

Supporting Information

Upgrading coal tar products into hypercrosslinked polymers by mechanosynthesis

A.M. Borrero-López^{1,2}, J. Castro-Gutiérrez^{1,}, E. Derveaux,^{3,4} W. Marchal^{3,4}, A. Celzard^{1,5},
V. Fierro^{1,*}*

¹ *Université de Lorraine, CNRS, Institut Jean Lamour (IJL), F-88000 Epinal, France*

² *Pro2TecS – Chemical Process and Product Technology Research Centre. Dept. Chemical Engineering, ETSI.
Campus de “El Carmen”. Universidad de Huelva. 21071 Huelva. Spain*

³ *Hasselt University, Institute for Materials Research (IUMAT), Metabolomics and Advanced Solid state NMR
group (MAS-NMR), Martelarenlaan 42, B-3500 Hasselt, Belgium*

⁴ *imec, IUMAT, Wetenschapspark 1, B-3590 Diepenbeek, Belgium*

⁵ *Institut Universitaire de France (IUF), F-75231, Paris, France*

Table S1. Main components of distilled coal tar pitch (DCTP).

Distilled coal tar pitch	
Abundance (wt.%)	Compound
18.26	Acenaphthene
10.50	Anthracene
8.35	Indane
7.21	Fluoranthene
4.74	Pyrene
3.00	Naphthalene
2.76	Fluorene
2.53	1H-Benzo[b]fluorene
2.45	Naphthalene, 2-methyl-
1.99	Naphthalene, 1-phenyl-
1.96	Triphenylene
1.75	Phenanthrene, 2-methyl-
1.74	Benzene, [1-(2,4-cyclopentadien-1-ylidene)ethyl]-
1.62	5H-Indeno[1,2-b]pyridine
1.45	4H-Cyclopenta[def]phenanthrene
1.44	Benz[a]anthracene
1.40	1,1'-Biphenyl, 4-methyl-
1.16	Pyrene, 1-methyl-
1.11	Naphthalene, 1-methyl-
1.02	Benzo[b]fluoranthene
0.98	Naphthalene, 2-ethyl-
0.94	1,1'-Biphenyl, 2-methyl-
0.90	Anthracene, 1,2,3,4-tetrahydro-
0.83	Dibenzofuran
0.81	Naphthalene, 2,7-dimethyl-
0.80	Ethylbenzene
0.71	Benzene, (2-methyl-1-propenyl)-
0.70	Benzene, 1-ethyl-3-methyl-
0.69	Benzene, 2-ethenyl-1,4-dimethyl-
0.69	9H-Fluorene, 2-methyl-
0.67	Dibenzofuran, 4-methyl-
0.67	Naphtho[2,1-b]thiophene
0.66	Anthracene, 9,10-dihydro-
0.65	1,2,3,4-Tetrahydro-1-phenyl-1,2,3-methanonaphthalene
0.61	o-Xylene
0.51	Cyclopenta(cd)pyrene, 3,4-dihydro-
0.51	o-Terphenyl
0.49	Acenaphthylene, 1,2,2a,3,4,5-hexahydro-
0.48	p-Xylene
0.46	1H-Indene, 2,3-dihydro-5-methyl-
0.46	1,2,4,8-Tetramethylbicyclo[6.3.0]undeca-2,4-diene
0.41	Benzo[b]naphtho[2,1-d]thiophene
0.40	Anthracene, 1-methyl-
0.40	4-Carbomethoxy-3-methoxy-4-methyl-2,5-cyclohexadien-1-one
0.39	Benzene, 2-butenyl-
0.38	Benzo[ghi]fluoranthene
0.38	4-O-Methoxyphenylhydrazono-3-methyl-2-pyrazolin-5-one
0.35	Benzene, 1-ethyl-3,5-dimethyl-
0.34	Phenanthrene, 1,2-dihydro-
0.33	Pyrene, 1,3-dimethyl-
0.32	Benzo[e]pyrene
0.31	Benzo[b]naphtho[2,1-d]furan
0.29	Benzo(c)carbazole
0.29	Perylene
0.25	4,4'-Bis(tetrahydrothiopyran)
0.24	4H-Benzo[def]carbazole

Table S1 (continued). Main components of distilled coal tar pitch (DCTP).

Distilled coal tar pitch	
Abundance (wt.%)	Compound
0.23	Naphthacene, 5,12-dihydro-
0.23	Naphthalene, 2,6-dimethyl-
0.22	1,8-Anthracenediamine
0.22	11H-Benzo[a]carbazole
0.22	Indeno[2,1-b]chromene,
0.20	Acridine, 9,10-dihydro-
0.20	Benzene, 1,2,4-trimethyl-
0.20	9H-Fluorene, 9-methyl-
0.20	Phenanthrene, 3,6-dimethyl-
0.20	Triphenylene, 2-methyl-
0.19	Benzo[g]quinoline
0.19	Naphthalene, 1-ethyl-
0.19	Phenanthrene, 2,5-dimethyl-
0.18	Naphthalene, 2,3,6-trimethyl-
0.17	Hydrazinecarboxamide, 2-(2,6-dimethylcyclohexylidene)-
0.17	Naphthalene, 1,7-dimethyl-
0.17	Naphthalene, 2,3-dimethyl-
0.16	Anthracene, 2-ethyl-
0.16	Benzene, 1,2,3-trimethyl-
0.14	Naphthalene, 1,2,3,4-tetrahydro-
0.13	o-Toluidine
0.12	Benzo[b]naphtho[2,3-d]furan
0.11	Benzene, cyclopentyl
0.06	Cyclohexane, hexaethylidene- (ISOMER 2)

Table S2. Main components of depleted naphthalene oil (DNO).

Depleted Naphthalene oil	
Abundance (wt.%)	Compound
50.42	Naphthalene
26.02	Naphthalene, 2-methyl-
7.35	Naphthalene, 1-methyl-
4.31	Quinoline
4.13	Benzo[b]thiophene
1.87	1-Methyl-2-phenylcyclopropane
1.13	Biphenyl
1.12	Indane
1.03	Phenol, 3,5-dimethyl-
0.78	3-Phenyl-1-propyne
0.67	p-Cresol
0.66	Quinoline
0.50	Benzene, 1-butyryl-

Table S3. Main components of wash oil.

Wash oil	
Abundance (wt.%)	Compound
21.67	Acenaphthene
16.11	Fluorene
12.16	Dibenzofuran
10.40	Naphthalene
6.61	Naphthalene, 1-methyl-
4.07	Biphenyl
3.62	Naphthalene, 2-methyl-
3.61	Dibenzofuran, 4-methyl-
2.39	Naphthalene, 2,7-dimethyl-
1.97	Anthracene
1.97	Diphenylmethane
1.81	1-Isopropenylnaphthalene
1.64	1,1'-Biphenyl, 4-methyl-
1.24	Naphthalene, 2-ethyl-
1.20	Naphthalene, 1,6,7-trimethyl-
1.01	Naphthalene, 2,3-dimethyl-
0.73	Quinoline
0.64	Naphthalene, 2,3,6-trimethyl-
0.59	9H-Fluorene, 2-methyl-
0.43	1-Naphthalenecarbonitrile
0.42	Naphthalene, 1,4,6-trimethyl-
0.35	Anthracene, 9,10-dihydro-
0.35	Naphthalene, 2,6-dimethyl-
0.28	Dibenzothiophene
0.28	Quinoline, 8-methyl-
0.25	Naphthalene, 1-ethyl-
0.24	Benzo[b]thiophene
0.20	Biphenylene
0.16	5-Methyl-5H-dibenzo[b,d]silole
0.12	4-Carbomethoxy-3-methoxy-4-methyl-2,5-cyclohexadien-1-one
0.11	1,1'-Biphenyl, 2-methyl-
0.10	1-Ethynyl-2-(methylsulfanyl)benzene

Table S4. Main components of naphthalene oil.

Naphthalene oil	
Abundance (wt.%)	Compound
87.40	Naphthalene
8.37	Naphthalene, 1-methyl-
2.67	Naphthalene, 2-methyl-
1.56	Cyclopenta[b]thiopyran

Table S5. Main components of chrysene oil.

