Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Thermal annealing effects on hydrothermally synthesized unsupported MoS_2 for enhanced deoxygenation of Propylguaiacol and Kraft lignin

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Aluminium, Al	18	mg/kg	Manganese, Mn	58	mg/kg
Antimony,Sb	0.06	mg/kg	Molybdenum, Mo	0.7	mg/kg
Arsenic, As	0.08	mg/kg	Sodium, Na	9300	mg/kg
Barium, Ba	2	mg/kg	Neodymium, Nd	0.005	mg/kg
Beryllium, Be	0.013	mg/kg	Niobium, Nb	<0.005	mg/kg
Lead, Pb	0.04	mg/kg	Nickel, Ni	0.4	mg/kg
Boron, B	22	mg/kg	Osmium, Os	<0.005	mg/kg
Bromine, Br	1.2	mg/kg	Palladium, Pd	<0.005	mg/kg
Cerium, Ce	0.012	mg/kg	Platinum, Pt	<0.005	mg/kg
Cesium, Cs	0.13	mg/kg	Praseodymium, Pr	<0.005	mg/kg
Dysprosium, Dy	<0.005	mg/kg	Rhenium, Re	<0.005	mg/kg
Erbium, Er	<0.005	mg/kg	Rhodium, Rh	<0.005	mg/kg
Europium, Eu	<0.005	mg/kg	Rubidium, Rb	4.2	mg/kg
Phosphorus, P	12	mg/kg	Ruthenium, Ru	<0.005	mg/kg
Gadolinium, Gd	<0.005	mg/kg	Samarium, Sm	<0.005	mg/kg
Gallium, Ga	0.15	mg/kg	Selenium, Se	0.09	mg/kg
Germanium, Ge	0.03	mg/kg	Silver, Ag	0.03	mg/kg
Gold, Au	<0.005	mg/kg	Scandium, Sc	<0.005	mg/kg
Hafnium, Hf	<0.005	mg/kg	Strontium, Sr	1	mg/kg
Holmium, Ho	<0.005	mg/kg	Sulphur, S	21000	mg/kg
Iridium, Ir	<0.005	mg/kg	Tantalum, Ta	<0.005	mg/kg
Iodine, I	0.5	mg/kg	Tellurium, Te	<0.005	mg/kg
Iron, Fe	30	mg/kg	Thallium, Tl	0.03	mg/kg
Cadmium, Cd	0.17	mg/kg	Tin, Sn	0.1	mg/kg
Calcium, Ca	200	mg/kg	Terbium, Tb	<0.005	mg/kg
Potassium, K	1100	mg/kg	Titanium, Ti	1.4	mg/kg
Silicon, Si	6000	mg/kg	Thorium, Th	<0.005	mg/kg
Cobalt, Co	0.08	mg/kg	Thulium, Tm	<0.005	mg/kg
Copper, Cu	0.9	mg/kg	Uranium, U	<0.005	mg/kg
Chromium, Cr	0.3	mg/kg	Vanadium, V	19	mg/kg
Mercury, Hg	<0.005	mg/kg	Bismuth, Bi	<0.005	mg/kg
Lanthanum, La	0.007	mg/kg	Tungsten, W	0.3	mg/kg
Lithium, Li	0.07	mg/kg	Ytterbium, Yb	<0.005	mg/kg
Lutetium, Lu	<0.005	mg/kg	Yttrium, Y	0.005	mg/kg
Magnesium, Mg	21	mg/kg	Zinc, Zn	13	mg/kg
			Zirconium, Zr	0.007	mg/kg

Figure S1 ICP analysis of impurities in kraft lignin.

Table S1 Elemental analysis for kraft lignin.

