Electronic Supplementary Information (ESI)

Enhanced production of phenol and debromination by co-pyrolysis of the non-metallic fraction of printed circuit boards and waste tire

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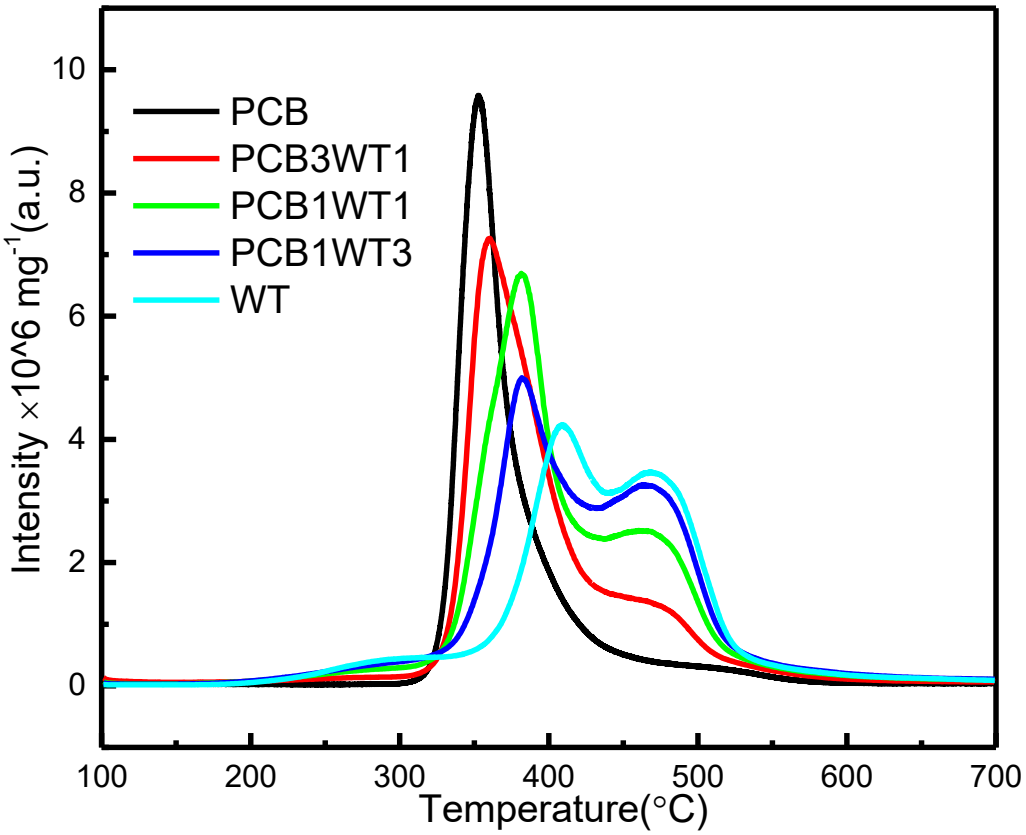

