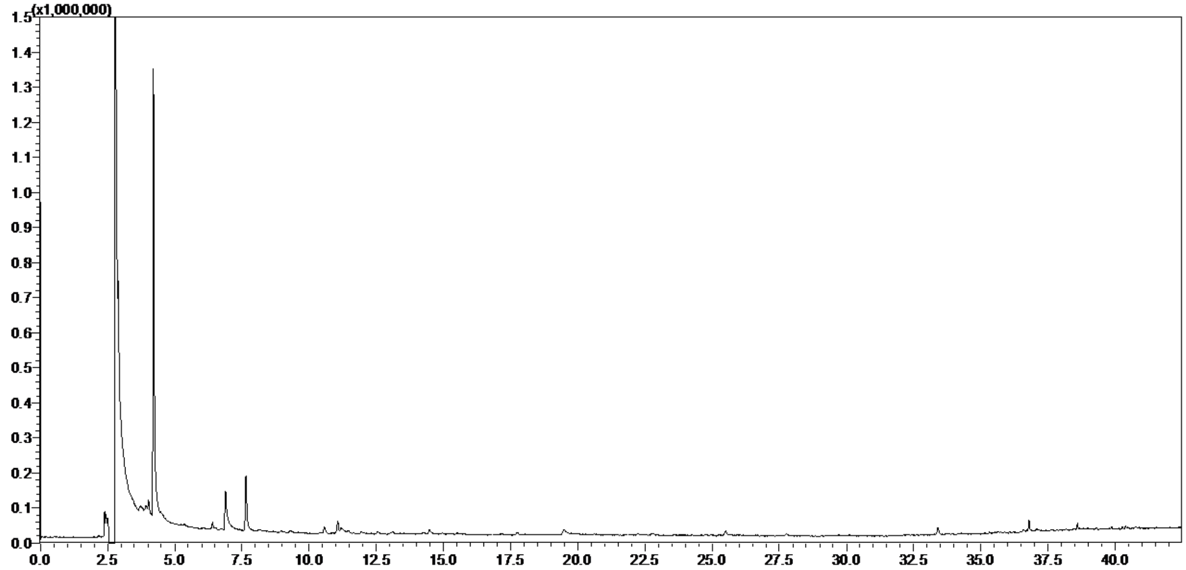
Table S. 2 Identified peaks from the GC-MS chromatograms. Species were identified automatically using the software GCMSsolution Version 2.70 and NIST library search. Identified species are marked with an x at the given reaction temperature. Reaction conditions: 10 g lignin treated for 4 h in 100 ml methanol.

Time [min]	Similarity index	Name	Drawing	Temperature			
				300°C	350°C	400°C	400°C (blind)
2.393	96	methanol		x	x	x	x
2.607	92	ethanol		x	x	x	x
2.813	96	acetone		x	x	x	x
3.093	95	methyl acetate		x	x	x	x
3.400	96	1-propanol			x	x	x
3.863	92	1,1-dimethoxyethane		x	x	x	
4.027	94	2-methylfurane		x	x	x	
4.450	94	2-methylpropan-1-ol			x	x	
4.570	95	methyl propanoate		x	x	x	x
5.900	97	methyl-2-methyl propanate			x	x	x
10.043	95	tetramethyl orthosilicate					x

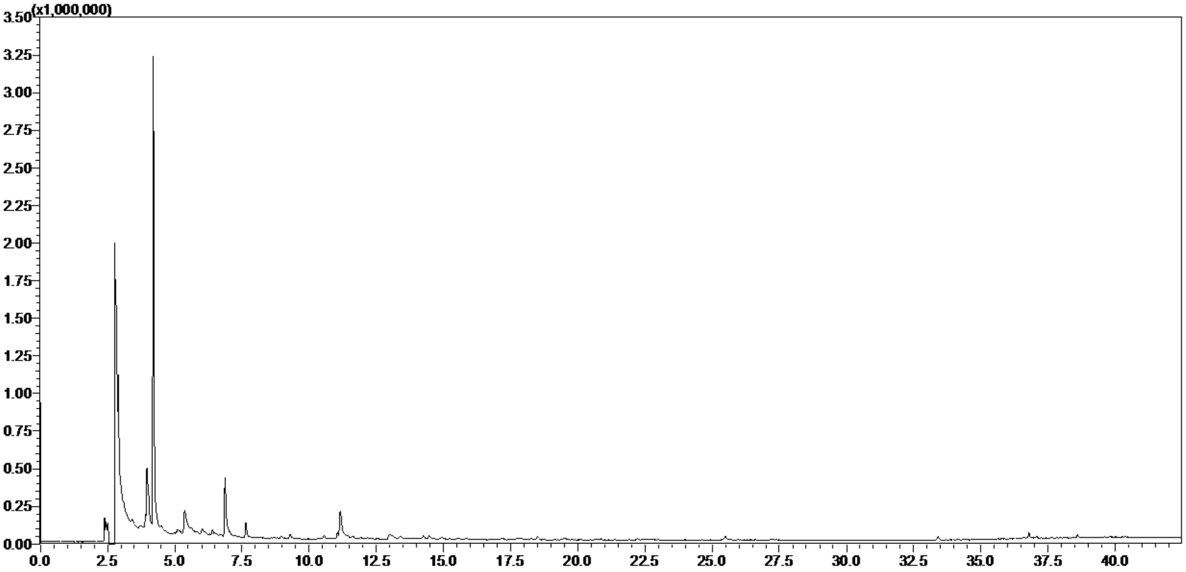
Ethanol:

Fig. S. 4 GC-MS chromatograms of the light solvent fraction after reaction. Reaction conditions: 10 g lignin, 100 ml ethanol and 4 h reaction at different reaction temperatures.

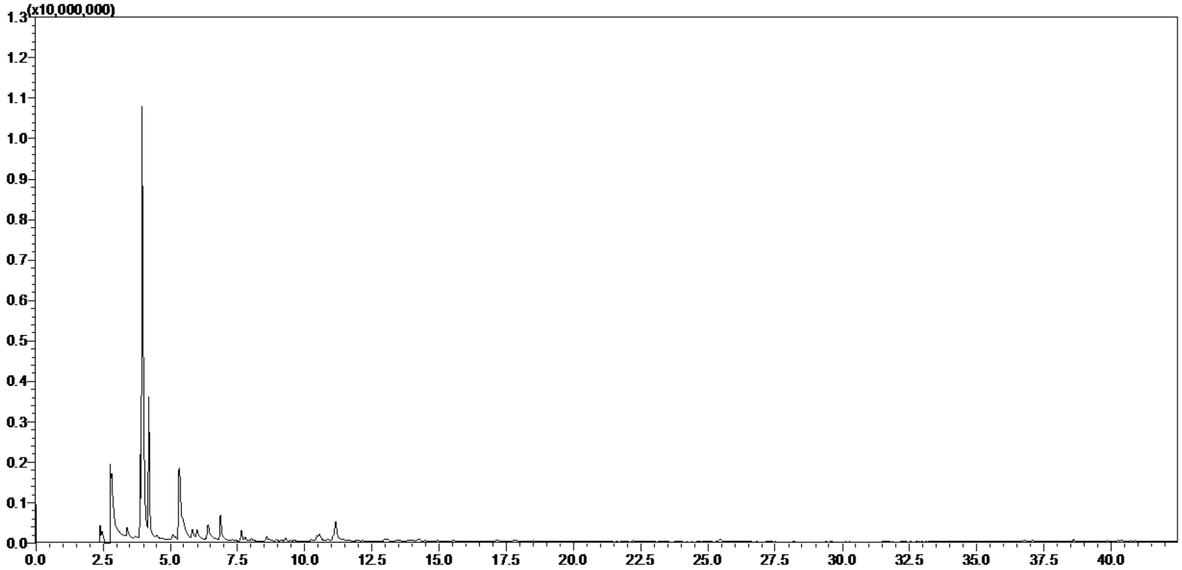
300˚C:

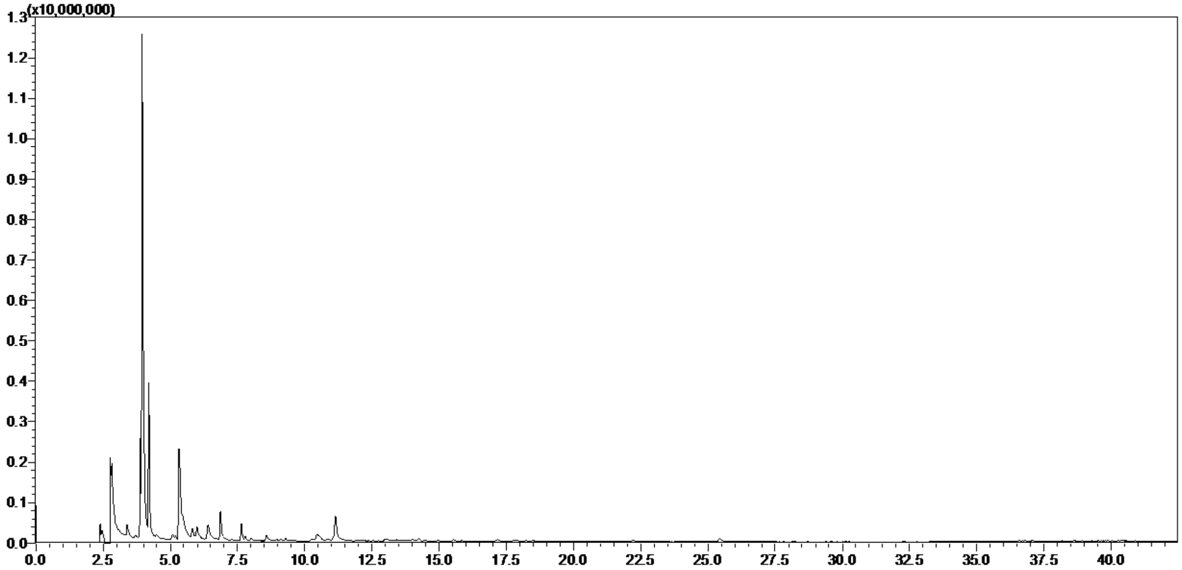


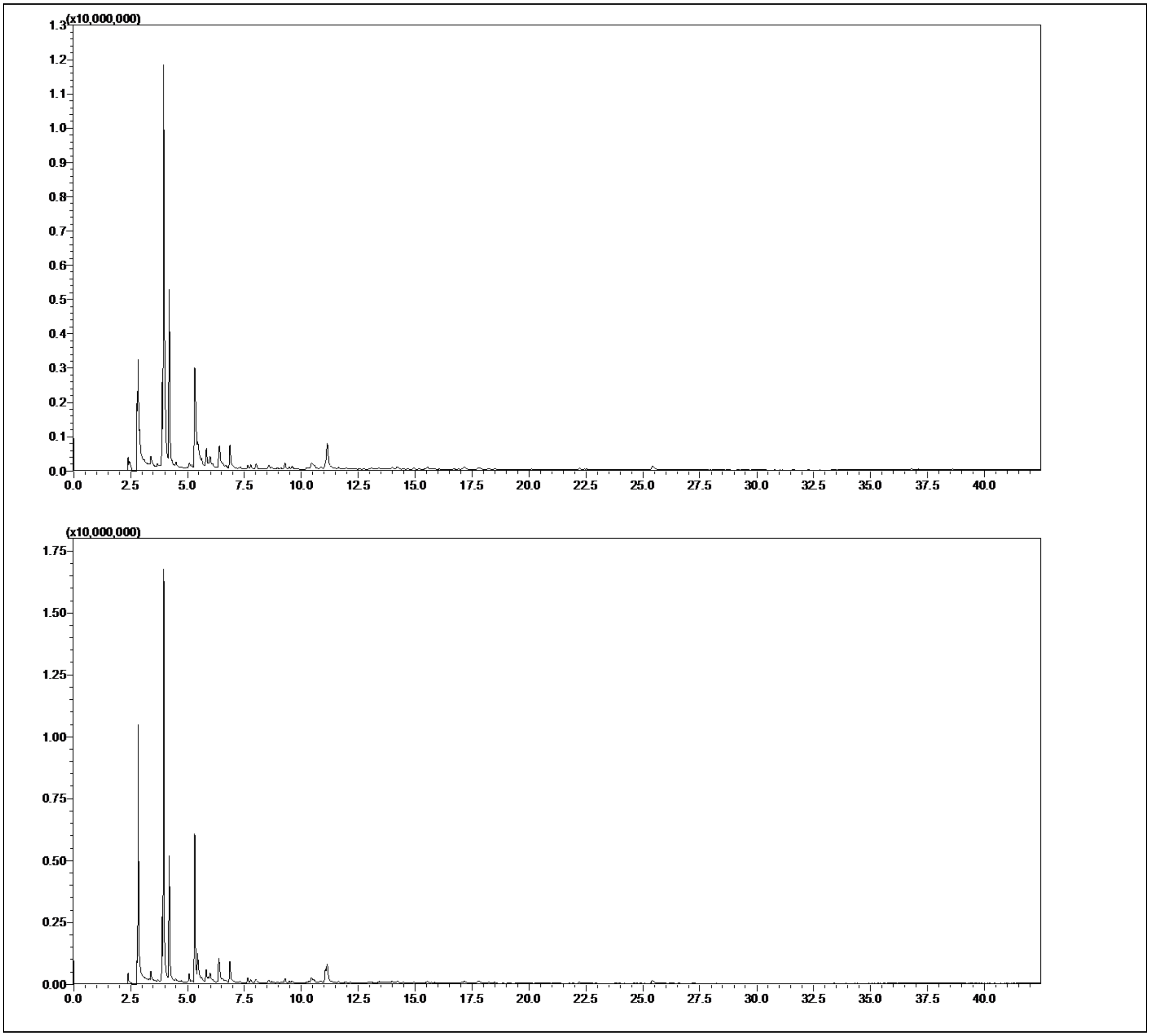
350˚C:



400˚C:


(x10,000,000)
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
40.0


(x10,000,000)
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
40.0


(x10,000,000)
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
40.0
(x10,000,000)
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
40.0

400˚C (solvent blank):

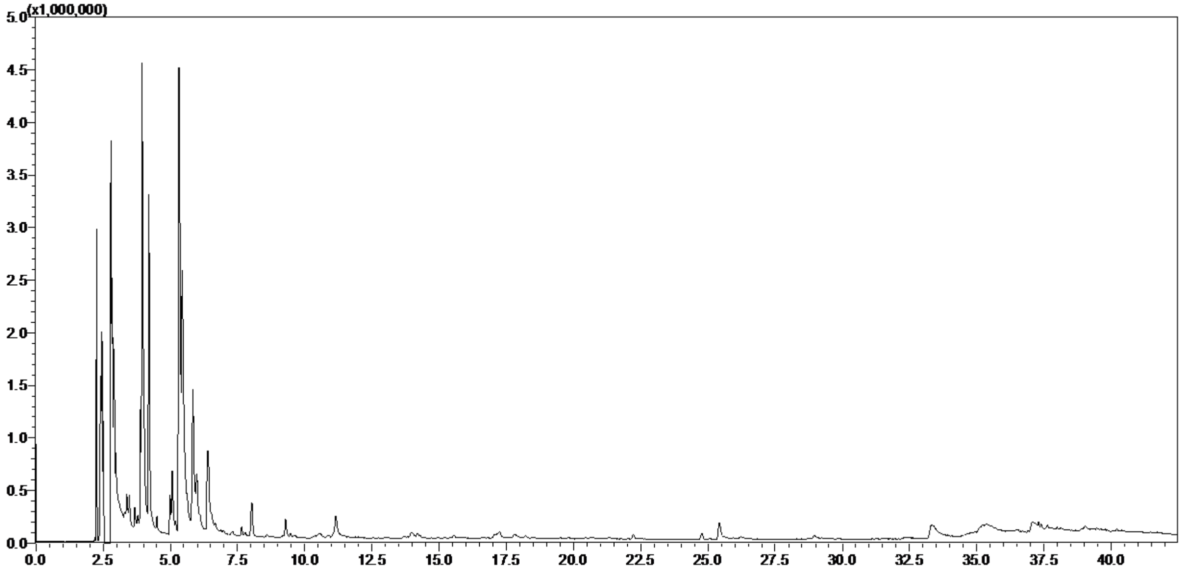
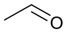
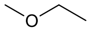
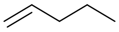
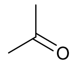
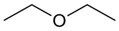
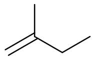
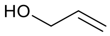
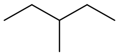
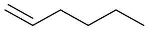
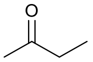
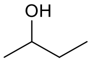
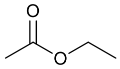
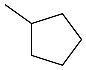
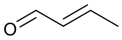
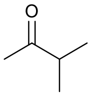
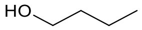
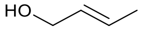
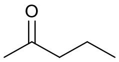
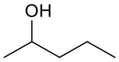
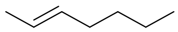
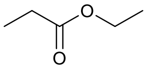
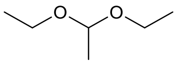
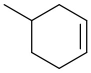
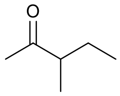
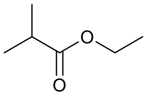
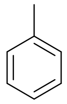
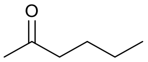
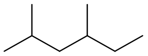
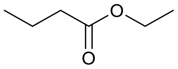
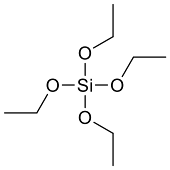
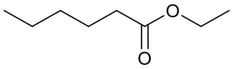
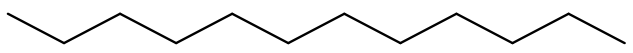