Elemental analysis (%)	Wt%
C	62.1
H	5.85
N	0.35
S	2.18
O	29.5*

*by difference and neglecting other impurities

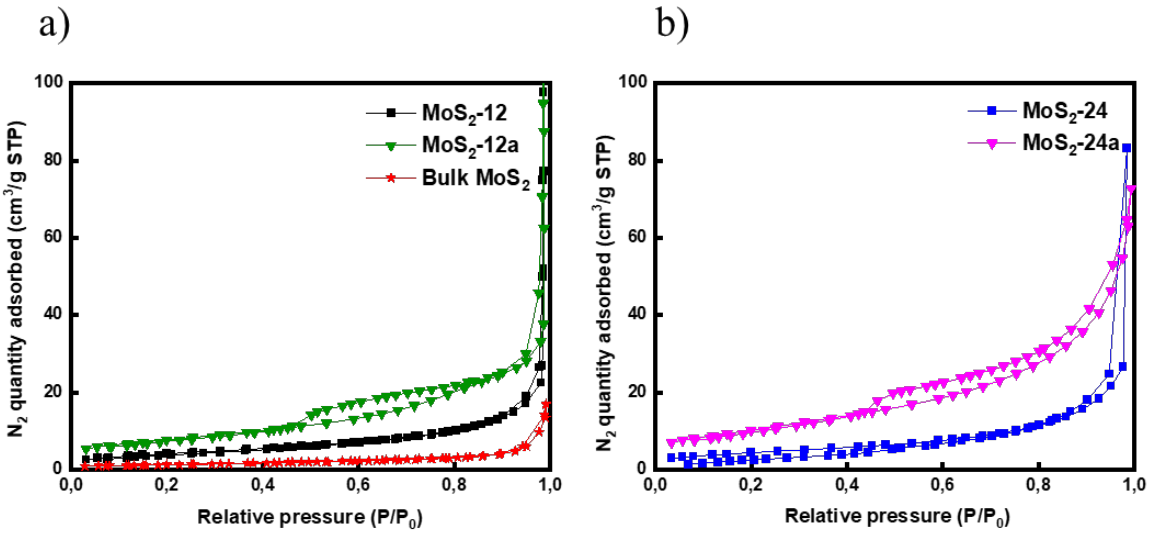

Figure S2 Nitrogen adsorption-desorption isotherms for studied catalysts.