Fig. S1 Total ion chromatograms of PCB, WT and their blends obtained by EGA-MS

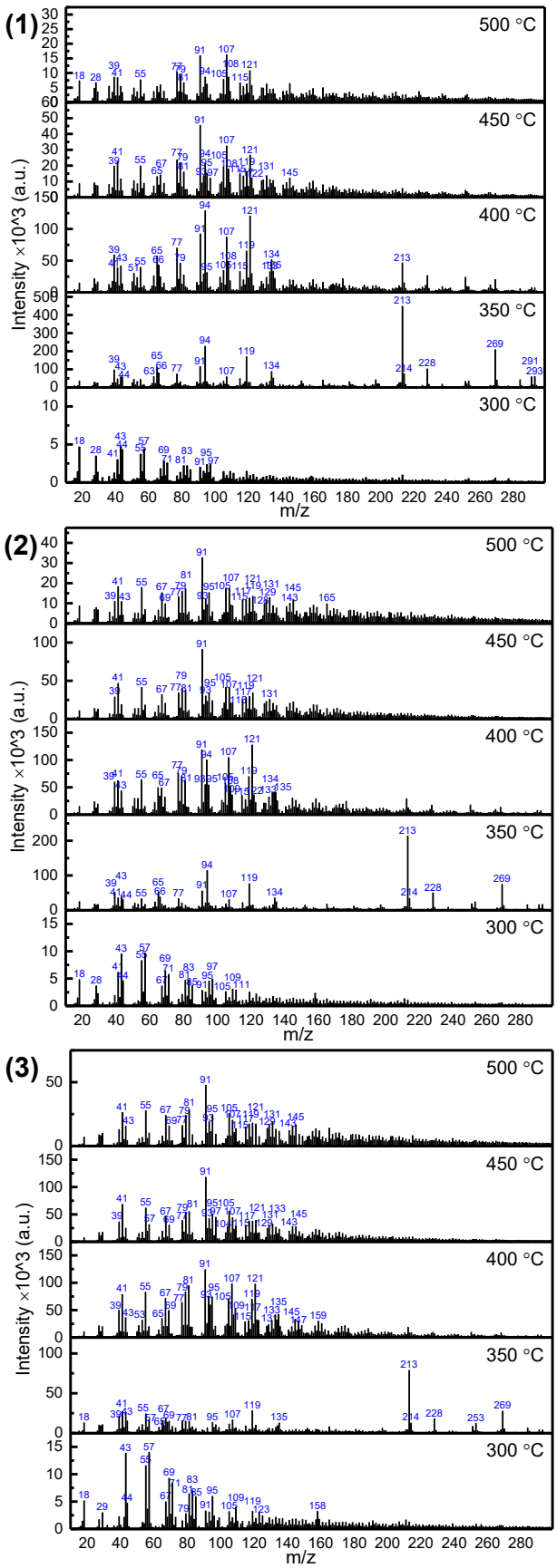

Fig. S2 The mass spectra of the evolved products from the co-pyrolysis of PCB and WT at different temperatures: (1) PCB3WT1; (2) PCB1WT1; (3) PCB1WT3