Chrysene oil	
Abundance (wt.%)	Compound
17.60	Fluoranthene
14.64	Pyrene
11.59	Anthracene
9.56	Triphenylene
6.18	1H-Benzo[a]fluorene
5.43	Benzo[b]fluoranthene
2.13	4H-Cyclopenta[def]phenanthrene
2.11	Pyrene, 1-methyl-
1.96	5H-Indeno[1,2-b]pyridine
1.50	Cyclopenta(cd)pyrene, 3,4-dihydro-
1.44	Phenanthrene, 2-methyl-
1.42	Naphthalene
1.37	Pyrene, 1,3-dimethyl-
1.15	Cyclopenta[cd]pyrene
1.13	Benzo[a]pyrene
1.10	Benzo[b]naphtho[2,3-d]furan
1.05	Benzo[b]naphtho[2,1-d]thiophene
1.01	Fluorene
0.91	1H-Benzo[a]carbazole
0.87	4H-Benz[de]anthracene, 5,6-dihydro-
0.78	Naphthalene, 1-phenyl-
0.76	Acenaphthene
0.73	2-Phenylnaphthalene
0.70	9-(Cyanomethylene)fluorene
0.69	Benzo[c]acridine
0.69	9H-Cyclopenta[a]pyrene
0.67	4H-Benzo[def]carbazole
0.66	Benzo(c)carbazole
0.57	Benz[a]anthracene, 1-methyl-
0.56	5-Bromothiophene-2-carboxylic acid
0.54	Anthracene, 1-methyl-
0.52	Benzo[ghi]perylene
0.52	Phenanthrene, 1-methyl-
0.49	Dibenzothiophene
0.48	Anthra(1,2-b)thiophene
0.48	Benzo[e]pyrene
0.46	9-Anthracenecarbonitrile
0.46	Dibenzofuran
0.45	Cyclohexane, hexaethylidene- (ISOMER 2)
0.45	Naphthacene, 5,12-dihydro-
0.40	9H-Carbazole, 2-methyl-
0.34	Acridine
0.34	Phenanthrene, 3,6-dimethyl-
0.29	Indeno[2,1-b]chromene,
0.25	Chrysene, 1-methyl-
0.24	Chrysene, 6-methyl-
0.24	8,9-Dihydro-7H-cyclopenta[a]pyrene

Table S5 (continued). Main components of chrysene oil.

Chrysene oil	
Abundance (wt.%)	Compound
0.23	Naphthalene, 1,8-di-1-propynyl-
0.23	Phenanthrene, 2,5-dimethyl-
0.22	Acridine, 9,10-dihydro-
0.22	1,4-Ethenoanthracene, 1,4-dihydro-
0.21	di-p-Tolylacetylene
0.18	7-Isopropenyl-1,4a-dimethyl-4,4a,5,6,7,8-hexahydro-3H-naphthalen-2-one
0.18	Anthracene, 2-ethyl-
0.18	Dinaphtho[1,2-b:1',2'-d]furan
0.15	Benzo[f]isoquinoline
0.15	Phenanthrene, 4,5-dimethyl-
0.14	Anthranilic acid, 2TMS derivative

Table S6. Main components of phenolic oil.

Phenolic oil	
Abundance (wt.%)	Compound
23.32	Indane
15.40	Naphthalene
13.34	Indene
9.59	Phenol
6.67	p-Cresol
5.94	p-Xylene
3.49	Phenol, 2-methyl-
2.93	Benzene, 1,2,3-trimethyl-
2.46	Benzene, 1-ethyl-3-methyl-
2.44	Mesitylene
2.02	Benzene, 1,3-dimethyl-
2.00	Benzofuran
1.70	Ethylbenzene
1.27	Benzene, (2-methyl-2-propenyl)-
1.05	Benzene, 1-ethyl-2,3-dimethyl-
0.99	Aniline
0.94	Benzene, 2-ethenyl-1,4-dimethyl-
0.92	Cinnamaldehyde, (E)-
0.79	Mesitylene
0.72	Benzene, 1-ethenyl-4-ethyl-
0.46	Benzofuran, 2-methyl-
0.45	Pyridine, 3,4-dimethyl-
0.41	Benzofuran, 2-methyl-
0.22	Benzene, 1,2,3,4-tetramethyl-
0.19	Benzene, 4-ethyl-1,2-dimethyl-
0.18	Benzene, (1-methylethyl)-
0.10	Benzo[b]thiophene

Table S7. Main components of creosote.

Creosote	
Abundance (wt.%)	Compound
21.65	Anthracene
13.22	Acenaphthene
8.64	Naphthalene
7.12	Fluorene
6.32	Dibenzofuran
4.09	Naphthalene, 1-methyl-
3.24	Fluoranthene
3.20	Dibenzofuran, 4-methyl-
2.92	Phenanthrene, 2-methyl-
2.57	4H-Cyclopenta[def]phenanthrene
2.30	Dibenzothiophene
2.28	Naphthalene, 2-methyl-
2.16	Naphthalene, 2,7-dimethyl-
2.00	Biphenyl
1.87	9H-Fluorene, 2-methyl-
1.44	Phenanthrene
1.36	Diphenylmethane
1.08	Indane
1.05	1-Isopropenylnaphthalene
1.05	Pyrene
0.78	Naphthalene, 2-phenyl-
0.67	5H-Indeno[1,2-b]pyridine
0.67	Naphthalene, 1,4-dimethyl-
0.63	Dibenzo[a,e]cyclooctene
0.61	Naphthalene, 2-ethyl-
0.59	Naphthalene, 1,6,7-trimethyl-
0.57	1,1'-Biphenyl, 3-methyl-
0.55	Acridine
0.52	Anthracene, 9,10-dihydro-
0.51	8-Dimethylaminonaphthalene-1-carbonitrile
0.47	Benzo[f]isoquinoline
0.39	Acridine, 9,10-dihydro-
0.38	Phenanthrene, 1-methyl-
0.38	Quinoline
0.36	Benzo[b]naphtho[2,3-d]furan
0.36	4-Carbomethoxy-3-methoxy-4-methyl-2,5-cyclohexadien-1-one
0.36	Naphthalene, 2,3,6-trimethyl-
0.34	1,1'-Biphenyl, 4-methyl-
0.33	Naphthalene, 2,3-dimethyl-
0.31	1-Naphthalenecarbonitrile
0.24	Naphthalene, 1,5-dimethyl-
0.14	Anthracene, 1,2,3,4-tetrahydro-9,10-dimethyl-
0.14	Phenanthrene, 1,2-dihydro-
0.12	Naphthalene, 1,4,6-trimethyl-

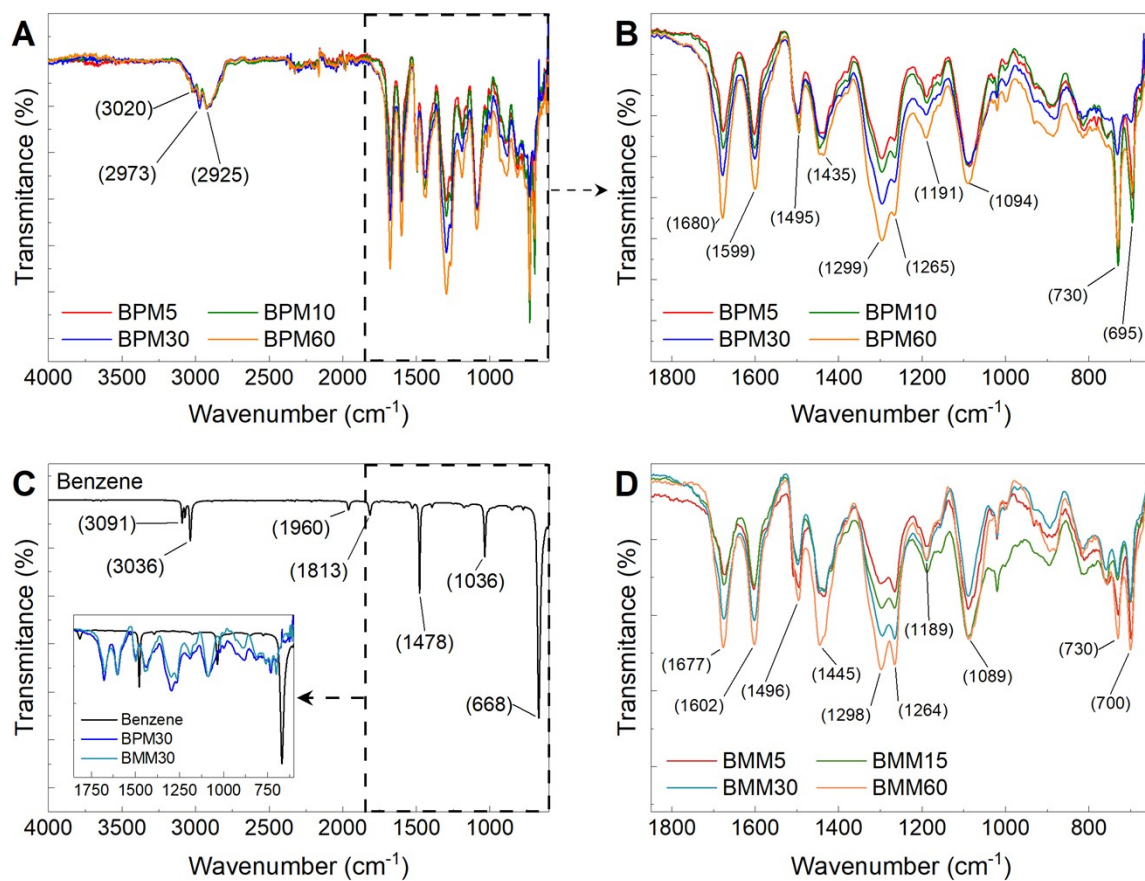


Figure S1. (A) FTIR spectra of benzene-derived HCPs at different reaction times prepared using a planetary mill (BPM t), (B) zoom in on the 2000 – 600 cm⁻¹ range to better observe the differences discussed. (C) FTIR spectrum of benzene. (D) FTIR spectra in the 2000 – 600 cm⁻¹ range of benzene-derived HCPs formulated at different reaction times using a mixer mill (BMM t). The inset in (C) compares the spectrum of the pristine benzene molecule to those of samples BPM30 and BMM30.