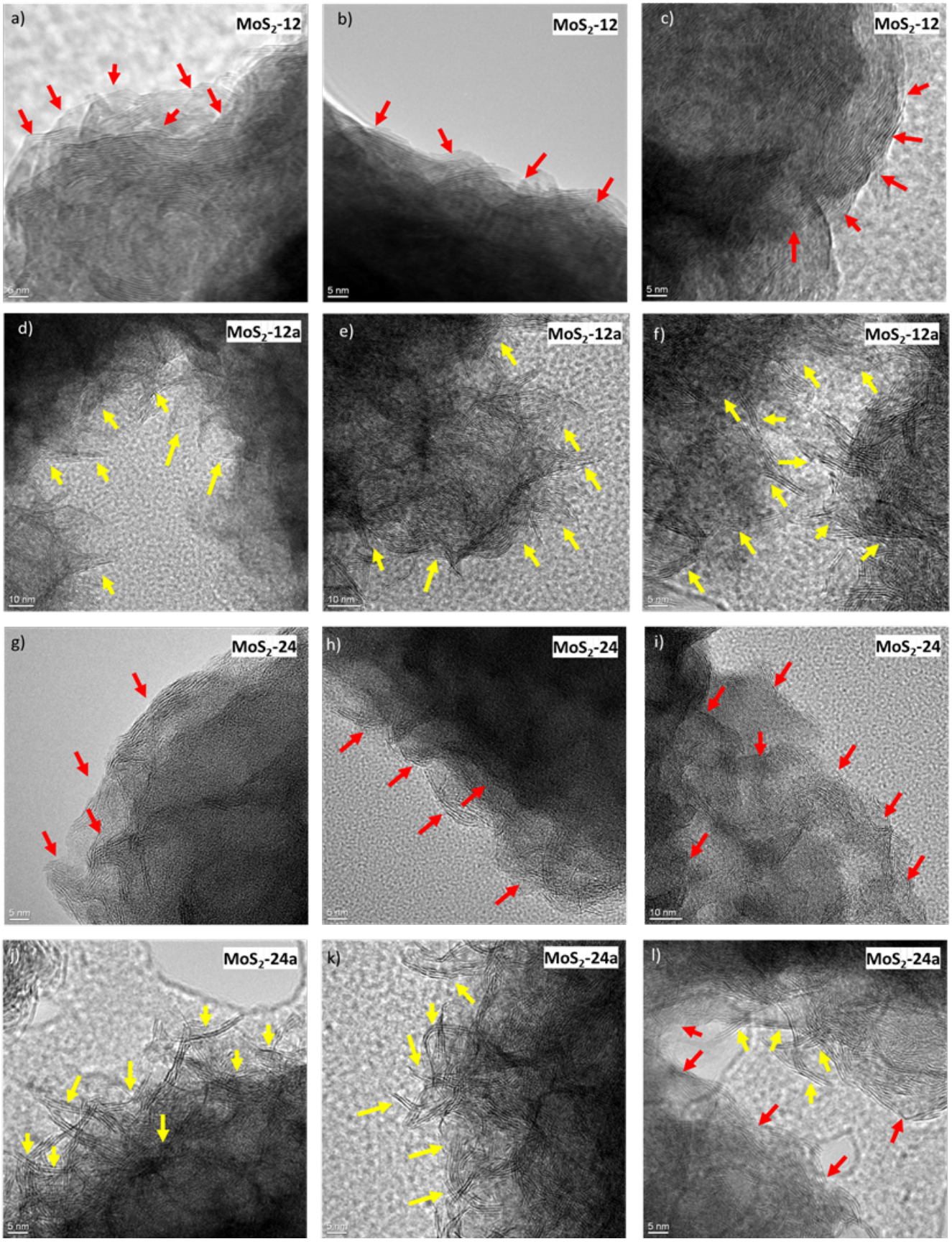

Figure S3 Additional HRTEM images of a-c) MoS_2-12, d-f) MoS_2-12a, g-i) MoS_2-24, and j-l) MoS_2-24a.

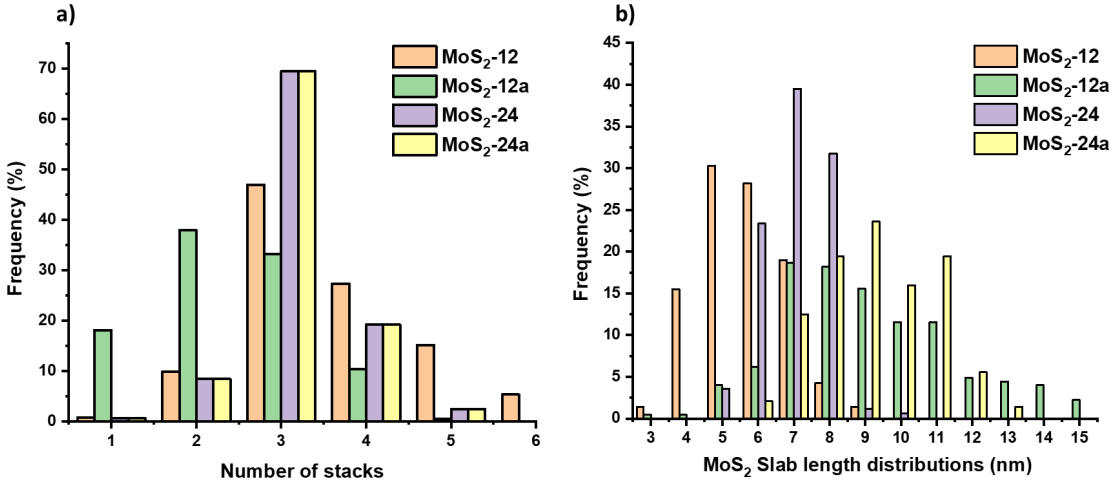

Figure S4a) Distribution of the number of stacks and b) MoS_2 slab length for different unsupported MoS_2.