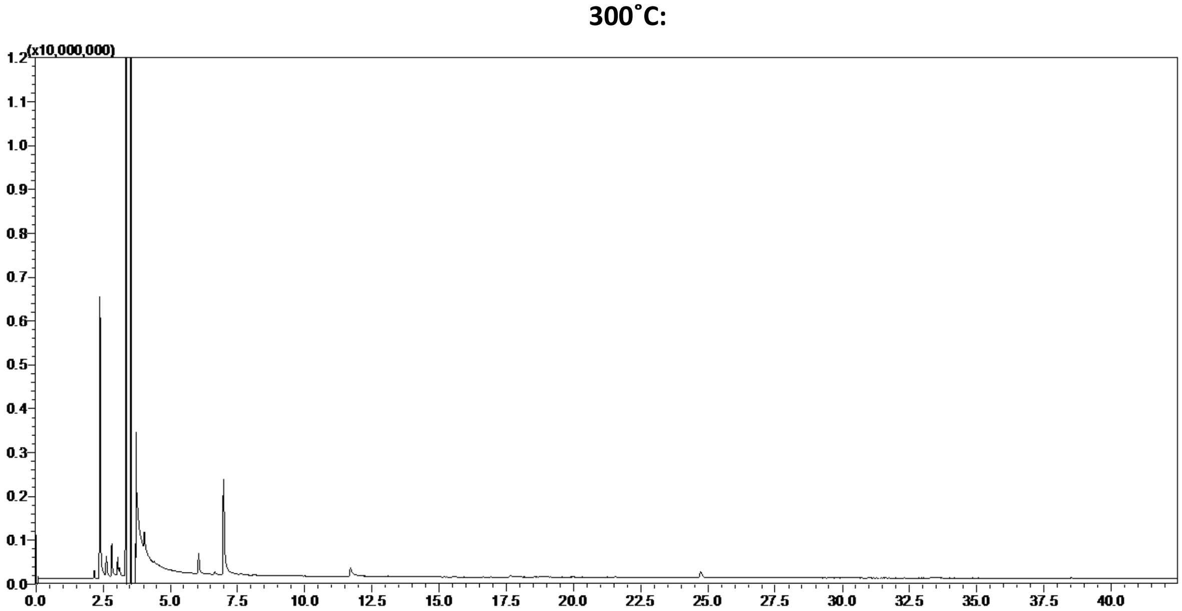
Table S. 3 Identified peaks from the GC-MS chromatograms. Species were identified automatically using the software GCMSsolution Version 2.70 and NIST library search. Identified species are marked with an x at the given reaction temperature. Reaction conditions: 10 g lignin treated for 4 h in 100 ml ethanol.

Time [min]	Similarity index	Name	Drawing	Temperature			
				300°C	350°C	400°C	400°C (blind)
2.45	98	acetaldehyde		x	x	x	x
2.51	94	ethyl methyl ether			x		
2.79	96	1-pentene					x
2.81	94	acetone			x		
2.90	96	diethyl ether		x	x		
2.98	98	2-methyl-1-butene					x
3.30	92	2-propen-1-ol					x
3.68	93	3-methyl-pentane					x
3.79	92	1-hexene					x
3.89	97	2-butanone			x	x	x
3.96	97	2-butanol			x	x	x
4.20	98	ethyl acetate		x	x	x	x
4.50	96	methyl-cyclopentane					x
4.99	95	2-butenal					x
5.20	96	3-methyl-2-butanone				x	x
5.34	91	1-butanol			x	x	x
5.44	94	2-buten-1-ol					x
5.99	96	2-pentanone				x	x
6.39	96	2-pentanol					x
6.68	93	2-heptene					x
6.87	96	ethyl propanoate		x	x	x	
7.65	96	1,1-diethoxy-ethane		x	x	x	x
8.03	97	4-methyl-cyclohexene					x
8.58	90	3-methyl-2-pentanone				x	

8.95	92	ethyl 2-methylpropanoate				x	
9.29	95	toluene				x	x
10.46	93	2-hexanone				x	
11.05	92	2,4-dimethylhexane			x		
11.15	94	ethyl butanoate			x	x	x
24.77	92	tetraethyl silicate					x
25.42	93	ethyl hexanoate					x
36.79	95	*n*-dodecane			x	x	

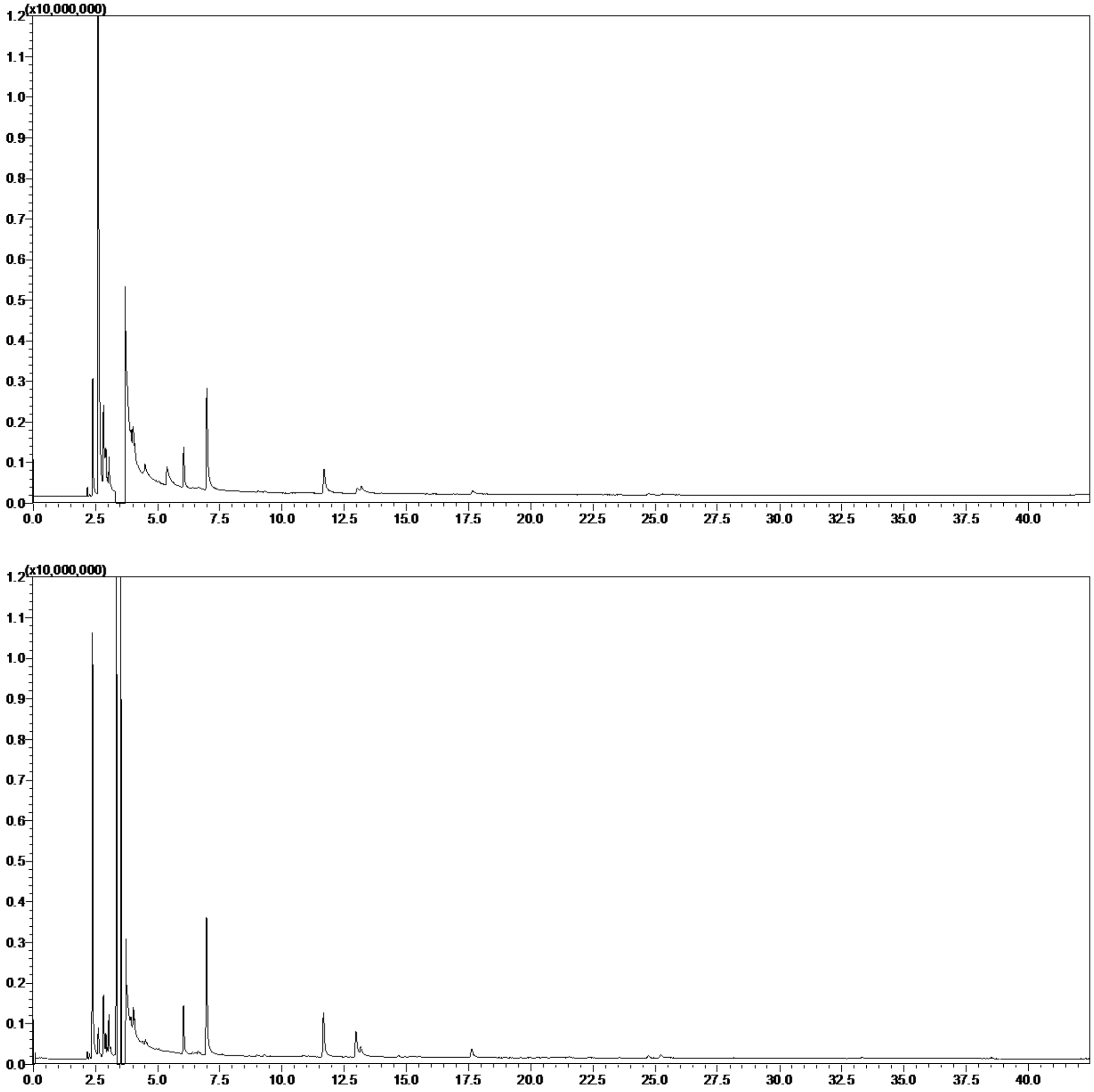
1-Propanol:

Fig. S. 5 GC-MS chromatograms of the light solvent fraction after reaction. Reaction conditions: 10 g lignin, 100 ml 1-propanol and 4 h reaction at different reaction temperatures.