Table S8. TG analysis of benzene-derived HCPs obtained using a planetary mill and a mixer mill, BPM t , and BMM t , respectively, where t stands for the milling time in minutes. Each thermal event is identified by its onset and end temperature (T_{onset} and T_{end} , respectively), as well as by the temperature at which maximum mass loss occurs during the corresponding event (T_{max}). The total mass loss at each thermal event and the final residue at 900 °C are also reported ($-\Delta M$ and R_{900} , respectively).

Sample	T_{center} (°C)	T_{onset} (°C)	T_{end} (°C)	$-\Delta M$ (wt.%)	R_{900} (wt.%)*
BPM3	315	214	377	9	68
	485	377	493	7	
	540	493	900	16	
BPM5	297	237	373	9	71
	477	373	481	5	
	539	481	900	15	
BPM10	305	243	381	11	72
	479	381	511	7	
	553	511	900	10	
BPM15	312	216	380	9	71
	481	380	500	7	
	548	500	900	13	
BPM20	324	225	388	11	68
	489	388	517	9	
	551	517	900	12	
BPM30	323	235	389	12	70
	486	389	517	8	
	546	517	900	10	
BPM60	327	252	391	12	68
	498	391	525	10	
	547	525	900	10	
BMM5	243	203	365	9	61
	520	365	900	30	
BMM15	243	202	254	2	68
	296	254	376	9	
	544	376	900	21	
BMM30	239	206	247	2	69
	285	247	378	10	
	460	378	494	6	
	551	494	900	13	

* Residual weight fraction at 900 °C from TG analysis in inert atmosphere.

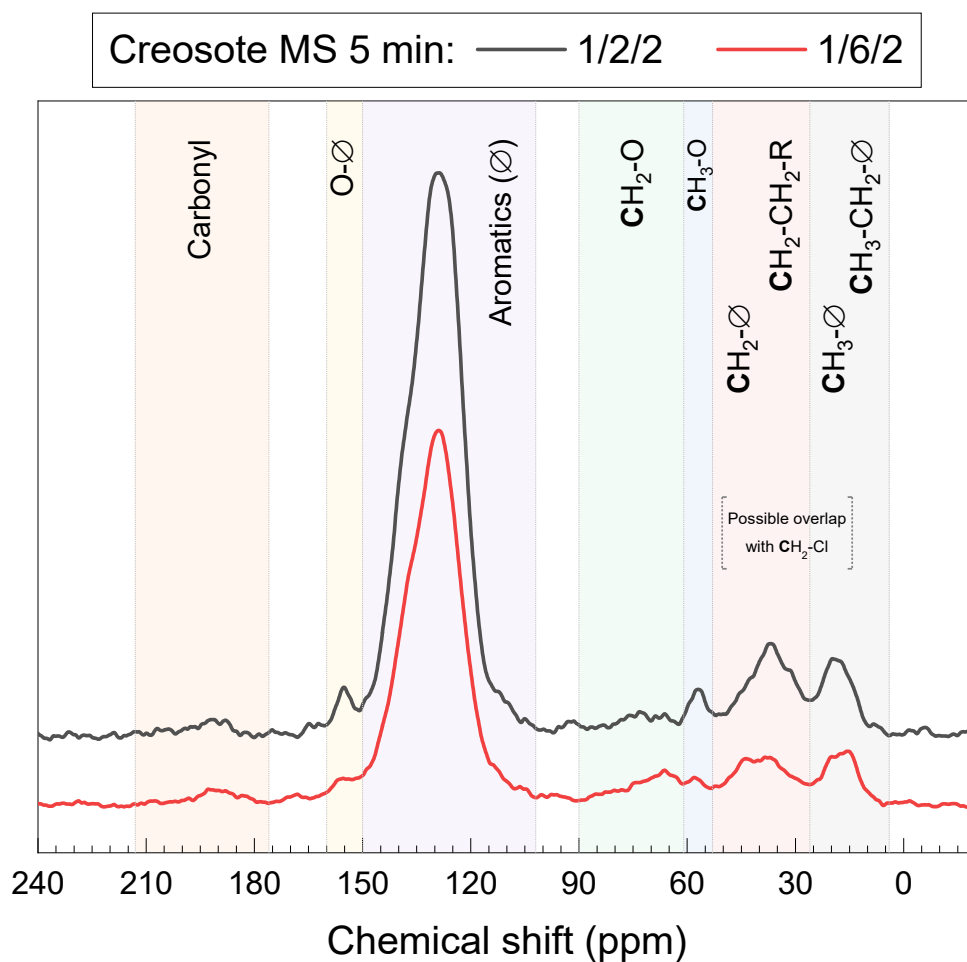


Figure S2. ^{13}C MAS solid-state NMR spectra for creosote-derived HCPs obtained using a 1/2/2 and 1/6/2 precursor/catalyst/crosslinker molar ratio and a reaction time of 5 min.

Table S9. ^{13}C MAS solid-state NMR signals and contributions for creosote MS 5 min 1/2/2 and 1/6/2 samples.

Signal	Contribution (%)	
	Creosote MS 5 min 1/2/2	Creosote MS 5 min 1/6/2
Carbonyl	1.50	2.73
O-∅	2.19	1.30
Aromatics (∅)	74.65	70.12
CH ₂ -O	2.91	5.70
CH ₃ -O	2.34	1.88
CH ₂ -∅ + CH ₂ -CH ₂ -R	9.78	9.30
CH ₃ -∅ + CH ₃ -CH ₂ -∅	6.06	6.48