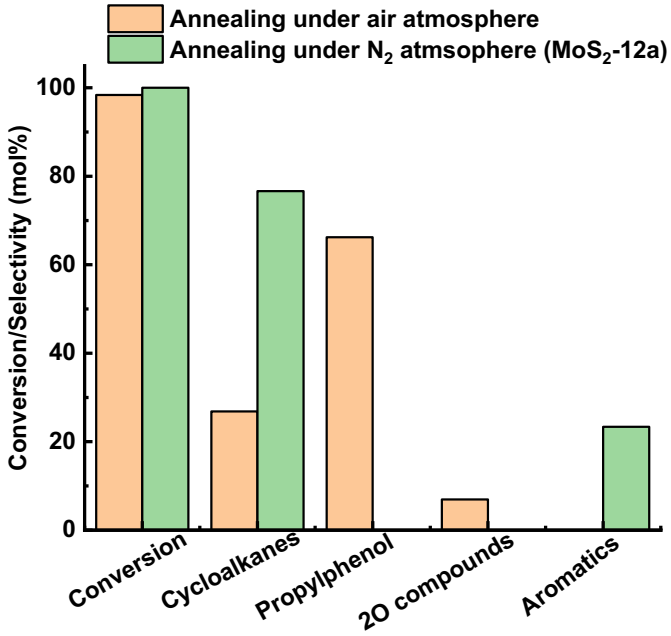

Figure S5 Comparison of PG conversion and product selectivity for HDO of PG over MoS_2-24 following an annealing treatment under different atmosphere (air or N_2) at 400 ˚C for 2 h. Reaction conditions: 50 bar total H_2 pressure, 300 ˚C, and 1000 rpm.

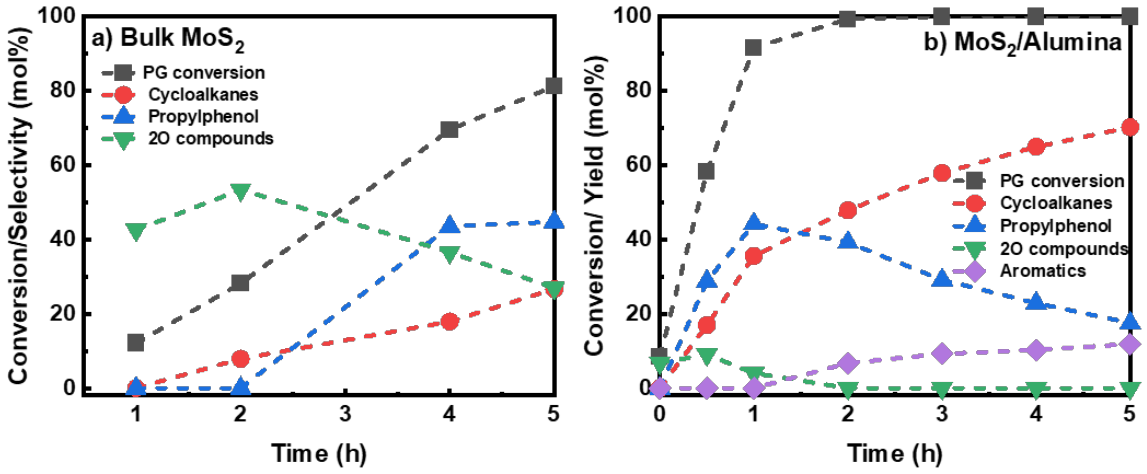

Figure S6 Reaction product distribution for HDO of PG over a) Bulk MoS_2 b) 13.2 wt% MoS_2 supported on alumina at 50 bar total H_2 pressure, 300 ˚C and 1000 rpm.