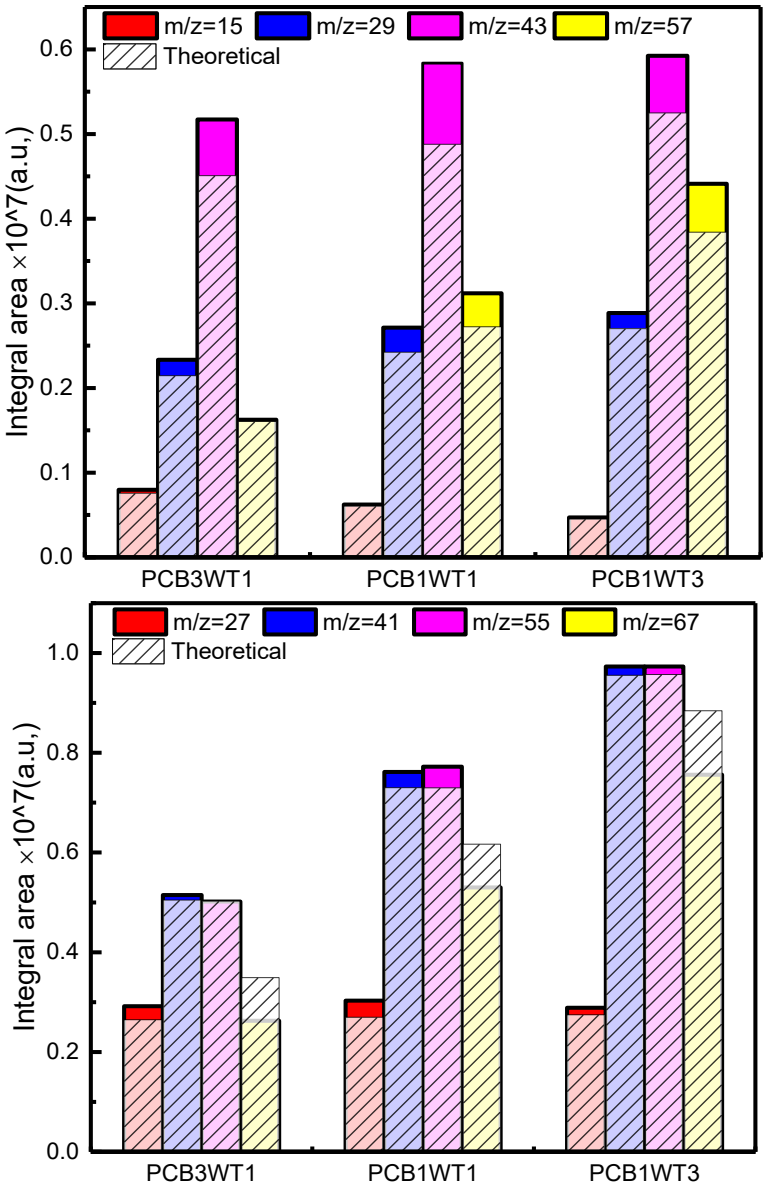

Fig. S3 Integral area of the specific fragment ions formed from the PCB and WT blends

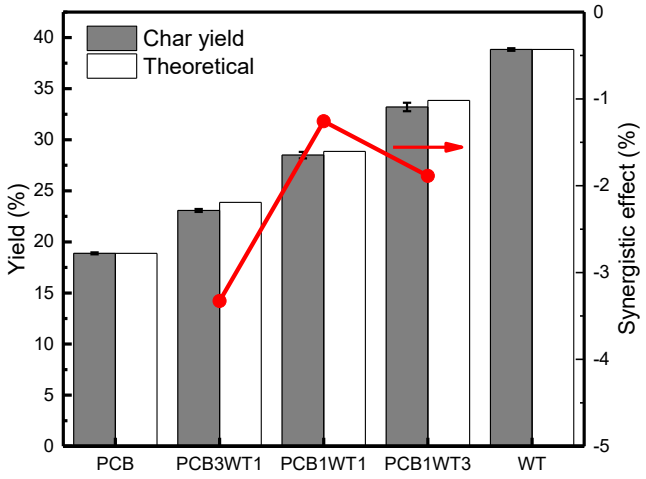

Fig. S4 Yield of char obtained from the pyrolysis of PCB, WT, and their blends at 500 °C