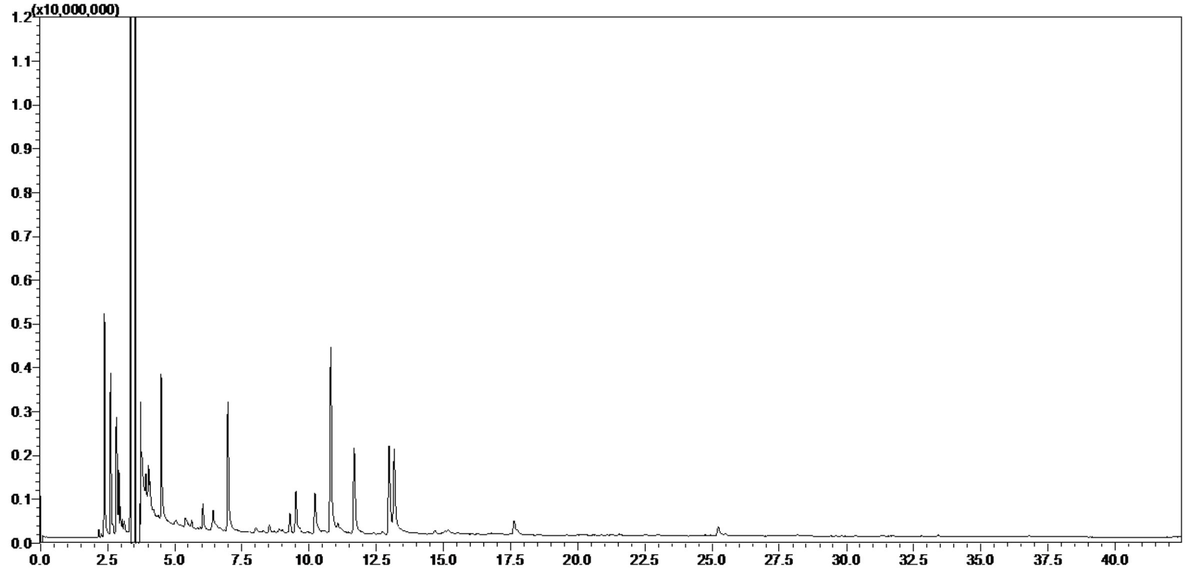


300˚C:

350˚C:


(x10,000,000)
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
40.0
(x10,000,000)
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
40.0

400˚C:



400˚C (solvent blank):

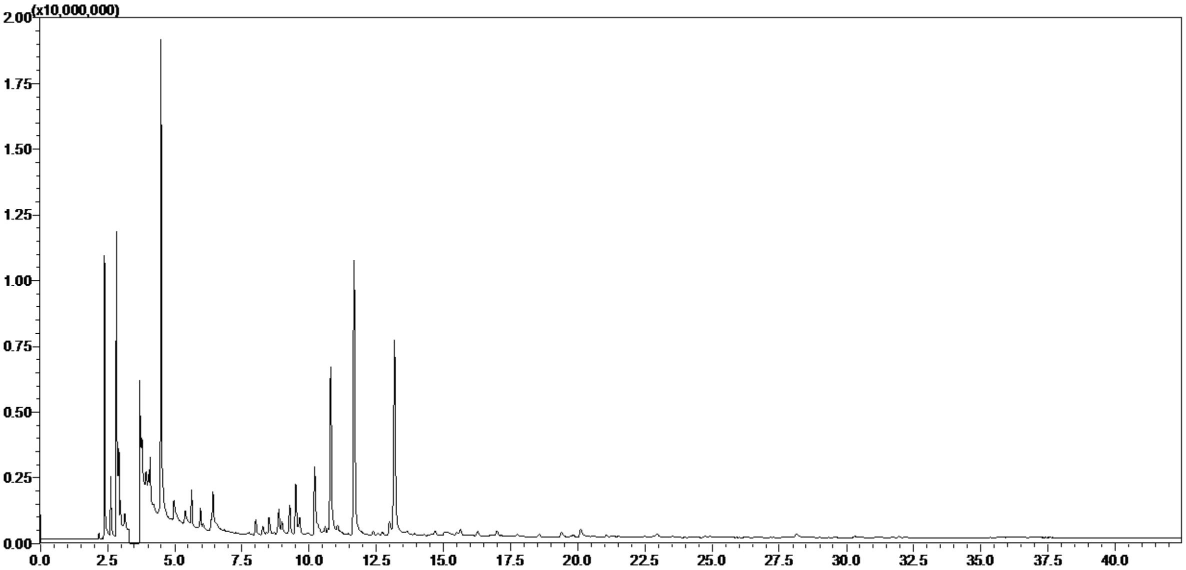
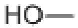
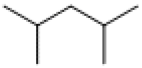
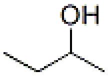
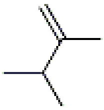
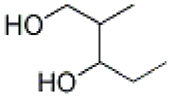
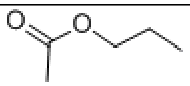
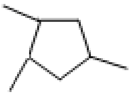
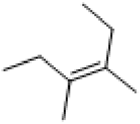
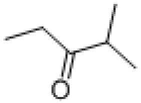
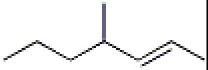
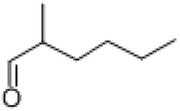
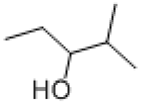
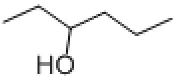
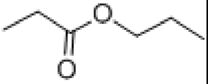
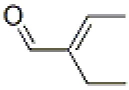
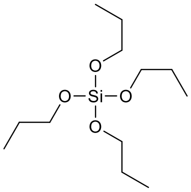


Table S. 4 Identified peaks from the GC-MS chromatograms. Species were identified automatically using the software GCMSsolution Version 2.70 and NIST library search. Identified species are marked with an x at the given reaction temperature. Reaction conditions: 10 g lignin treated for 4 h in 100 ml 1-propanol.