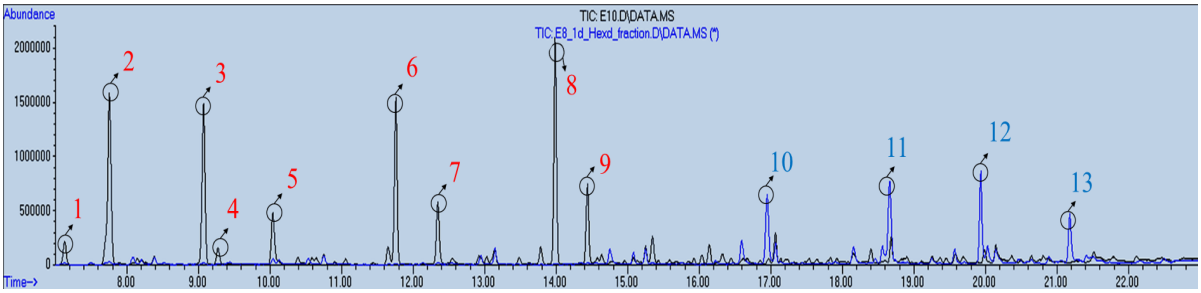

Figure S7 GC spectrum of the lignin fraction obtained from the hydrotreatment of kraft lignin over commercial MoS_2 (blue line) and MoS_2-12a (black line). Reaction conditions: 3:1 lignin to catalyst ratio, 340 ˚C, 40 bar initial H_2 pressure, and 1000 rpm. The major compounds were labeled in the spectrum as (1) Methylcyclopentane, (2) Cyclohexane, (3) Methylcyclohexane, (4) Ethylcyclopentane, (5) Toluene, (6) Ethylcyclohexane, (7) 1,3-dimethylbenzene, (8) Propylcyclohexane, (9) Propylbenzene, (10) Guaiacol, (11) Creosol, (12) 4-ethyl-2-methoxyphenol and (13) Propylguaiacol.

Table S2 Products identified from GC-MS spectra and product yields for hydrotreatment of Kraft lignin over bulk MoS_2 and MoS_2-12a. Reaction conditions: 3:1 lignin to catalyst mass ratio, 340 ˚C, 40 bar initial H_2 pressure, and 1000 rpm.

Retention time (min)	Compound identified	Compound chemical formula	FID peak area (Bulk MoS_2)	Bulk MoS_2 Product yield (area %)	FID peak area (MoS_2-12a)	MoS_2-12a Product yield (area %)
7.135	Methylcyclopentane	C_6H_{12}	-	-	2.10×10^6	2.53
8.089	Cyclohexane	C_6H_{10}	6.19×10^5	1.9	1.56×10^7	18.83