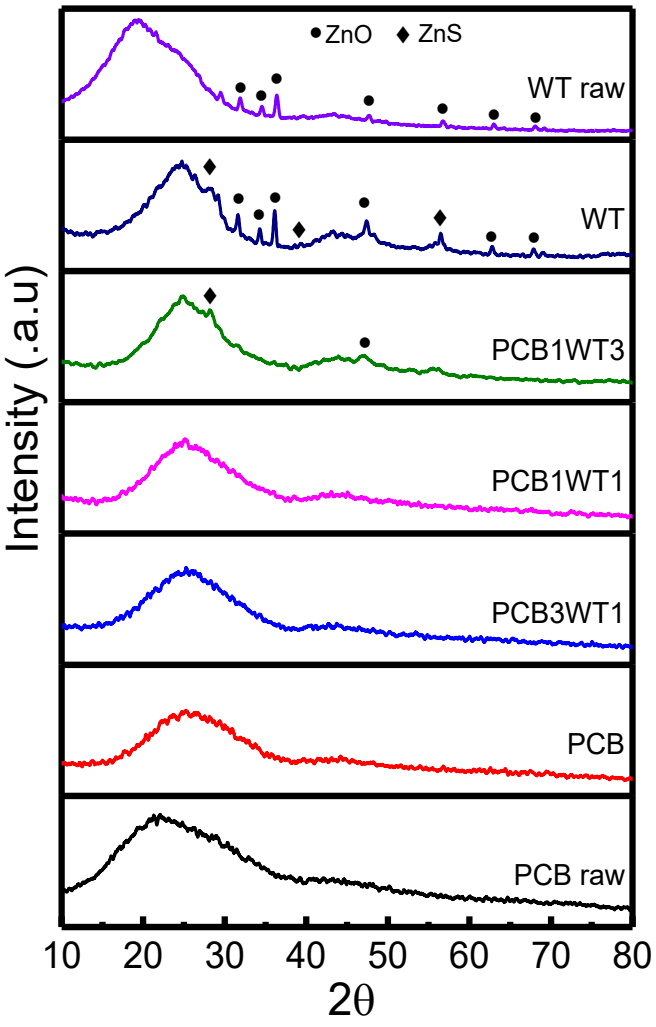

Fig. S5 XRD patterns of the pyrolysis char derived from PCB, WT, and their blends

Table S1 Trace elements in sample by ICP/MS

Element (wt%)	PCB	WT
B	1.63	-[a]
Na	0.26	0.11
Mg	0.21	0.07
Al	4.31	0.04
Si	18.35	1.25
P	-	0.02
K	-	1.01
Ca	10.57	0.35
Fe	0.13	0.09
Ni	-	0.01
Cu	-	0.01
Zn	-	1.01

[a] **Not detected**

Table S2. Py-GC/MS and EGA-MS equipment and method characteristics.

Equipment	**EGA/PY-3030D, Agilent 6890 GC & 5975C MS**
Py-GC	
Py heating program	50 °C → 10 °C min^{-1} → 500 °C (10 min)
Column	Ultra ALLOY® Capillary Column UA^{+}-5, 30 m × 0.25 mm × 0.25 μm, 95 % polydimethylsiloxane and 5 % polydiphenyldimethylsiloxane stationary phase
GC oven program	35 °C (5 min) → 5 °C min^{-1} → 300 °C (10 min)
Py-EGA	
Py heating program	50 °C → 10 °C min^{-1} → 800 °C
Column	Ultra ALLOY® deactivated metal capillary tube, 3 m ×0.15 mm
GC oven program	hold at 300 °C
Common conditions	
Sample volume	1.0 mg
Carrier gas	He
Carrier gas flow	1.0 mL/min
Split mode	Split ratio 100:1
Py-GC/MS interface temperatures	300 °C/300 °C/280 °C
MS detector temperature (quad/source)	150 °C/230 °C
EI mode	70 eV
Acquisition mode	scan
Mass range	10–600 a.m.u.

Table S3 Identified compounds from the pyrolysis of PCB, WT and their blends by Py-GC/MS