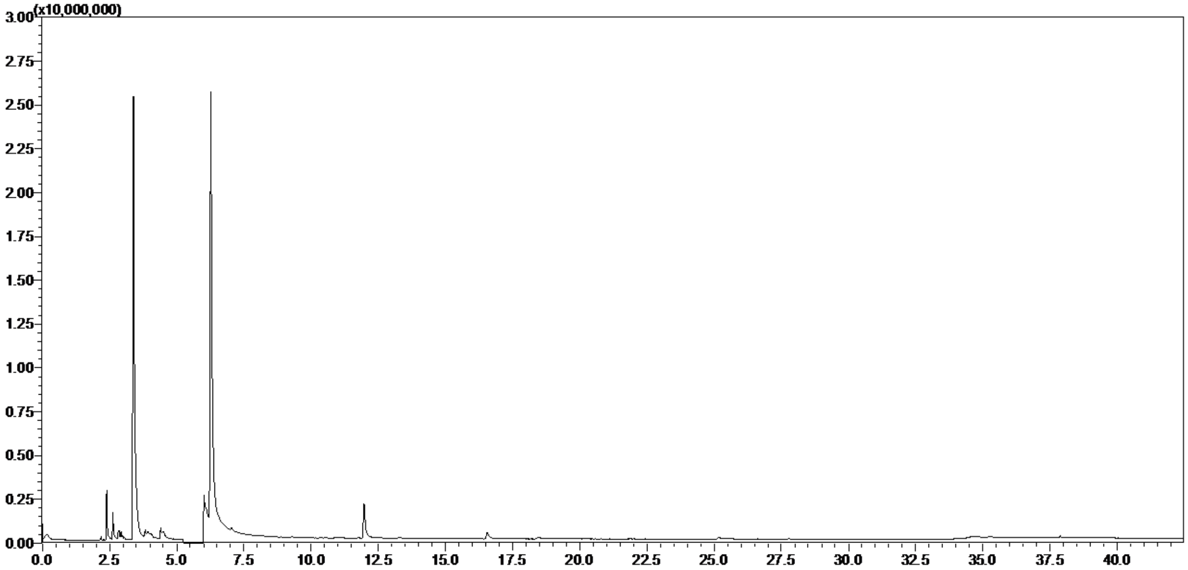
Time [min]	Similarity index	Name	Drawing	Temperature			
				300°C	350°C	400°C	400°C (blind)
2.393	96	methanol		x	x	x	x
2.607	92	ethanol		x	x	x	x
2.980	96	2-pentene			x	x	x
3.043	97	methyl propyl ether		x	x	x	
3.117	90	propanal				x	x
3.400	96	1-propanol		x	x	x	x
3.920	93	2,4-dimethylpentane			x	x	x
4.023	93	1-methylpropan-1-ol		x	x	x	
4.080	91	2,3-dimethylbut-1-ene			x	x	x
4.450	94	2-methylpropan-1-ol		x	x	x	x
4.963	94	2-methylprop-2-en-1-ol					x
5.373	93	1-butanol			x	x	x
5.630	96	3-methylhexane				x	x
5.957	97	3-ethylpentane				x	x
6.053	91	dipropyl ether		x	x	x	x
6.430	91	2-methyl-1,3-pentandiol				x	x
6.90	97	propyl acetate		x	x	x	
8.017	95	1,2,4-trimethylcyclopentane					x

8.283	93	2,3-dimethylhex-3-ene					x
8.520	94	2-methylpentan-3-one				x	x
8.867	95	4-methylhept-2-ene					x
8.983	92	2-methylhexanal					x
9.507	96	2-methyl-pentan-3-ol				x	x
10.223	98	hexan-3-one				x	x
10.807	94	hexan-3-ol				x	x
11.707	96	propyl propanoate		x	x	x	x
12.967	95	2-ethyl-but-2-enal			X	x	x
13.167	94	2-methyl-1-pentanol			x	x	x
38.360	86	tetrapropyl orthosilicate					x

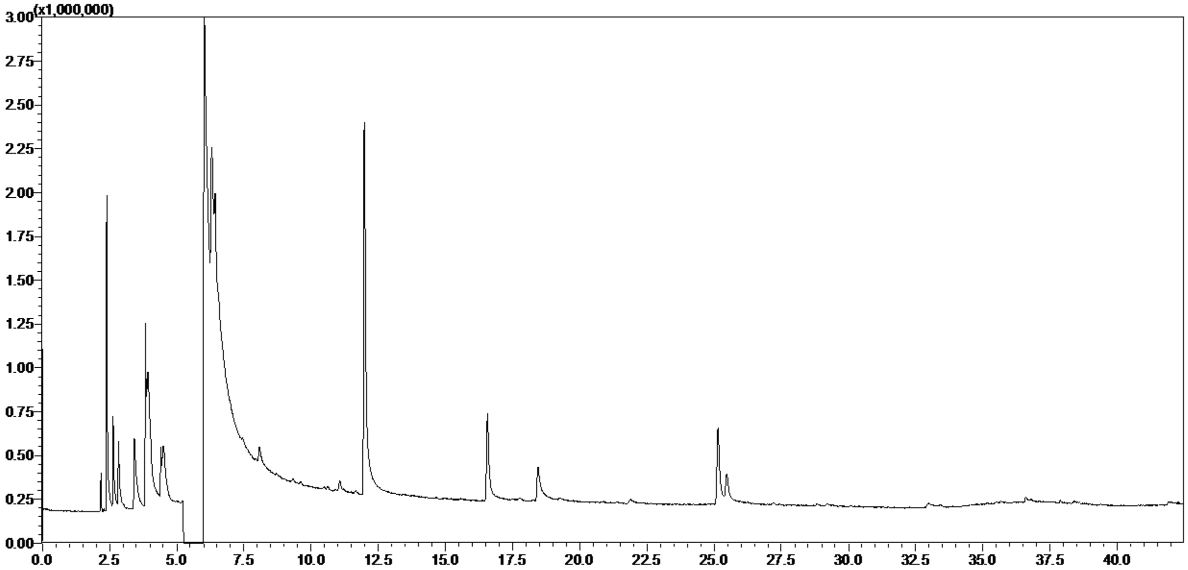
1-Butanol:

Fig. S. 6 GC-MS chromatograms of the light solvent fraction after reaction. Reaction conditions: 10 g lignin, 100 ml 1-butanol and 4 h reaction at different reaction temperatures.

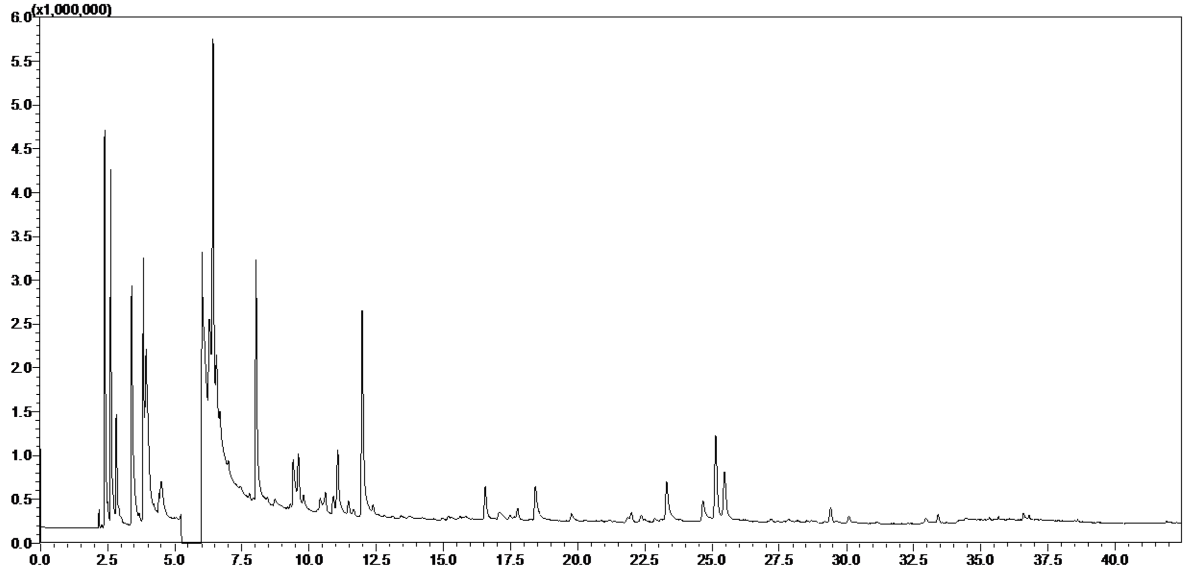
300˚C:



350˚C:



400˚C:



400˚C (solvent blank):