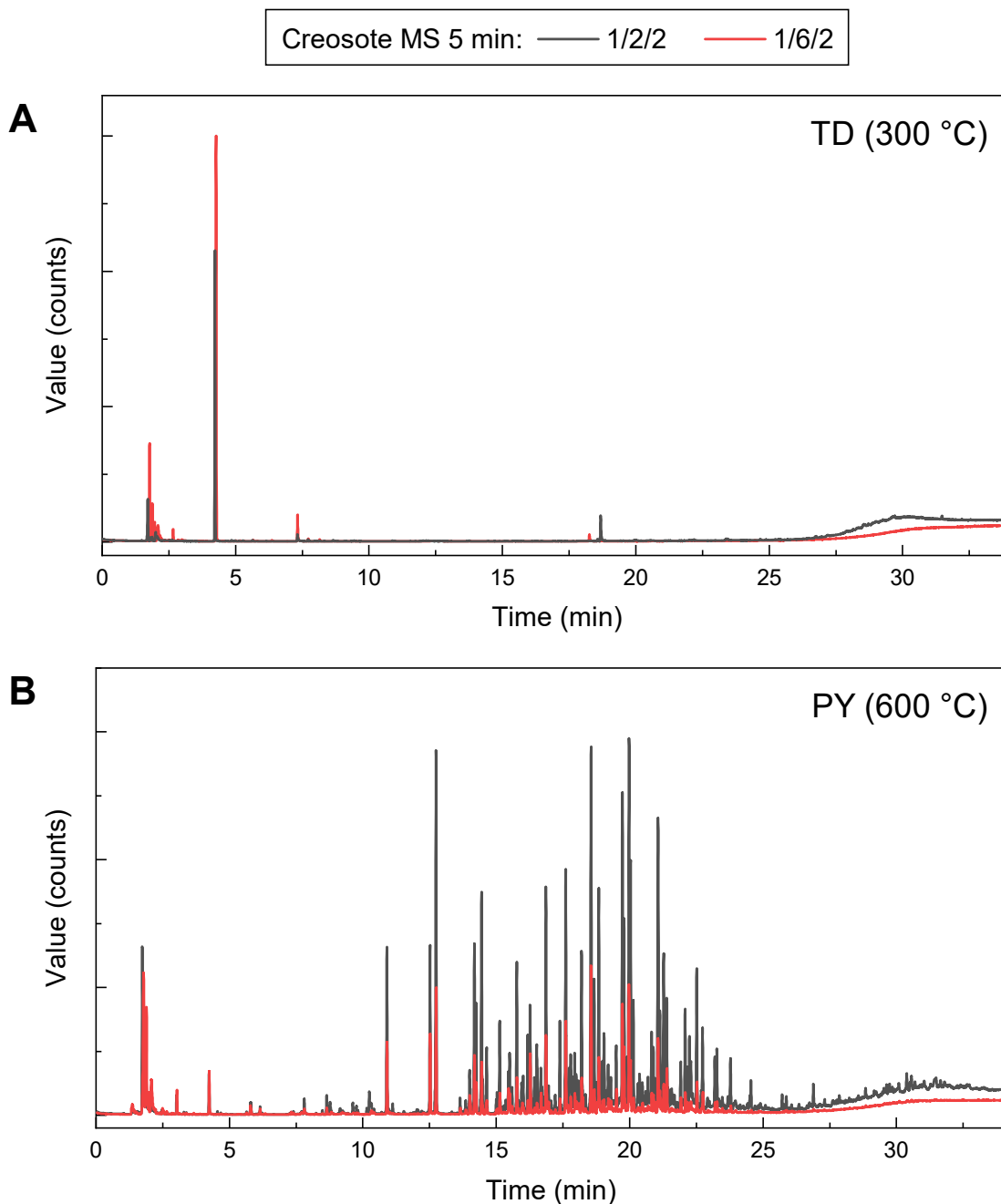


Figure S3. Chromatograms from TP-PY-GC/MS analysis for creosote MS 5 min 1/2/2 and 1/6/2 at (A) 300 °C and (B) 600 °C. For comparison, the 1/6/2 chromatograms were normalized by a factor of 0.756, which is the ratio of the sample sizes used for 1/2/2 and 1/6/2 samples.

Table S10. TP-GC/MS decomposition products for creosote MS 5 min 1/2/2 at 300 °C.

Creosote MS 5 min 1/2/2	
Compound	Relative area (%)
Carbon dioxide	11.48
Ethanol	6.61
Toluene	69.58
Benzaldehyde	2.71
Anthracene	9.61

Table S11. PY-GC/MS decomposition products for creosote MS 5 min 1/2/2 at 600 °C.

Creosote MS 5 min 1/2/2	
Compound	Relative area (%)
Carbon dioxide	1.76
Propane	0.19
Sulfur dioxide	0.44
Cyclopropyl carbinol	0.33
Toluene	0.37
Benzene	0.16
Benzene, C2-	0.20
Benzene, C3-	0.32
Phenol, C1-	0.22
Phenol, C2-	0.40
Phenol, C3-	0.12
Naphthalene	1.80
Naphthalene, C1-	6.40
Naphthalene, C2-	7.61
Naphthalene, C3-	5.11
Naphthalene, C4-	1.24
Biphenyl	0.16
Biphenyl, C2-	1.08
Biphenyl, C4-	0.73
1,1'-Biphenyl, C1-	1.13
1,1'-Biphenyl, C2-	0.67
Acenaphthene	0.24
Dibenzofuran	0.48
Fluorene	1.44
1-Isopropenylnaphthalene	0.46
9H-Fluorene-3-ol	0.39
9H-Fluorene, C1-	4.21
9H-Fluorene, C2-	0.43
9H-Xanthene	2.82
6H-Dibenzo[b,d]-pyran	0.26
Naphtho[2,1-b]furan, 1,2-dimethyl-	2.02
Phenanthrene	4.82
Anthracene	1.40
Acridine	0.22
Anthracene, 9,10-dihydro-2-methyl-	2.41
4-Phenanthrenol, 1,2,3,4-tetrahydro-4-methyl-	0.85
Dibenzothiophene, C1-	0.98
Dibenzothiophene, C2-	0.24
Anthracene / Phenanthrene, C1-	15.45
Anthracene / Phenanthrene, C2-	10.06
Anthracene / Phenanthrene, C3-	3.02
Acenaphthylene, C4-	1.19
Fluoranthene	1.18
Pyrene	0.48
Pyrene, C2-	1.22
Fluoranthene / Pyrene, C1-	3.46
Retene	0.59
7,12-Dihydro-2-methylbenz[a]anthracene	0.16
Naphthalene, 1,1'-methylenebis-	0.14
9,10-(1,2-Benzo)anthracene, 2,3-dimethyl-9,10-dihydro-	0.22

Table S12. TD-GC/MS decomposition products for creosote MS 5 min 1/6/2 at 300 °C.

Creosote MS 5 min 1/6/2	
Compound	Relative area (%)
Carbon dioxide	8.78
Chloromethane	1.68
Acetaldehyde	3.06
Ethyl Chloride	1.33
Ethanol	6.38
Ethyl Acetate	1.28
Toluene	68.92
Benzaldehyde	3.93
Benzyl chloride	0.25
Dibenzothiophene	1.20
Anthracene	0.32

Table S13. PY-GC/MS decomposition products for creosote MS 5 min 1/2/2 at 600 °C.

Creosote MS 5 min 1/2/2	
Compound	Relative area (%)
Carbon dioxide	7.11
Sulfur dioxide	1.76
Acetaldehyde	2.52
Ethyl Chloride	0.35
Ethanol	2.64
Methyl vinyl ketone	0.15
Benzene	0.52
Toluene	1.14
Benzene, C2-	0.58
Benzene, C3-	0.52
Phenol, C1-	0.16
Naphthalene	2.36
Naphthalene, C1-	6.68
Naphthalene, C2-	6.32
Naphthalene, C3-	3.52
Naphthalene, C4-	0.74
Biphenyl	0.19
Biphenyl, C2-	0.32
Acenaphthylene	0.27
Acenaphthylene, C4-	0.64
1,1'-Biphenyl, C1-	0.88
1,1'-Biphenyl, C2-	0.51
1,1'-Biphenyl, C4-	0.77
Acenaphthene	0.18
Dibenzofuran	0.77
Fluorene	2.12
1-Isopropenyl-naphthalene	0.17
9H-Fluoren-3-ol	0.66
9H-Fluorene, C1-	4.18
9H-Fluorene, C2-	0.40
9H-Xanthene	2.87
6H-Dibenzo[b,d]-pyran	0.43
Naphtho[2,1-b]furan, 1,2-dimethyl-	1.17
Phenanthrene	5.34
Anthracene	1.03
Anthracene / Phenanthrene, C1-	12.87
Anthracene / Phenanthrene, C2-	6.51
Anthracene / Phenanthrene, C3-	2.96
Acridine	0.37
Anthracene, 9,10-dihydro-2-methyl-	1.91
4-Phenanthrenol, 1,2,3,4-tetrahydro-4-methyl-	0.44
Dibenzothiophene, C1-	1.18
Dibenzothiophene, C2-	0.12
Fluoranthene	1.48
Pyrene	0.63
Pyrene, C2-	0.80
Fluoranthene / Pyrene, C1-	2.51
Retene	0.37

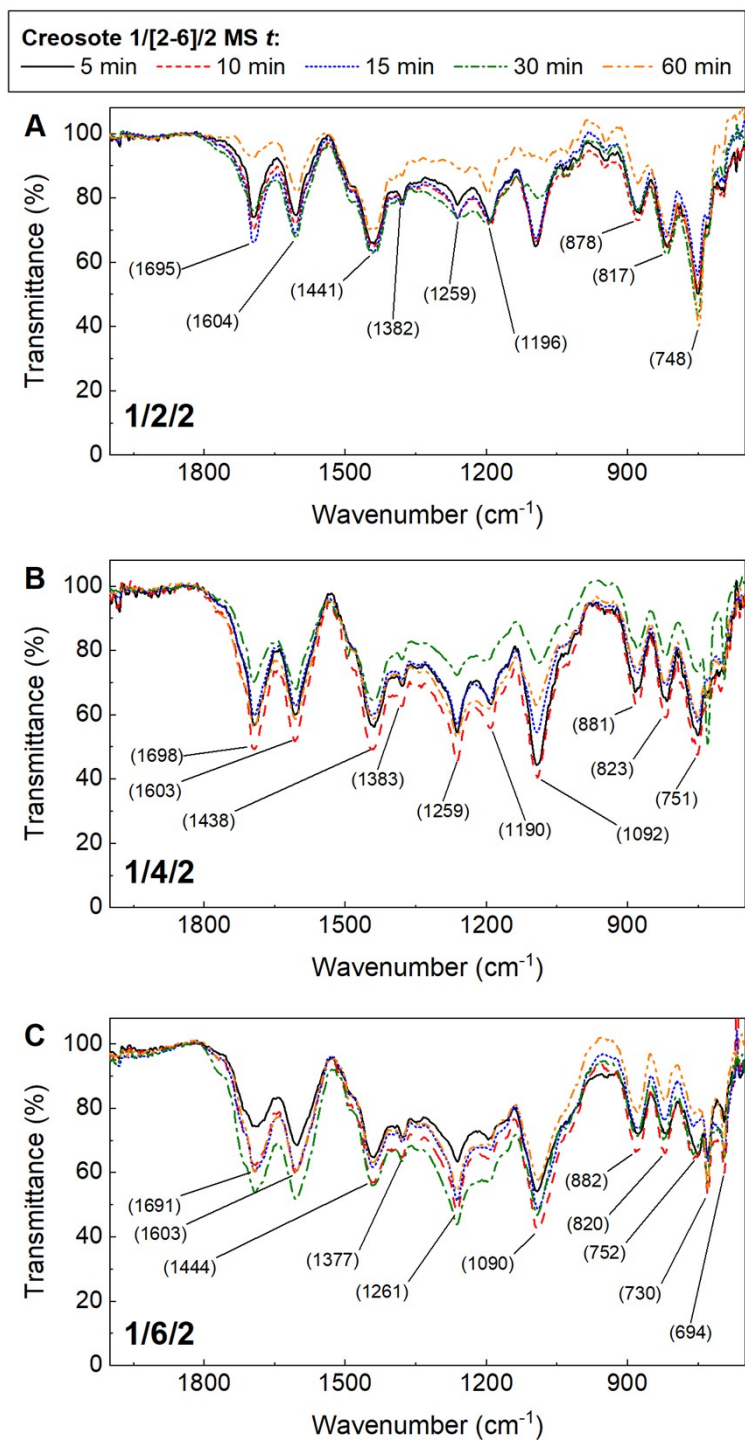


Figure S4. FTIR spectra of creosote-derived HCPs synthesized by MS using a precursor/catalyst/crosslinker molar ratio of: (A) 1/2/2, (B) 1/4/2, and (C) 1/6/2.