Compounds	Absolute peak area for each sample ($\times 10^7$ PA mg^{-1})				
	PCB	**PCB3 WT1**	**PCB1 WT1**	**PCB1 WT3**	**WT**
Alkene	***0.6±0.1***	***6.9±0.5***	***16.5±1.0***	***20.7±0.7***	***33.3±0.9***
Propene	0.5±0.1	1.1±0.3	1.4±0.2	0.0±0.0	0.2±0.0
Isobutene	-[a]	3.1±0.7	6.4±1.2	0.6±0.1	1.1±0.3
Isoprene	-	1.1±0.0	2.0±0.3	2.3±0.2	5.2±0.6
Cyclopentene	-	0.3±0.0	0.5±0.1	0.5±0.2	0.4±0.1
trans-1,4-Hexadiene	-	-	-	0.4±0.1	0.3±0.1
2-Methylpentene	-	-	0.6±0.2	0.9±0.3	0.3±0.0
2-Methyl-1,3-pentadiene	-	-	0.2±0.0	0.5±0.1	0.4±0.3
1-Methyl-1,3-cyclopentadiene	-	-	-	0.3±0.2	0.4±0.1
1-Methylcyclopentene	-	0.1±0.0	0.3±0.1	0.6±0.3	0.6±0.1
1,3-Cyclohexadiene	-	-	0.1±0.1	0.3±0.1	0.3±0.0
Cyclohexene	-	0.1±0.1	0.2±0.1	0.3±0.1	0.2±0.1
2,4,4-Trimethyl-1-pentene	-	0.1±0.0	0.2±0.0	0.3±0.2	0.4±0.3
4-Ethenylcyclohexene	-	0.2±0.0	0.5±0.4	0.9±0.5	0.9±0.4
2,5,5-trimethylcyclopentadiene	-	-	-	0.3±0.1	-
2,5,5-Trimethyl-1,3,6-heptatriene	-	-	-	0.5±0.1	0.6±0.3
1,6-Dimethylhepta-1,3,5-triene	-	-	-	1.0±0.4	0.7±0.2
p-Cymene	0.1±0.0	0.2±0.0	0.4±0.1	0.5±0.1	0.3±0.0
D-limonene	-	0.6±0.1	3.8±0.3	10.5±0.5	21.1±0.7
Alkane	***-***	***0.7±0.1***	***3.4±0.5***	***3.3±0.2***	***3.2±0.4***
Butane	-	-	1.4±0.5	0.7±0.2	0.5±0.1
1,1-Dimethylcyclopropane	-	0.3±0.0	0.9±0.2	0.7±0.2	1.1±0.5
Isopropylidenecyclobutane	-	0.4±0.1	0.9±0.3	1.2±0.4	0.9±0.3
Do-/Tetra-/Nonacosane	-	-	0.2±0.2	0.7±0.2	0.8±0.4
Aromatics	***0.3±0.1***	***4.0±0.3***	***6.7±0.3***	***13.4±0.5***	***13.9±0.3***
Benzene	0.1±0.0	0.2±0.0	0.2±0.0	0.4±0.1	0.4±0.1
Toluene	-	1.2±0.2	1.4±0.4	2.8±0.7	3.0±0.5
Ethylbenzene	-	0.2±0.0	0.5±0.2	1.0±0.3	0.8±0.1
p-Xylene	0.1±0.0	0.5±0.1	0.8±0.2	1.4±0.4	0.9±0.2
Styrene		1.5±0.1	2.9±0.1	4.9±0.2	5.4±0.4
3-Ethyltoluene	0.1±0.0	0.2±0.0	-	0.5±0.1	-
α-Methylstyrene	-	0.1±0.0	0.6±0.1	1.7±0.2	2.1±0.4
4-Allyltoluene	-	-	-	0.2±0.0	0.2±0.0
1,3-Diphenylpropane	-	0.2±0.0	0.4±0.0	0.6±0.3	0.7±0.1
1,3,5-Triphenylcyclohexane	-	-	-	-	0.4±0.2
Phenolic compounds	***337.1±8.1***	***227.1±10.3***	***140.1±5.4***	***71.1±3.2***	***2.2±0.2***
Phenol	62.5±1.5	65.4±5.4	45.1±3.2	23.6±1.0	-
2-/4-methylphenol	19.0±1.4	14.3±1.1	9.0±0.8	5.6±0.4	0.1±0.0
2,6-/2,4-Dimethylphenol	8.9±0.4	5.5±1.3	4.5±0.7	3.1±0.4	0.7±0.1
Ethylphenol	2.3±0.3	1.6±0.3	1.3±0.1	0.5±0.0	-
2-Allylphenol	0.5±0.2	0.8±0.3	0.8±0.2	0.8±0.1	-