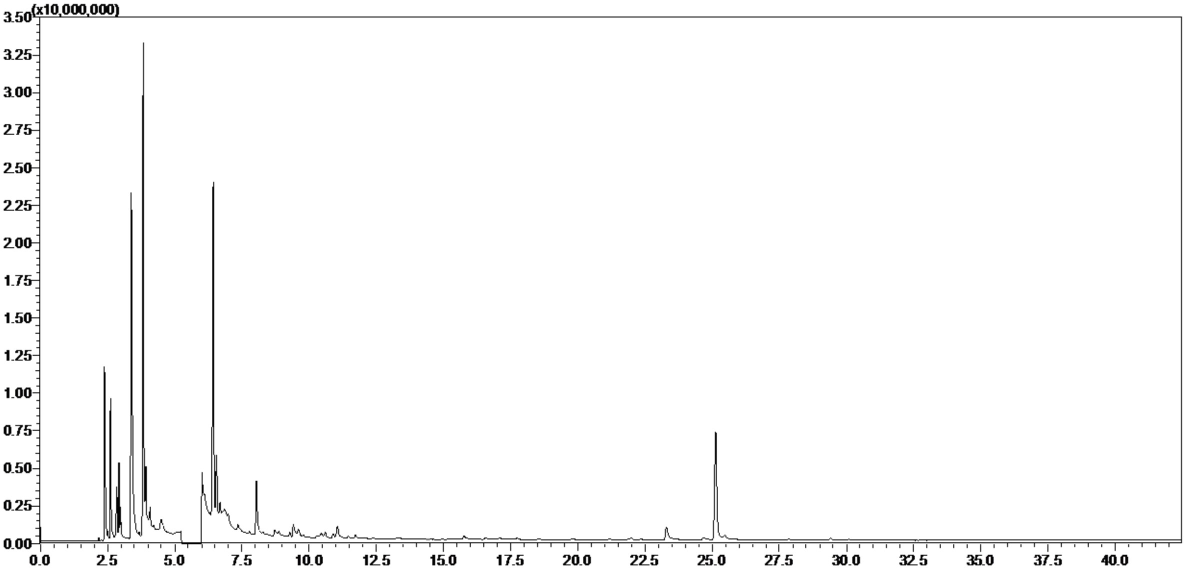
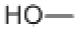
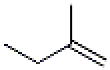
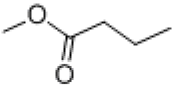
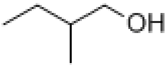
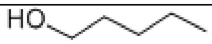
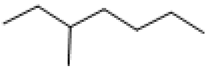
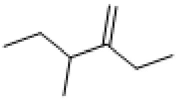
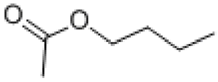
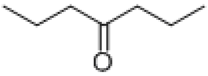
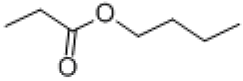
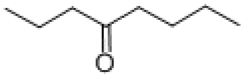
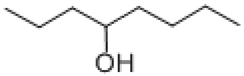
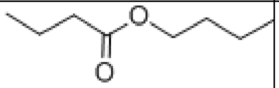
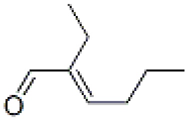


Table S. 5 Identified peaks from the GC-MS chromatograms. Species were identified automatically using the software GCMSsolution Version 2.70 and NIST library search. Identified species are marked with an x at the given reaction temperature. Reaction conditions: 10 g lignin treated for 4 h in 100 ml 1-butanol.

Time [min]	Similarity index	Name	Drawing	Temperature			
				300°C	350°C	400°C	400°C (blind)
2.393	97	methanol		x	x	x	x
2.620	95	ethanol		x	x	x	x
2.823	90	acetone		x	x	x	x
2.927	97	2-methylbut-1-ene		x	x	x	x
3.433	96	1-propanol		x	x	x	x
3.830	94	butanal		x	x	x	x
3.933	92	hexane		x	x	x	x
4.407	96	methyl butyl ether		x	x	x	x
4.450	90	2-methylpropan-1-ol		x	x	x	x
5.373	93	1-butanol		x	x	x	x
6.293	91	*n*-butyl formate		x	x	x	
6.423	90	*n*-heptane				x	x
6.557	96	hept-3-ene					x
7.030	96	propyl acetate		X	x	x	
7.363	94	methyl butanoate					x
8.067	98	2-methylbutan-1-ol			x	x	x
9.407	94	1-pentanol				x	x
9.603	93	3-methylheptane				x	x

10.613	94	3-methyl-4-methylenehexane				x	x
11.070	91	2,4-dimethylhexane				x	x
11.463	96	2-octene				x	x
11.977	97	butyl acetate		x	x	x	
15.767	96	4-heptanone					x
16.567	96	*n*-butyl ether		x	x	x	x
17.763	93	*n*-nonane				x	
18.447	98	butyl propanoate			x	x	
23.310	94	4-octanone				x	x
24.657	95	4-octanol				x	x
25.160	94	butyl butanoate		x	x	x	x
25.473	95	2-ethylhex-2-enal			x	x	x

S. 5. Full Size Exclusion Chromatography Data

Size Exclusion Chromatography (SEC) was carried out as described in the main text. Full SEC data is shown in Fig. S. 7.

For all alcohols a clearly visible trend of lowered molecule mass of the oil is seen as a function of reaction temperature showing similar effects of all solvents. At a reaction temperature of 350˚C and 400˚C there is shift towards heavier molecular weight species as the chain length of the alcohol solvent is increased. This may be due to the primary alcohol solvent alkylating depolymerised oil species. At 300˚C in particular the shoulders in the SEC curves represent monomer and dimer species and there is a clear shift towards more dimmers relative to monomers as the chain length of the alcohol solvent is increased.

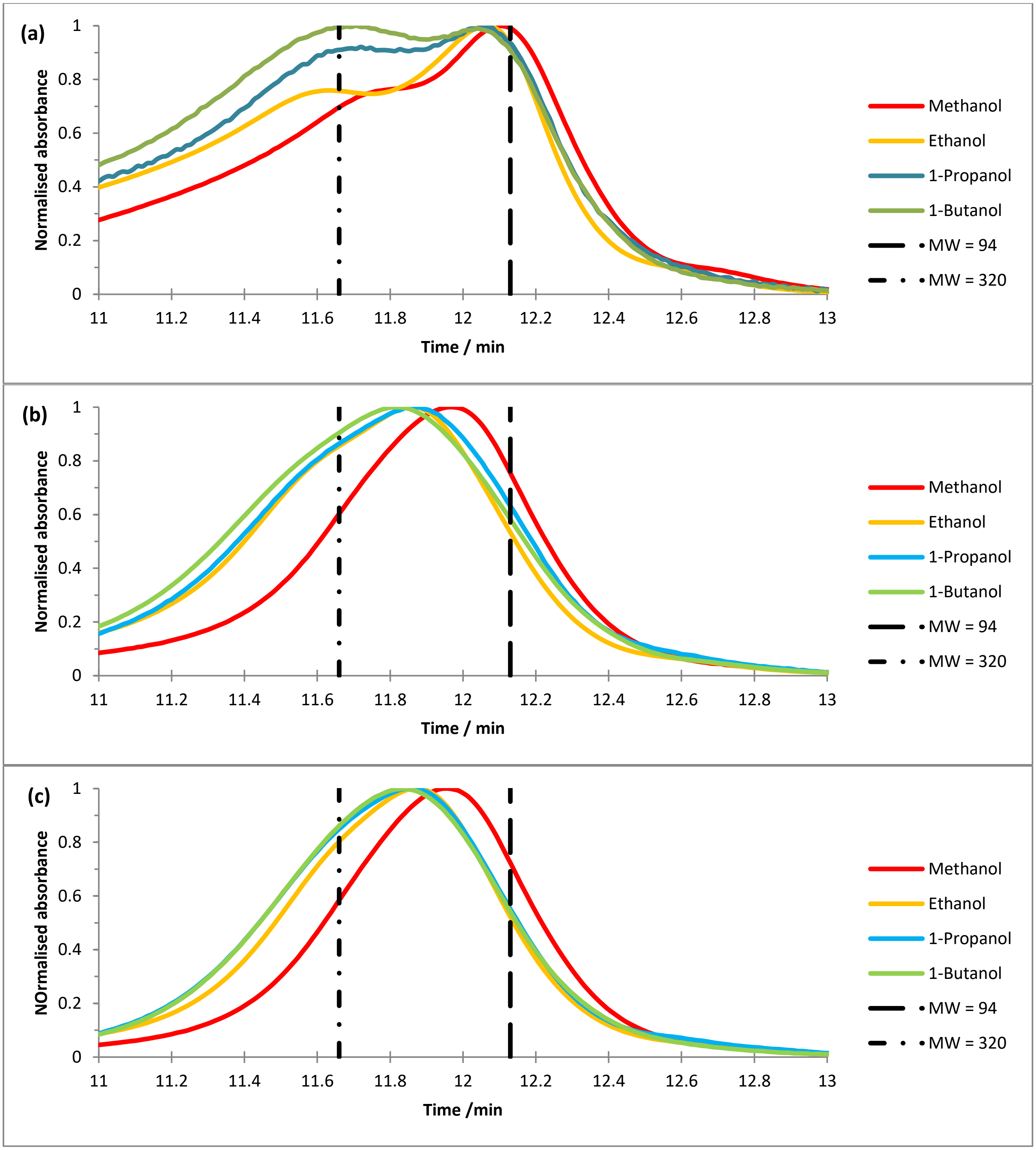
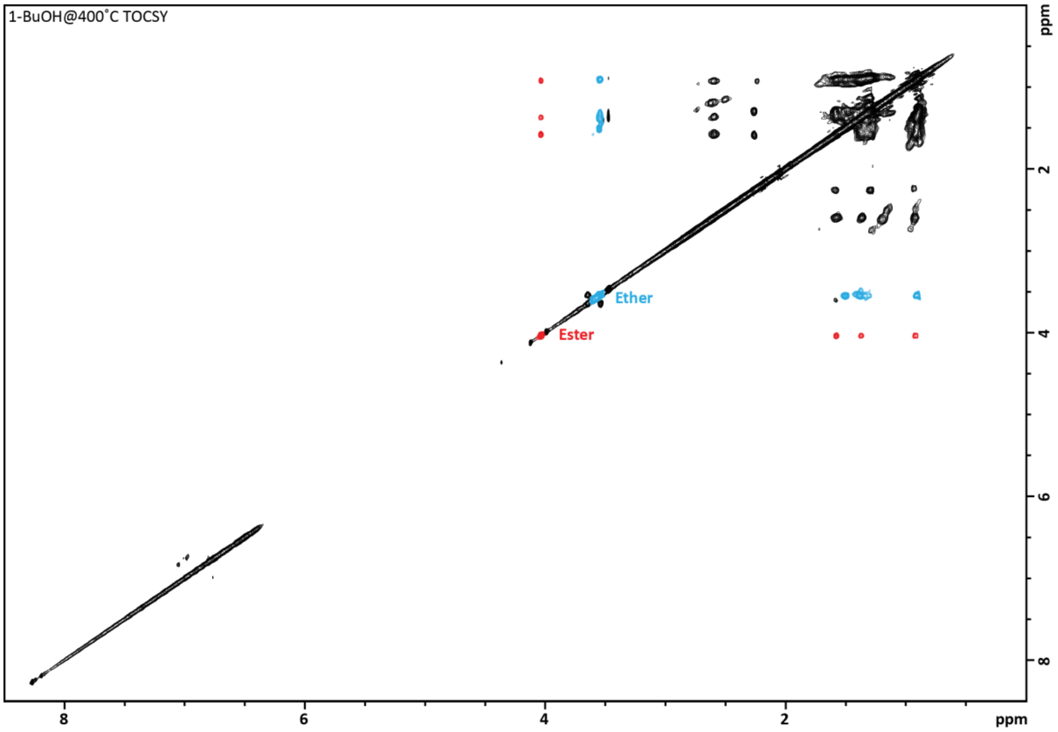