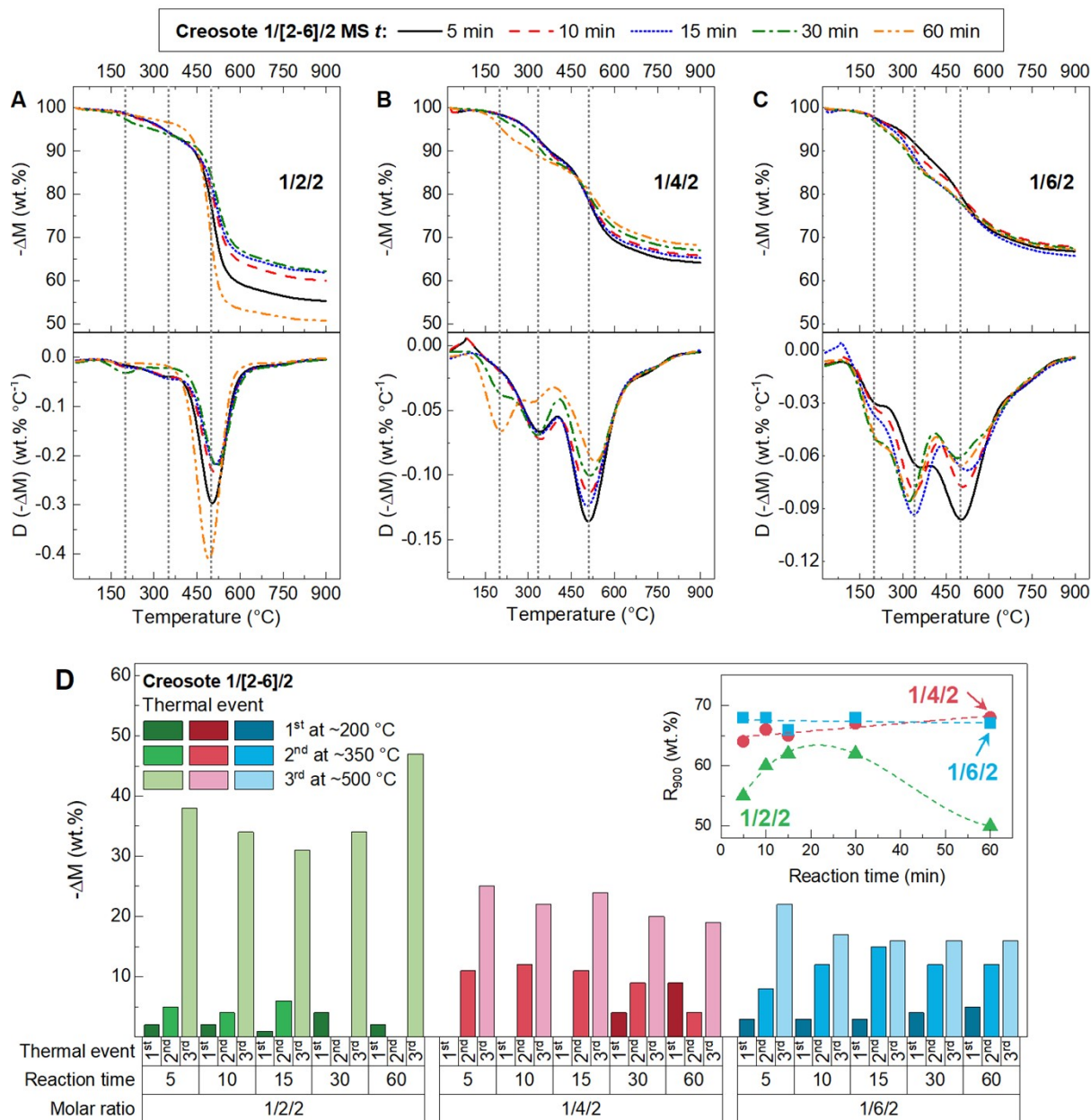


Figure S5. TG analysis of creosote-derived HCPs obtained using different catalyst contents (1/[2-6]/2 molar ratio) and reaction times (5 – 60 min): (A - C) Mass loss, $-\Delta M$, and its derivative, $D(-\Delta M)$, curves; (D) $-\Delta M$ for each thermal event and (D, inset) final residual weight fraction at 900 °C, R_{900} . The temperatures of the thermal events in (D) are given for reference, the exact values for each case are reported in Table S9.

Table S14. TG analysis of creosote-derived HCPs prepared by MS using a planetary mill. Each thermal event is identified by its onset and end temperature (T_{onset} and T_{end} , respectively), as well as by the temperature at which maximum mass loss occurs during the corresponding event (T_{max}). The total mass loss at each thermal event and the final residue at 900 °C are also reported ($-\Delta M$ and R_{900} , respectively).

Sample	T_{max} (°C)	T_{onset} (°C)	T_{end} (°C)	$-\Delta M$ (wt.%)	R_{900} (wt.%)*
Creosote 1/2/2 MS 5min	203	119	259	2	55
	344	259	374	5	
	504	374	900	38	
Creosote 1/2/2 MS 10min	204	99	254	2	60
	354	254	369	4	
	514	369	900	34	
Creosote 1/2/2 MS 15min	214	124	254	1	62
	354	254	384	6	
	519	384	900	31	
Creosote 1/2/2 MS 30min	204	94	279	4	62
	519	279	900	34	
	199	109	239	2	
Creosote 1/2/2 MS 60min	494	239	900	47	50
	339	84	404	11	
	509	404	900	25	
Creosote 1/4/2 MS 5min	344	84	409	12	66
	514	409	900	22	
	339	119	404	11	
Creosote 1/4/2 MS 10min	509	404	900	24	65
	214	94	239	4	
	334	239	409	9	
Creosote 1/4/2 MS 15min	514	409	900	20	67
	204	89	284	9	
	314	284	389	4	
Creosote 1/4/2 MS 30min	534	389	900	19	68
	211	90	242	3	
	360	242	394	8	
Creosote 1/6/2 MS 5min	503	394	900	22	67
	207	93	229	3	
	342	229	423	12	
Creosote 1/6/2 MS 10min	510	423	900	17	68
	200	85	231	3	
	337	231	436	15	
Creosote 1/6/2 MS 15min	525	436	900	16	66
	217	90	228	4	
	320	228	409	12	
Creosote 1/6/2 MS 30min	493	409	900	16	68
	214	83	242	5	
	332	242	418	12	
Creosote 1/6/2 MS 60min	500	418	900	16	67
	219	109	259	5	
	324	259	379	6	
Creosote 1/6/1 MS 30min	499	379	900	18	71
	204	104	264	4	
	324	264	359	4	
Creosote 1/6/0.5 MS 30min	504	359	654	17	73
	724	654	900	2	
	179	109	204	1	
Creosote 1/6/0 MS 30min	274	204	329	3	74
	469	329	644	18	
	730	644	900	4	

* Residual weight fraction at 900 °C from TG analysis in inert atmosphere.

Table S15. Elemental analysis of creosote-derived HCPs prepared by MS for 30 min reaction time.