8.148	1,3-dimethylcyclopentane	C_7H_{14}	-	-	9.45×10^5	1.14
9.073	Methylcyclohexane	C_7H_{14}	-	-	1.90×10^7	13.20
9.276	Ethylcyclopentane	C_7H_{14}	-	-	1.34×10^6	1.61
10.044	Toluene	C_7H_8	3.98×10^5	1.22	3.47×10^6	4.18
10.126	Cyclopentene	C_7H_{12}	3.27×10^5	1.00	-	-
10.392	1,3-dimethylcyclohexane	C_8H_{16}	-	-	5.77×10^5	0.69
10.536	Pentylcyclopentane	C_8H_{16}	7.76×10^5	2.38	-	-
10.587	1-ethyl-3-methylcyclopentane	C_8H_{16}	-	-	9.70×10^5	1.17
10.906	1,2-dimethylcyclohexane	C_8H_{16}	-	-	5.65×10^5	0.68
11.650	Propylcyclopentane	C_8H_{16}	-	-	1.44×10^6	1.74
11.757	Ethylcyclohexane	C_8H_{16}	-	-	1.06×10^7	12.78
12.343	1,3-dimethylbenzene	C_8H_{10}	-	-	3.68×10^6	4.44
12.547	Xylene	C_8H_{10}	-	-	7.12×10^5	0.86
12.920	1-methyl-2-propylcyclopentane	C_9H_{18}	-	-	1.39×10^6	1.69
12.946	Octylcyclopentane	$C_{11}H_{22}$	9.91×10^5	3.04	-	-
13.480	1-ethyl-4-methylcyclohexane	C_9H_{18}	-	-	6.73×10^5	0.82
13.782	(1-methylethyl)cyclohexane	$C_{10}H_{20}$	-	-	1.11×10^6	1.34
13.984	Propylcyclohexane	C_9H_{18}	-	-	1.42×10^7	17.16
14.433	Propylbenzene	C_9H_{12}	-	-	4.24×10^6	5.12
14.573	1-ethyl-3-methylbenzene	C_9H_{12}	-	-	4.48×10^5	0.54
14.748	Phenol	C_6H_6O	1.87×10^6	5.71	-	-
15.077	1-methyl-2-propylcyclohexane	$C_{10}H_{20}$	-	-	4.39×10^5	0.53
15.132	(2-methylpropyl)-cyclohexane	$C_{10}H_{20}$	-	-	2.31×10^5	0.28
15.424	1-Methyl-4-(1-methylethyl)-cyclohexane	$C_{10}H_{18}$	-	-	2.22×10^5	0.27
15.924	(1-methylpropyl)-Cyclohexane	$C_{10}H_{20}$	-	-	3.29×10^5	0.40
16.034	n-butylbenzene	$C_{10}H_{14}$	-	-	5.67×10^5	0.68
16.136	Cyclopropylbenzene	C_9H_{10}	-	-	1.08×10^5	1.31
16.321	1-methyl-3-propylbenzene	$C_{10}H_{14}$	-	-	9.61×10^5	1.16
16.441	n-butylbenzene	$C_{10}H_{14}$	-	-	3.89×10^5	0.47
16.588	3-methylphenol	C_7H_8O	2.04×10^6	6.25	-	-
16.944	Guaiacol	$C_7H_8O_2$	5.13×10^6	15.71	-	-
17.134	(2-Methylbutyl)cyclohexane	$C_{11}H_{22}$	-	-	3.31×10^5	0.40
17.832	Pentylcyclohexane	$C_{11}H_{22}$	-	-	5.45×10^5	0.66
17.888	2,4-dimethylphenol	$C_8H_{10}O$	2.89×10^5	0.88	-	-
17.919	(3-methyl-2-butenyl)-benzene	$C_{11}H_{14}$	-	-	3.36×10^5	0.41

18.151	3-ethylphenol	$C_8H_{10}O$	1.43×10^6	4.37	-	-
18.152	2,5-Dimethylphenyl methyl carbinol	$C_{10}H_{14}O$	-	-	1.03×10^6	1.24
18.395	1,2,3,4-tetrahydro-Naphthalene	$C_{10}H_{12}$	-	-	8.78×10^5	1.06
18.658	Creosol	$C_8H_{10}O_2$	7.09×10^6	21.71	-	-
19.247	3,4-dimethoxyltoluene	$C_9H_{12}O_2$	4.63×10^5	1.42	-	-
19.249	1,2,3,4-tetrahydro-2-methyl- Naphthalene	$C_{11}H_{14}$	-	-	5.24×10^5	0.63
19.563	3-propylphenol	$C_9H_{12}O$	1.21×10^6	3.69	-	-
19.927	4-ethyl-2-methoxyphenol	$C_9H_{12}O_2$	4.73×10^6	14.50	-	-
20.460	4-ethyl-1,2-dimethoxybenzene	$C_{10}H_{14}O_2$	3.93×10^5	1.20	-	-
20.634	2,5-diol-p-cymene	$C_{10}H_{14}O_2$	2.71×10^5	0.83	-	-
20.884	4-(2-propenyl)-phenol	$C_9H_{10}O$	6.56×10^5	2.01	-	-
21.171	2-methoxy-4-propylphenol	$C_{10}H_{14}O_2$	2.76×10^6	8.28	-	-
21.502	4-(1-methylethyl)-benzaldehyde	$C_{10}H_{12}O$	1.27×10^6	3.89	-	-