Compositional Modification of Pyrogenic Products Using $CaCO_3$ and CO_2 from the Thermolysis of Polyvinyl Chloride (PVC)

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Table S1. Calibrations and QA/QC of micro-GC

1. Calibrations

Order	H2	CH4	CO
A. Concentration (mol. %)			
1	4.99	5.00	5.01
2	9.99	10.00	10.01
3	19.97	20.00	20.02
B. peak area (unitless)			
1	2748230	603940	176650
2	5442482	1005081	475080
3	11187164	2104563	890161
C. Calibration			
Retention Time (min)	0.637	1.278	1.438
Slope	556,852.91	105,070.05	44,597.81
Intercept	0	0	0
Coefficient of determination (R^2)	0.9995	0.9932	0.9883

2. RSE

Order	H_2	CH_4	CO
1	137,827	25,946	11,919
2	134,048	25,948	10,453
3	133,603	25,990	11,269
Mean	135,159	25,961	11,214
SD	2,321	25	735
RSE (%)	**0.99**	**0.06**	**3.78**

3. MDL

Order	H_2	CH_4	CO
1	14748	3512	2255
2	15076	4213	2110
3	14477	4568	2942
4	13809	4015	2013
5	15587	3566	1814
6	15497	3481	1974
7	15723	3935	2538
Mean	14988.14	3898.57	2235.14

SD	692.17	407.49	387.8
SD*3.14	2173.42	1279.52	1217.69
MDL (ppm)	**3.9**	**12.18**	**27.3**

Table S2. Calibrations and QA/QC of GC/TOF-MS

1. Indoor air 50 components STD

1.1. Calibrations

Order	Benzene	Toluene	Ethylbenzene	m-Xylene	p-Xylene	o-Xylene
A. Concentration (ppm)						
1	5.02	4.98	5.00	5.00	5.00	5.02
2	10.03	9.95	9.99	9.99	9.99	10.03
3	30.09	29.85	29.97	29.97	29.97	30.09
4	50.15	49.75	49.95	49.95	49.95	50.15
5	100.30	99.50	99.90	99.90	99.90	100.30
B. peak area (unitless)						
1	20,871,500	-	-	3,789,254	3,514,294	4,624,153
2	74,683,400	-	59,502,700	14,744,900	14,744,900	109,108,000
3	233,668,000	212,212,000	245,518,000	72,202,500	72,202,500	383,511,000
4	477,967,000	484,312,000	569,515,000	236,485,500	236,485,500	741,729,000
5	878,538,000	882,464,000	965,115,000	424,619,000	424,619,000	1,171,110,000
C. Calibration						
Retention Time (min)	9.278	15.260	20.938	21.451	21.451	21.526
Slope	9,072,443.72	9,405,698.60	10,192,182.97	4,615,568.32	4,617,149.06	12,264,520.09
Intercept	-17,741,200.84	-36,813,955.31	-23,731,887.15	-29,458,926.47	-29,575,505.79	2,265,198.14
Coefficient of determination (R^2)	0.9952	0.9896	0.9797	0.9786	0.9786	0.9748

Order	3-Ethyltoluene	4-Ethyltoluene	2-Ethyltoluene	1,3,5-Trimethylbenzene	1,2,3-Trimethyl benzene
A. Concentration (ppm)					
1	4.98	4.98	5.02	4.97	5.00
2	9.95	9.95	10.03	9.93	10.00
3	29.85	29.85	30.09	29.79	30.00
4	49.75	49.75	50.15	49.65	50.00
5	99.50	99.50	100.30	99.30	100.00
B. peak area (unitless)					
1	N.D.	N.D.	N.D.	17,919,300	7,845,570
2	27,321,500	27,321,500	47,086,100	93,465,100	69,886,900
3	130,293,500	130,293,500	241,678,000	318,003,000	360,348,000
4	305,839,000	305,839,000	570,457,000	659,050,000	723,512,000
5	514,825,000	514,825,000	978,745,000	1,080,720,000	1,169,960,000
C. Calibration					
Retention Time (min)	26.273	26.273	26.432	26.684	29.171
Slope	5,499,726.00	5,499,726.00	10,430,197.95	11,395,936.91	12,464,457.86
Intercept	-15,361,050.28	-15,361,050.28	-37,429,181.01	-7,498,968.83	-19,803,362.47
Coefficient of determination (R^2)	0.9778	0.9778	0.9806	0.9827	0.9786