Sample	N (wt.%)	C (wt.%)	H (wt.%)	S (wt.%)	O (wt.%)
Creosote 1/2/2 MS 30min	0.3	87.8	5.2	0.4	6.9
Creosote 1/4/2 MS 30min	0.3	80.9	4.8	0.4	9.1
Creosote 1/6/2 MS 30min	0.3	77.2	4.3	0.3	10.3

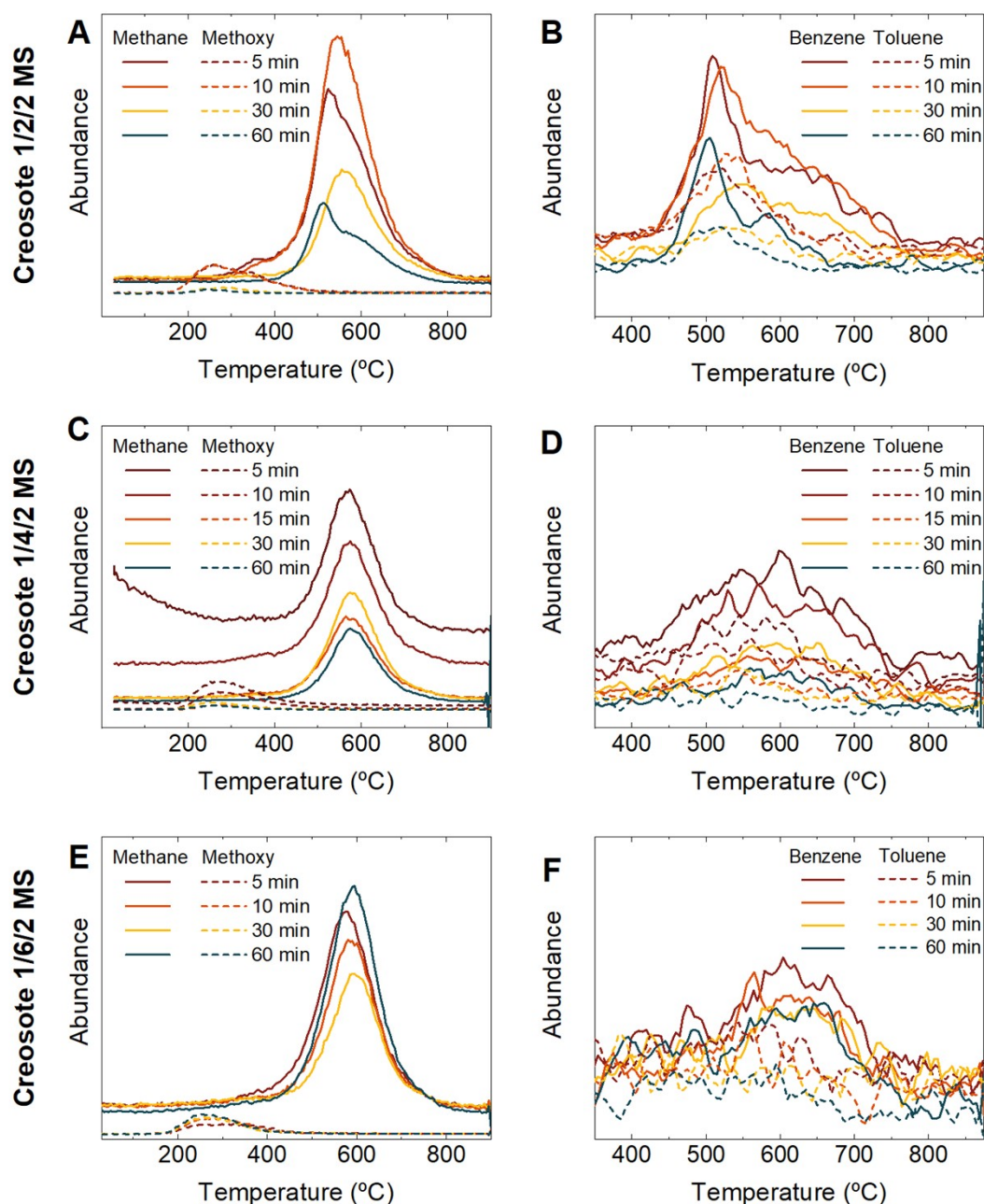


Figure S6. MaSp spectra for the release of (A, C, E) methane and methoxy moieties, (B, D, E) benzene and toluene moieties for creosote-derived HCPs prepared by MS using precursor/catalyst/crosslinker molar ratios of: (A, B) 1/2/2, (C, D) 1/4/2, and (E, F) 1/6/2.

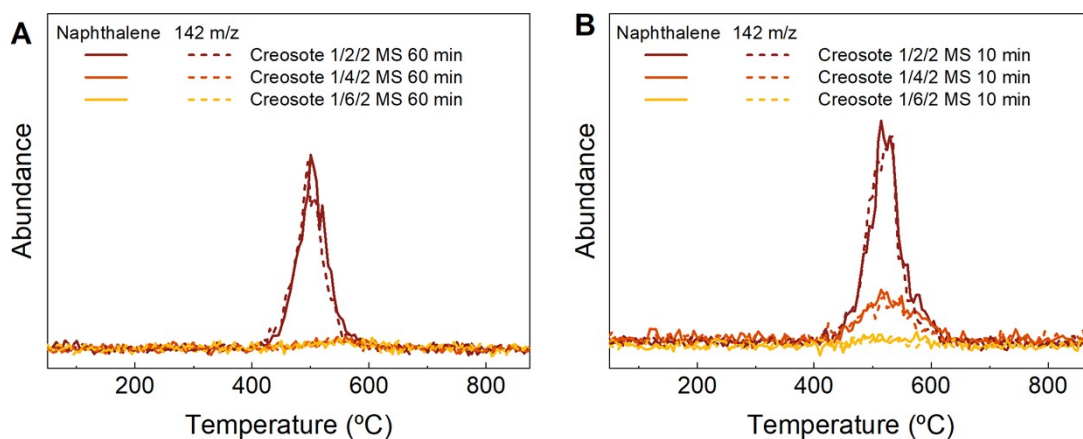


Figure S7. MaSp spectra for the release of naphthalene and 142 m/z moieties for creosote-derived HCPs using 1/[2 – 6]/2 precursor/catalyst/crosslinker molar ratios and a reaction time of: (A) 60 min, and (B) 10 min.

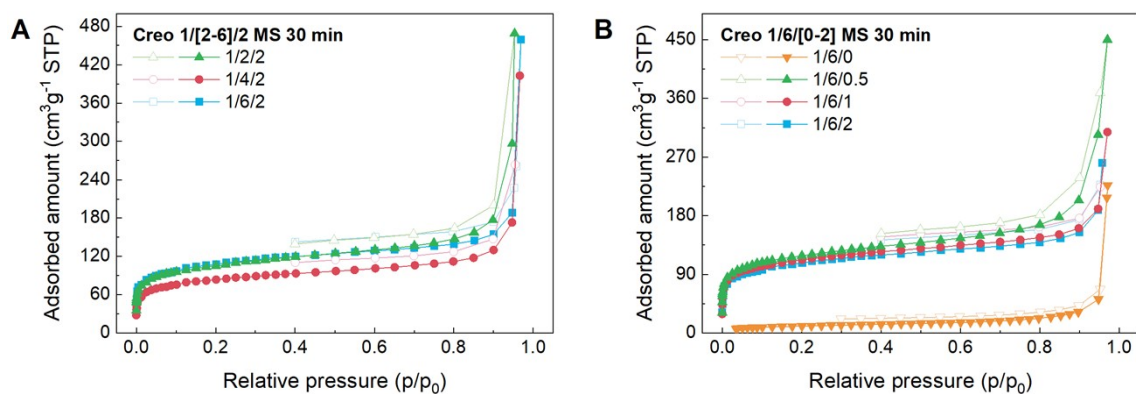


Figure S8. N₂ adsorption-desorption isotherms of creosote-derived HCPs obtained using different (A) catalyst (1/[2-6]/2) and (B) crosslinker contents and a reaction time of 30 min.