2,4,6-Trimethylphenol	1.1±0.4	0.8±0.5	0.6±0.2	0.4±0.3	0.3±0.0
p-Isopropylphenol	10.2±1.4	12.1±0.5	9.5±0.6	5.4±0.1	-
Thymol	0.6±0.2	0.6±0.3	0.5±0.1	-	-
p-Isopropenylphenol	2.1±0.5	0.6±0.3	1.9±0.5	3.1±0.7	-
4-Phenylphenol	1.9±0.4	1.8±0.5	0.8±0.3	0.2±0.0	-
4-Cumylphenol	-	0.4±0.1	0.2±0.0	-	0.4±0.1
2,2'-Methylenediphenol	2.0±0.2	1.6±0.3	1.6±0.1	0.7±0.1	-
2,2'-Methylenebis(4-methylphenol)	10.4±2.3	5.8±1.2	3.6±1.8	-	-
2-(4'-Hydroxyphenyl)-2-(4'-methoxyphenyl)propane	0.9±0.2	0.9±0.3	0.7±0.1	0.6±0.2	-
Bisphenol A	166.6±2.7	94.7±3.6	50.4±1.1	23.4±0.5	-
2-(1,1-dimethylethyl)-4-(1-methyl-1-phenylethyl)phenol	3.6±1.2	3.3±1.1	2.5±0.9	1.5±0.5	-
Tetramethylbisphenol A	42.7±8.2	15.1±3.5	6.6±2.2	2.1±1.0	0.7±0.4
Bisphenol A diglycidyl ether	1.9±1.2	1.9±1.3	0.6±0.5	-	-
Brominated compounds	***39.5±4.3***	***21.9±2.3***	***14.1±1.3***	***7.8±0.4***	-
Bromomethane	5.4±1.3	4.8±0.5	3.3±0.3	3.4±0.4	-
Hydrogen bromide	6.1±2.1	2.7±1.8	-	-	-
Bromoethane	0.2±0.0	0.3±0.1	0.2±0.0	0.1±0.0	-
1-bromopropane	0.3±0.1	0.2±0.0	0.2±0.1	0.1±0.0	-
3-Bromopropene	0.6±0.1	0.3±0.1	0.3±0.0	0.1±0.0	-
Bromoacetone	1.6±0.3	0.3±0.0	0.1±0.1	-	-
1-Bromobutane	0.6±0.1	-	-	-	-
2-Bromophenol	3.3±0.1	1.8±0.4	1.4±0.0	0.5±0.0	-
2,6-Dibromophenol	7.7±0.3	3.8±0.4	2.6±0.4	0.8±0.0	-
2,5-Dibromobenzo(b)thiophene	2.2±0.7	1.7±0.3	1.9±0.5	1.4±0.3	-
TBBPA	11.5±0.7	6.1±0.6	4.2±0.6	1.5±0.5	-
Nitrogen compounds	***1.2±0.5***	***2.1±0.5***	***2.6±0.2***	***3.3±0.3***	***4.1±0.5***
Benzothiazole	-	0.2±0.0	0.3±0.1	0.6±0.1	1.6±0.2
2,2,4-Trimethyl-1,2-dihydroquinoline	-	0.2±0.0	0.5±0.0	1.1±0.2	1.2±0.4
1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-	-	0.1±0.0	0.4±0.0	0.8±0.1	1.3±0.5
4,4'-Bis(dimethylamino)stilbene	1.2±0.5	1.6±0.7	1.3±0.5	0.9±0.3	-
Others	***8.0±2.0***	***11.8±1.2***	***12.2±0.8***	***11.6±0.5***	***12.2±0.3***
Carbon dioxide	5.0±2.0	6.2±1.7	4.5±1.0	1.4±0.5	0.6±0.1
Acrylaldehyde	-	-	0.5±0.1	0.4±0.0	-
Acetone	2.9±0.5	3.4±0.7	1.4±0.5	0.9±0.3	-
Benzofuran, 3-methyl-2-(1-methylethenyl)-	-	-	-	0.9±0.3	0.4±0.2
n-Hexadecanoic acid	-	1.8±0.1	3.9±0.2	5.1±0.1	6.8±0.3
Cembrene A	-	-	-	0.5±0.0	0.6±0.1
Heptadecanolide	-	-	-	-	0.5±0.0
Octadecanoic acid	-	0.5±0.1	2.0±0.1	2.5±0.2	3.4±0.2

[a]: not detected or $< 0.01 \times 10^7$ PA mg^{-1}

Table S4 The major fragment ions of specific compounds identified by Py-GC/MS and NIST library