Fig. S. 7 molecular size distribution of oil product obtained from solvolysis in the different alcohols at similar reaction conditions. 10 g lignin was treated for 4 h in 100 ml of alcohol solvent at different reaction temperatures: (a) 300°C; (b) 350°C; (c) 400°C.

S. 6. NMR

^{1}H-TOCSY NMR, ^{13}C-HMBC NMR and ^{13}C-HSQC NMR was conducted on isolated oil products as described in the main text. Spectral data from ^{1}H-TOCSY NMR and ^{13}C-HMBC NMR on isolated oil from treatment of 10 g lignin at 400°C in 1-butanol is shown in Fig. S. 8 and alkylation is identified as both butyl ether and ester. Fig. S. 9 shows ^{13}C-HSQC NMR data on oil isolated after treatment of 10 g lignin at 400°C in the four different alcohols. The spectral data shows very similar oil composition independent on alcohol chain length; however, methoxy groups are presented in a noticeably higher amount in the oil produced in methanol solvent. This shows that a transetherification takes place.



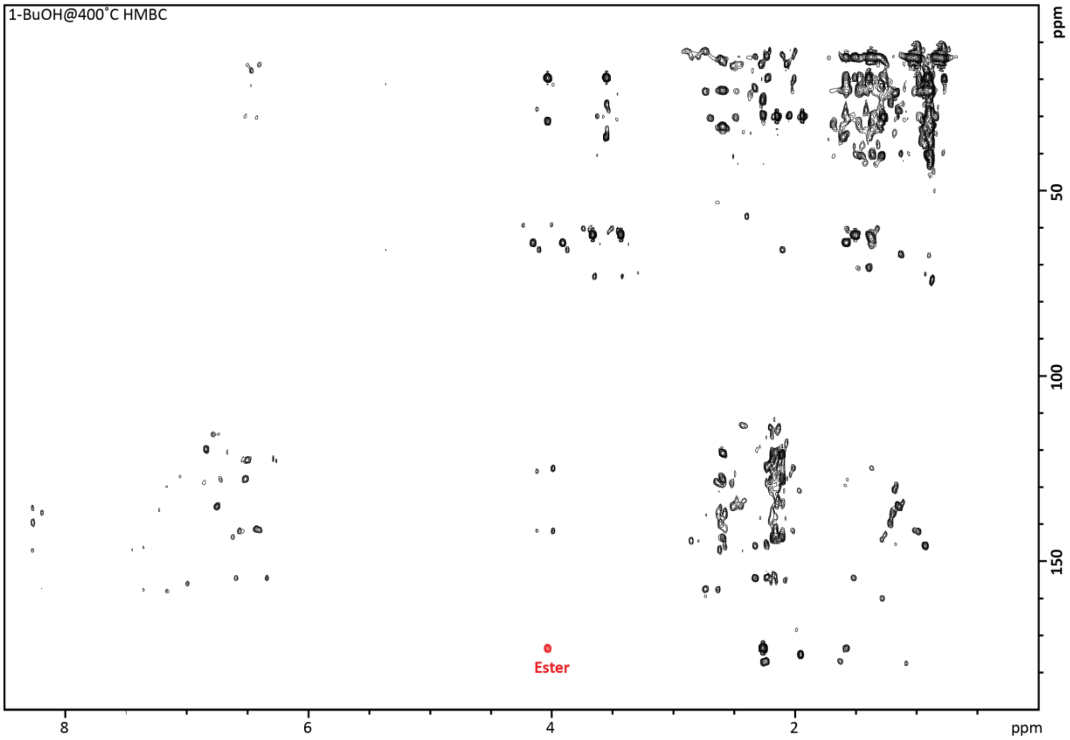
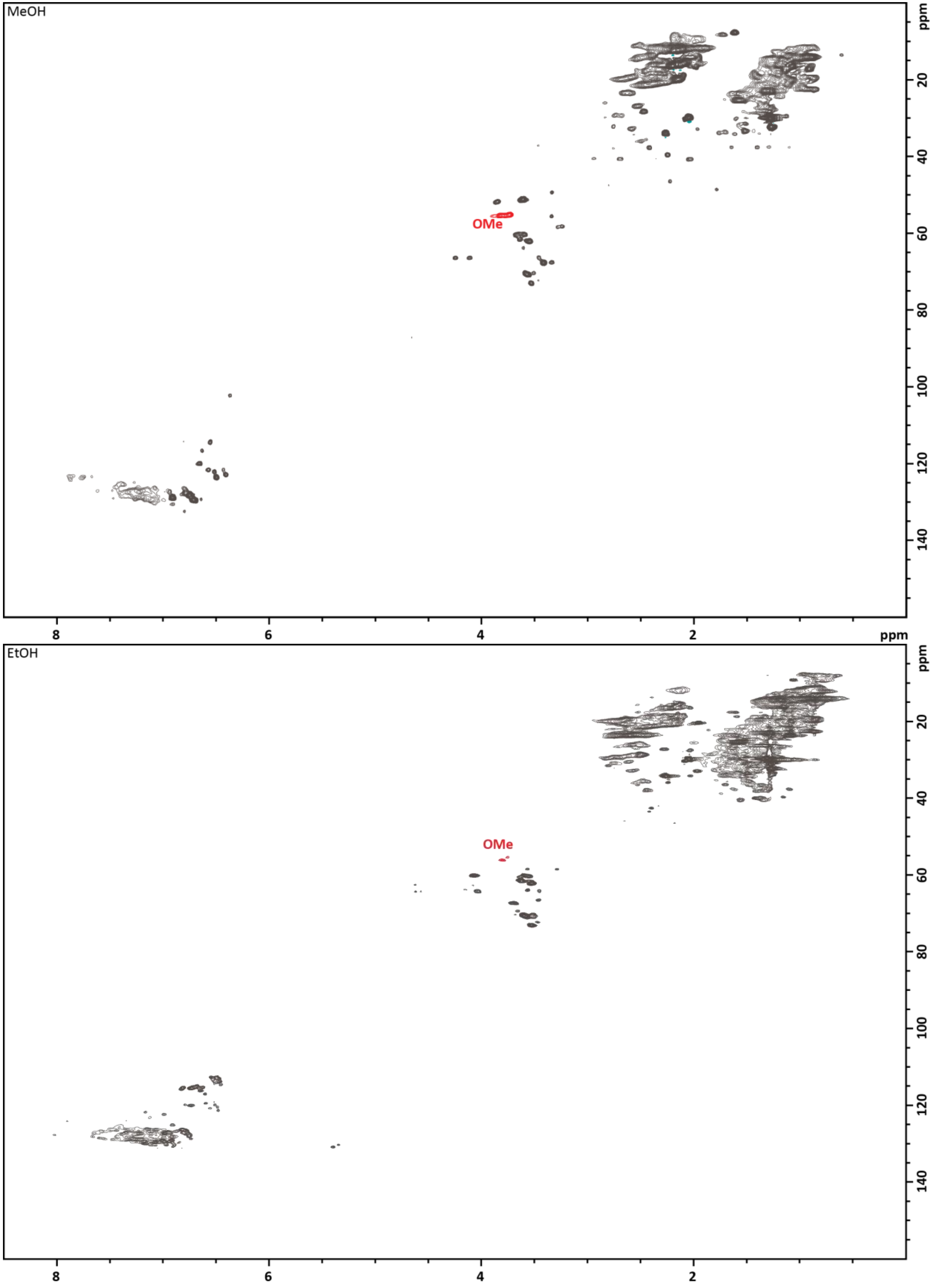
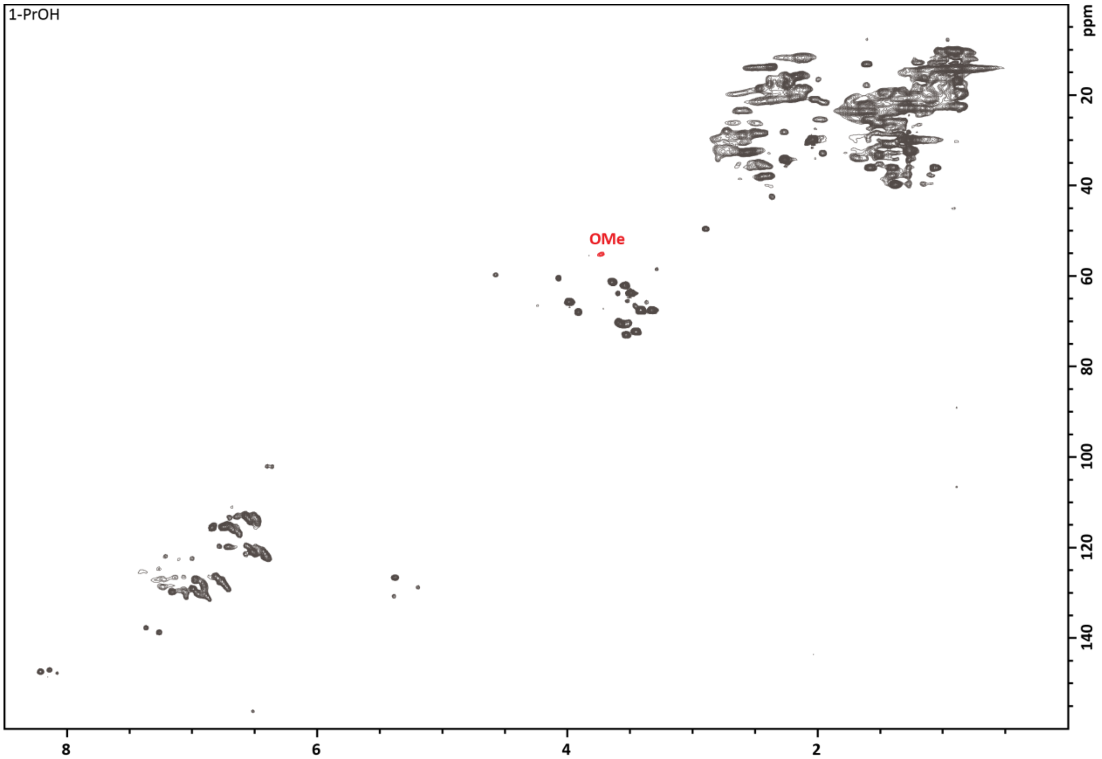
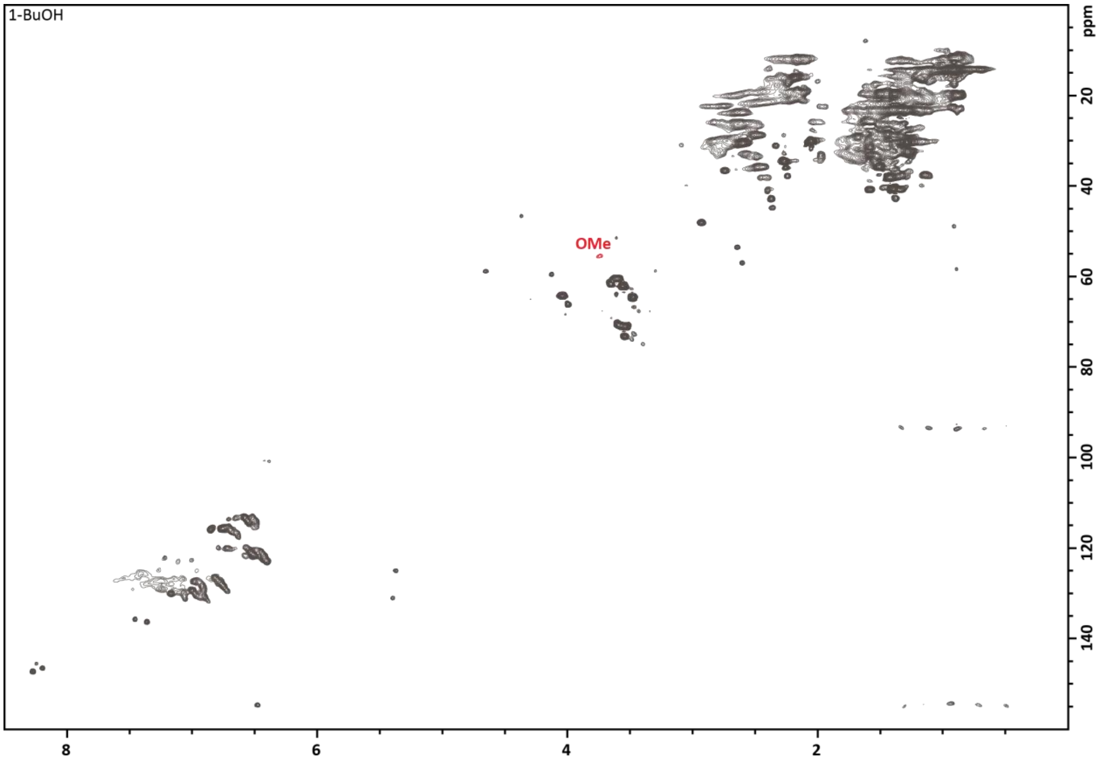


Fig. S. 8 ^{1}H-TOCSY and ^{13}C-HMBC spectra of oils produced at 400°C for 4 h in 100 ml 1-butanol. Butyl ester and butyl ether is highlighted in the figure.

Fig. S. 9 ^{13}C-HSQC NMR of oil produced from 10 g lignin reacted for 4 h at 400°C in 100 ml alcohol. The methoxy groups are highlighted.




1-PrOH
OMe
ppm
20
40
60
80
100
120
140
8
6
4
2


1-BuOH
OMe
ppm
20
40
60
80
100
120
140
8
6
4
2