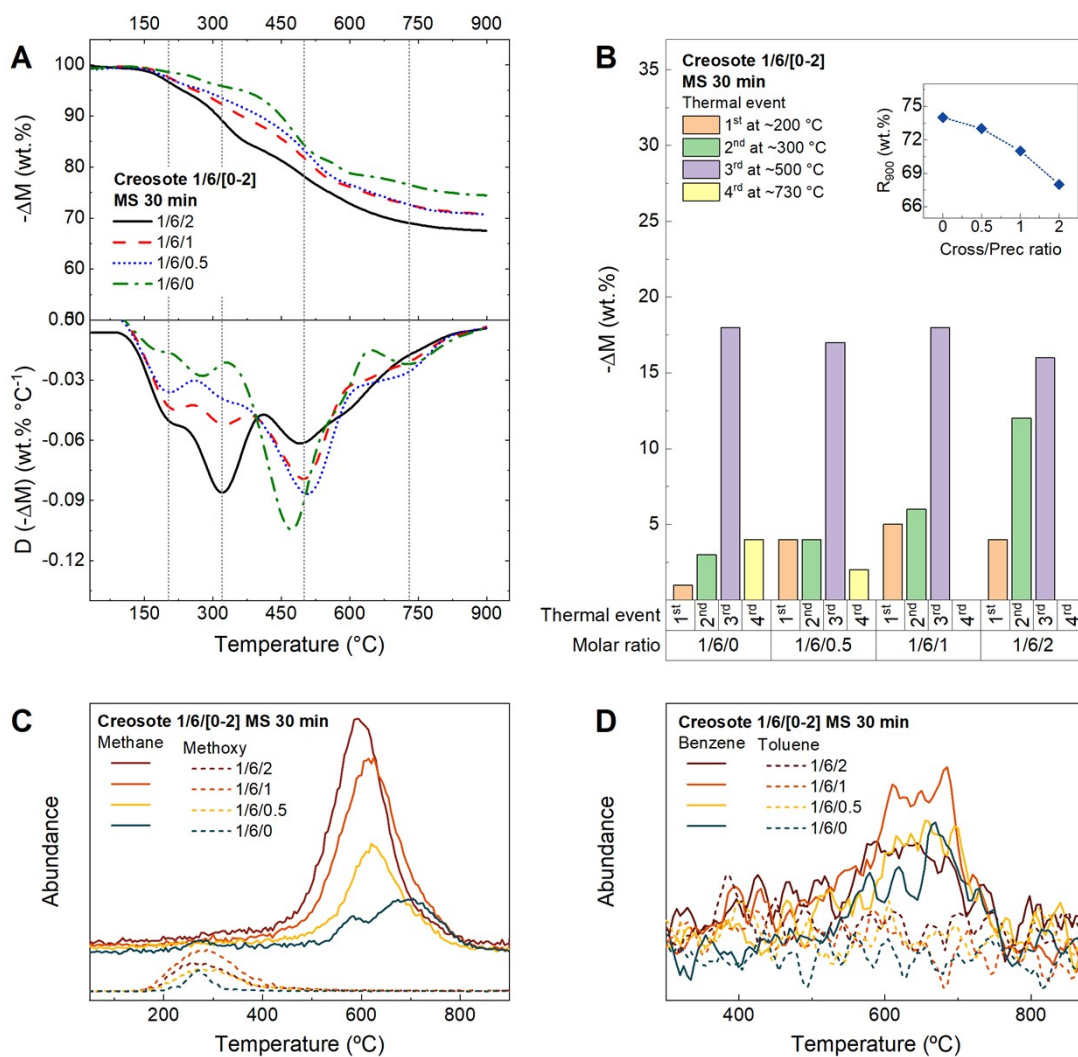


Figure S9. (A) TG analysis (mass loss and its derivative) and (B) $-\Delta M$ during each thermal event, (B inset) R_{900} observed during TG analysis. MaSp spectra for the release of (C) methane and methoxy moieties and (D) benzene and toluene moieties of creosote-derived HCPs obtained by MS using 1/6/[0-2] precursor/catalyst/crosslinker molar ratios.

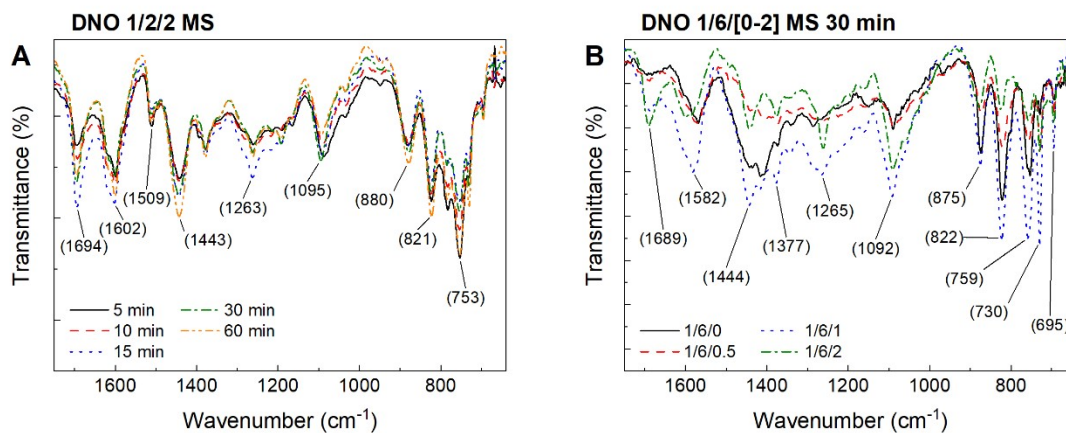


Figure S10. FTIR spectra of DNO-derived HCPs prepared by MS with: (A) 1/2/2 molar ratio and different reaction times (DNO 1/2/2 MS), and (B) different crosslinker contents and 30 min reaction time (DNO 1/6/[0-2]).

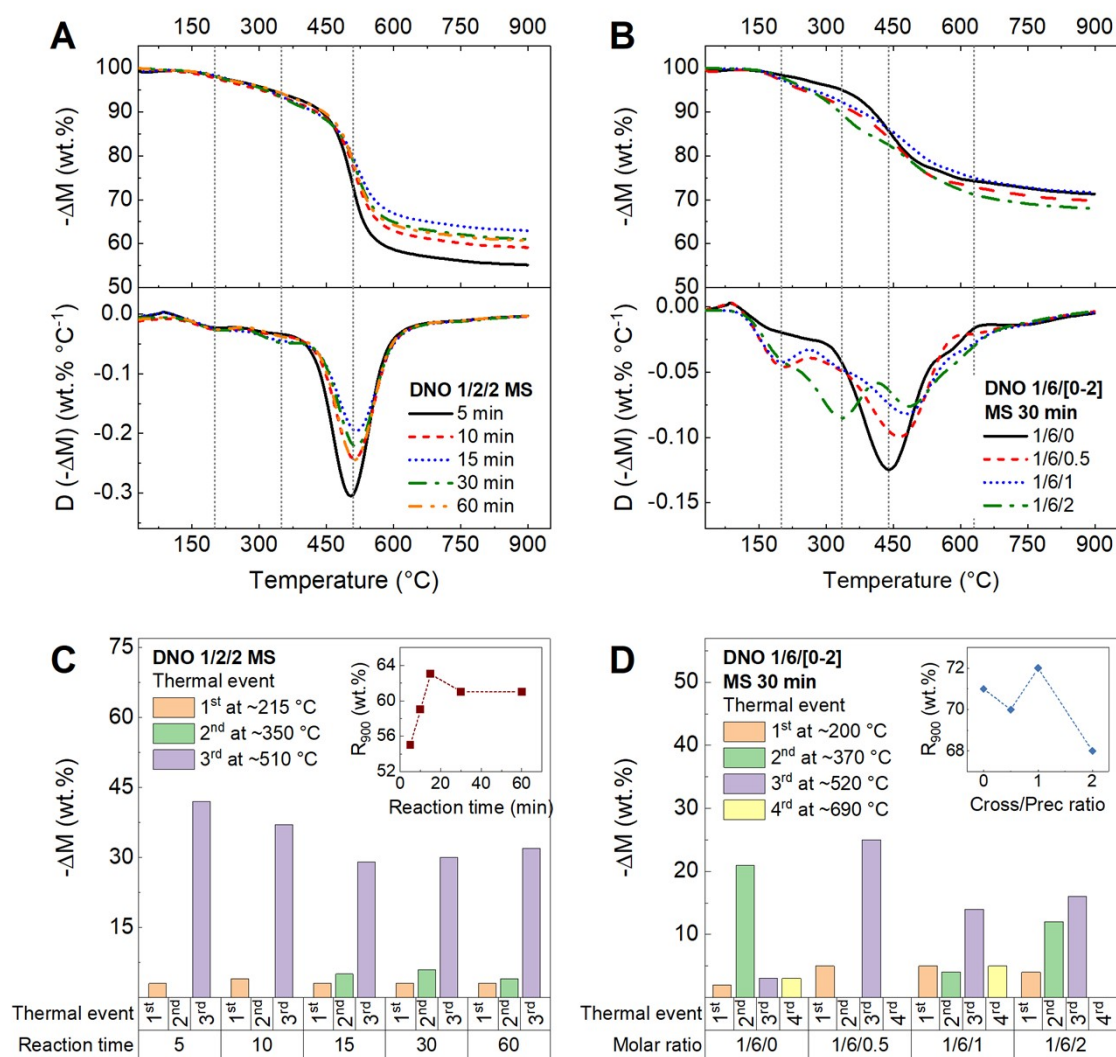


Figure S11. (A, B) Mass loss, $-\Delta M$, during each thermal event and (A,B insets) final residual weight fraction at 900 °C, R_{900} , observed during TG analysis of DNO-derived HCPs obtained by MS: (A) 1/2/2 molar ratio and different reaction times (DNO 1/2/2 MS), and (B) different crosslinker contents and 30 min reaction time (DNO 1/6/[0-2]). The temperatures of the thermal events in (A) and (B) are given for reference; the exact values for each case are reported in Table S11.

Table S16. TG analysis of DNO-derived HCPs prepared by MS using a planetary mill. Each thermal event is identified by its onset and end temperature (T_{onset} and T_{end} , respectively), as well as by the temperature at which the maximum mass loss occurs during the corresponding event (T_{max}). The total mass loss at each thermal event and the final residue at 900 °C are also reported ($-\Delta M$ and R_{900} , respectively).