Identification	**Mn**	**ESI-MSn *m,z* [Intensity,%][a,b]**
H_2O	18	**18**
CH_4	16	**16**;15[88]
CO	28	**28**
Carbon dioxide	44	**44**
Propene	42	**41**;42,29[75];27[40]
Propane	44	**29**;28[60];27[40];44,43[30]
Isobutene	54	**41**;39,56[45]
1,3-Butadiene	54	**39**;54,53[70]
Butene	56	**41**;56[39];39[34]
Butane	58	**43**;29[45];27[40]
Acetone	58	**43**;58[25]
Isoprene	68	**67**;68,53[65];39[50];27[22]
Cyclopentene	68	**67**;68[45];39,53[25]
1,1-Dimethylcyclopropane	70	**55**;39,70[45];41[35]
1,3-Cyclohexadiene	80	**79**;77,80[45];39,51[20]
1-Methylcyclopentene	82	**67**;82[30];81[18]
Cyclohexene	82	**67**;54[67];39[45];82,41[30]
4-Ethenylcyclohexene	108	**54**;79[65];80[40];66[38];67,39,93[30]
p-Cymene	134	**119**;134[30];91[18]
D-Limonene	136	**68**;93[60];67[45];136,121,107,94,79[20-25]
Benzene	78	**78**;77[30];51,50,52[20]
Toluene	92	**91**;92[78]
Ethylbenzene	106	**91**;106[30]
p-Xylene	106	**91**;106[65];105[30]
Styrene	104	**104**;103[50]78[50]
α-Methylstyrene	118	**118**;117[65];103[45];78[30];77,91[20]
Phenol	94	**94**;66[40];65,39[35]
2-Methylphenol	108	**108**;107[70];79[35];77,90[20]
4-Methylphenol	108	**107**;108[70];77[35];79[20]
2,6-Dimethylphenol,	122	**122**;107[90];77[42];121,91,77[30]
3-Ethylphenol	122	**107**;122[45];77[20]
p-Isopropylphenol	136	**121**;136[35];91,77[25]
p-Isopropenylphenol	134	**134**;119[80]
p-Hydroxybiphenyl	170	**170**;141,115[30]
Bisphenol A	228	**213**;228[25];119[20]
Hydrogen bromide	81	**80**;82[96];79,81[40]
Bromomethane	95	**94**;96[95];15[45]
Bromoethane	109	**29**;27[95];108,110[60];26[45]
1-Bromopropane	123	**43**;41[35];27[35];122,124[10]

3-Bromopropene	121	**41**;39[75];120,122[20]
Bromoacetone	137	**43**;136,138[10]
1-Bromobutane	137	**57**;41[70];29[55]27[50]
4-Bromobutene	135	**55**;39,29,27[17-20]
2-Bromophenol	173	**172**;174[95];65[45]64[35]63[30]
2,6-Dibromophenol	252	**252**;250,254[50];63[48]
TBBPA	543	**529**;527[70];531[65];152,293[33];544[25]
Benzothiazole	135	**135**;108[35];69[25]
Quinoline, 1,2-dihydro-2,2,4-trimethyl-	173	**158**;159[15];157[10]
1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-	268	**211**;268[50];183[20];167,105[18]
n-Hexadecanoic acid	256	**43**;73[90];60[85];41[75];57,55[65];29[40]
9-Octadecenoic acid	282	**55**;69[85]41,83[70]43,97,264[50]
Octadecanoic acid	284	**43**;73[90];60,57,55[85];41[70];129[50]
Tetracosane	338	**57**;43[80];71[70];85[55]
Docosane		**57**;43[75];71[65];85[45]

[a]: *Bold is the base peak with 100% intensity.*

[b]*:Reference: NIST Standard Reference Database Number 69, Available from: https://doi.org/10.18434/T4D303.*

Table S5 Elemental analysis of the pyrolysis chars at 500 °C

Sample[a]	Content (wt%)				
	C	H	N	S	Br
PCB	92.4	5.6	0.8	-	0.5
PCB3WT1	87.3	3.2	0.2	0.3	1.3
PCB1WT1	89.7	2.0	0.2	0.7	1.6
PCB1WT3	88.2	1.3	0.4	1.5	1.8
WT	80.2	0.7	0.2	1.7	-

[a]: *The fraction of glass fiber in the solid residue was excluded.*