Sample	T_{max} (°C)	T_{onset} (°C)	T_{end} (°C)	$-\Delta M$ (wt.%)	R_{900} (wt.%)*
DNO 1/2/2 MS 5min	201	91	261	3	55
	504	261	900	42	
DNO 1/2/2 MS 10min	212	95	270	4	59
	512	270	900	37	
DNO 1/2/2 MS 15min	234	95	262	3	63
	349	262	386	5	
DNO 1/2/2 MS 30min	516	386	900	29	61
	219	113	264	3	
DNO 1/2/2 MS 60min	354	264	397	6	61
	516	397	900	30	
DNO 1/6/2 MS 30min	215	111	264	3	68
	349	264	377	4	
DNO 1/6/1 MS 30min	513	377	900	32	72
	202	89	243	4	
DNO 1/6/0.5 MS 30min	335	243	413	12	70
	490	413	900	16	
DNO 1/6/0 MS 30min	204	90	261	5	71
	336	261	366	4	
DNO 1/6/0 MS 30min	480	366	592	14	71
	628	592	900	5	
DNO 1/6/0 MS 30min	206	86	265	5	71
	463	265	900	25	
DNO 1/6/0 MS 30min	170	88	243	2	71
	440	243	551	21	
DNO 1/6/0 MS 30min	599	551	660	3	71
	755	660	900	3	

* Residual weight fraction at 900 °C from TG analysis in inert atmosphere.

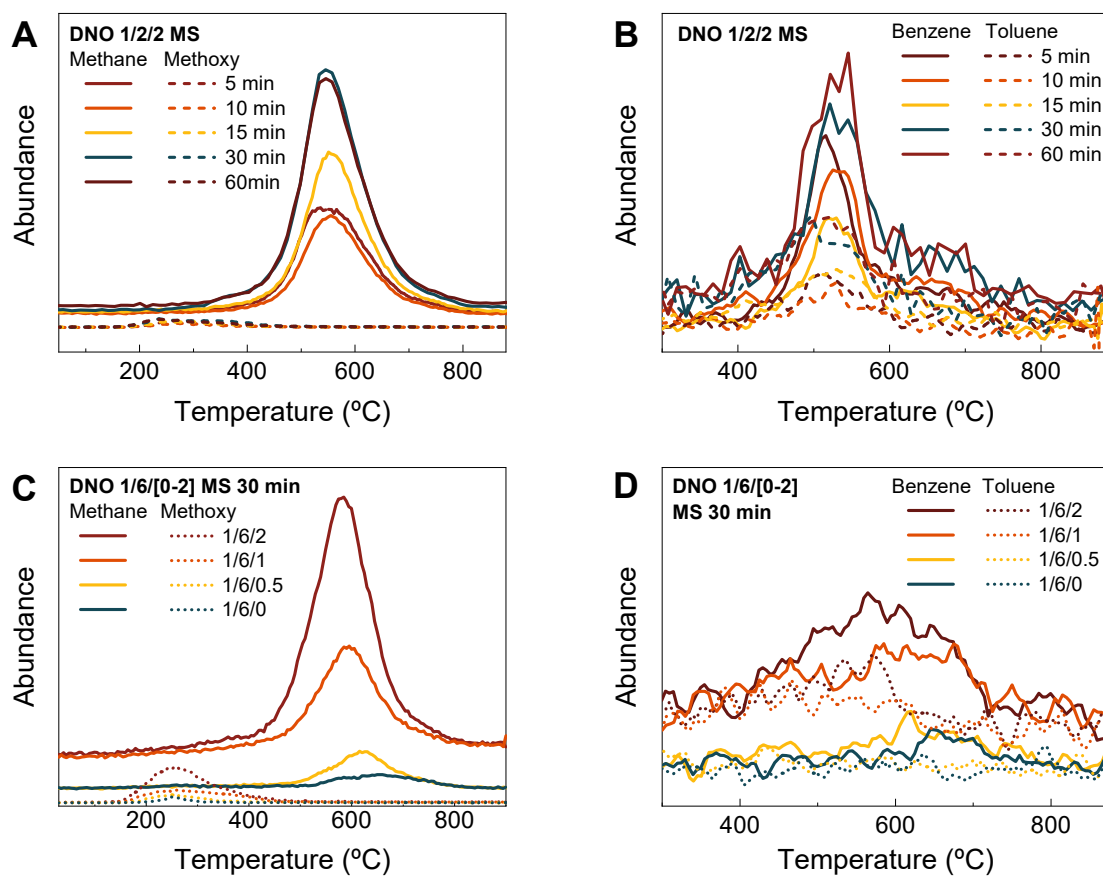


Figure S12. MaSp spectra for the release of: (A, B) methane and methoxy moieties, (C, D) benzene and toluene moieties of (A, B) DNO 1/2/2, and (C, D) DNO 1/6/[0-2] series of MS-based HCPs.

Table S17. A_{BET} and MB adsorption capacity of the tested HCPs from this study and those of other HCPs reported in the literature.

Sample	Precursor	A_{BET} ($\text{m}^2 \text{g}^{-1}$)	MB adsorption ($\text{mg}_{\text{MB}} \text{g}_s^{-1}$)	Ref.
DNO 1/2/2 MS 15 min	DNO	443	87	This study
Creosote 1/4/2 MS 60min	Creosote	497	102	
Creosote 1/2/2 MS 5 min	Creosote	153	26	
Creosote 1/4/2 MS 5 min	Creosote	165	36	
Creosote 1/6/2 MS 5 min	Creosote	161	9	
BE-XDC	Benzene, p-dichloroxylylene	706	105	1
CMB-CMB	4, 4'-bis-(chloromethyl)-1, 1'-biphenyl	1253	143	
HCP-3	Styrofoam	1007	106	2
AHCP-1	Sodium tetraphenylboron	939	120	3
TPP-PP	Triptycene, pyrrole	698	160	4
HCP-TPP	Tris(o-phenylenedioxy) cyclotriphosphazene	1642	505	5
HCP-TNP	Tris(2, 3-naphthalenedioxy) cyclotriphosphazene	1700	409	
HCP-MAH	Phenyl maleic anhydride	755	348	6
HCP-COOH		332	422	
HCPS-OH-1	Hydroxylated polystyrene	247	78	7
HCPS-OH-2		315	75	
HCPS-OH-3		119	172	
HCP _{TPB} -COOH		720	371	8
HCP-NH ₂	Benzylamine, benzene	890	480	9
Fe ₃ O ₄ @HCP-NH ₂		533	580	
Th-1	Thiophene	43	59	10

References

1. Zhao, L. X., Yuan, S. G., Sha, J. & Li, S. B. Hypercrosslinked Polymers Preparation VS Methylene Blue Adsorption. *MSF* **743–744**, 539–544 (2013).
2. Dong, X. *et al.* Recycling Plastic Waste for Environmental Remediation in Water Purification and CO₂ Capture. *ACS Appl. Polym. Mater.* **2**, 2586–2593 (2020).
3. Shen, R. *et al.* One-pot synthesis of a highly porous anionic hypercrosslinked polymer for ultrafast adsorption of organic pollutants. *Polym. Chem.* **9**, 4724–4732 (2018).
4. He, Y. *et al.* Efficient adsorption of methyl orange and methyl blue dyes by a novel triptycene-based hyper-crosslinked porous polymer. *RSC Advances* **12**, 5587–5594 (2022).
5. Xiong, G. *et al.* High porosity cyclotriphosphazene-based hyper-crosslinked polymers as efficient cationic dye MB adsorbents. *Polymer* **247**, 124787 (2022).
6. Song, S., Ai, J., Hu, A., Liao, G. & Wang, D. Synthesis of carboxyl-modified hyper-cross-linked polymers with conspicuous removal capability for various water-soluble contaminants. *Journal of Environmental Chemical Engineering* **9**, 106047 (2021).
7. Li, F. *et al.* Preparation of hyper-cross-linked hydroxylated polystyrene for adsorptive removal of methylene blue. *RSC Advances* **11**, 25551–25560 (2021).
8. Liu, K. *et al.* One-Pot Synthesis of Carboxyl-Functionalized Hyper-Cross-Linked Microporous Polymer Based on the Dual-Purpose Reagent Strategy for the Efficient Removal of Methylene Blue from Water. *ACS Appl. Polym. Mater.* **5**, 9807–9816 (2023).
9. Hu, A. *et al.* Magnetically hyper-cross-linked polymers with well-developed mesoporous: a broad-spectrum and highly efficient adsorbent for water purification. *J Mater Sci* **54**, 2712–2728 (2019).
10. Wei, J., Jia, J. & Liao, T. Highly selective adsorption of dyes by functional hypercrosslinked-polymers prepared in a facile and chemically stable manner. *Journal of Environmental Chemical Engineering* **11**, 110555 (2023).