1.2 RSE

Order	Benzene	Toluene	Ethylbenzene	m-Xylene	p-Xylene	o-Xylene
1	477967000	484312000	569515000	236485500	236485500	741729000
2	524219000	514975000	583144000	255147900	255147900	711127000
3	615472000	500275000	542224000	253314800	253314800	782229000
Mean	539219333.3	499854000	564961000	248316066.7	248316066.7	745028333.3
SD	69969019.98	15335834.6	20836645.29	10286486.02	10286486.02	35665638.94
RSE (%)	**7.49**	**1.77**	**2.13**	**2.39**	**2.39**	**2.76**

Order	3-Ethyltoluene	4-Ethyltoluene	2-Ethyltoluene	1,3,5-Trimethylbenzene	1,2,3-Trimethyl benzene
1	305839000	305839000	570457000	659050000	723512000
2	422178000	288719000	524479000	622487000	733248000
3	355879000	347552000	579524000	651115000	751187000
Mean	361298666.7	314036666.7	558153333.3	644217333.3	735982333.3
SD	58358549.68	30261060.4	29513101.6	19232696.02	14038655.22
RSE (%)	**9.33**	**5.56**	**3.05**	**1.72**	**1.10**

2. PAH-mix A STD

2.1. Calibrations

Order	Fluorene	Anthracene	Phenanthrene	Pyrene	Benzo(a)anthracene	Chrysene	Benzo(a)pyrene
A. Concentration (ppm)							
1	19.79	19.82	19.88	18.32	19.86	19.98	19.86
2	29.69	29.72	29.82	27.49	29.80	29.97	29.79
3	49.48	49.54	49.70	45.81	49.66	49.95	49.65
4	98.96	99.08	99.40	91.62	99.32	99.90	99.30
B. peak area (unitless)							
1	79,164,800	79,896,400	N.D.	66,611,600	24,833,943	47,970,557	N.D.
2	252,199,000	283,528,000	96,584,200	225,380,000	120,920,278	233,576,000	N.D.
3	951,671,000	1,027,150,000	499,758,000	877,071,000	225,050,000	922,448,000	240,331,000
4	2,769,350,000	2,608,580,000	2,083,360,000	2,689,590,000	1,264,720,000	2,443,000,000	894,832,000
C. Calibration							
Retention Time (min)	51.382	57.170	57.514	65.579	72.652	72.862	80.775
Slope	34,848,895.89	32,499,401.87	29,190,254.60	36,757,531.68	15,916,806.96	30,567,241.79	16,614,324.11
Intercept	-711,227,168.42	-610,231,768.42	-847,672,717.95	-719,199,376.32	-381,547,578.38	-615,085,088.27	-657,598,846.15
Coefficient of determination (R^2)	0.9956	0.9980	0.9923	0.9939	0.9528	0.9979	0.9974

2.2. RSE

Order	Fluorene	Anthracene	Phenanthrene	Pyrene	Benzo(a)anthracene	Chrysene	Benzo(a)pyrene
1	951671000	1027150000	499758000	877071000	225050000	922448000	240331000
2	934724000	972240000	502114000	882717000	231470000	972442000	251147000
3	961114000	1073240000	514428000	887924000	223550000	953381000	234478000
Mean	949169666.7	1024210000	505433333.3	882570666.7	226690000	949423666.7	241985333.3
SD	13371631.4	50564144.41	7878179.062	5427979.581	4206994.176	25230841.73	8456743.128
RSE (%)	**0.81**	**2.85**	**0.90**	**0.36**	**1.07**	**1.53**	**2.02**

Table S3. Conditions for micro-GC and GC/TOF-MS

1. Method of micro-GC

Gas chromatography (GC)		
GC model	INFICON 3000A, Switzerland	
Channel A, column	Molssieve, 10 m × 0.32 mm × 30 μm	
Channel B, column	PLOTU, 8 m × 0.32 mm × 30 μm	
Injector and Oven setting		
A. Injection	Channel A	Channel B
Inject time (msec)	5	5
Sample pump (sec)	1	1
Pump flow (ml min-1)	10	10
Backflush (sec)	10	10
B. Temperature control	Channel A	Channel B
Sample inlet (°C)	100	100
Injector (°C)	100	80
Column (°C)	80	70
C. Pressure control	Channel A	Channel B
Equilibration time (sec)	0	0
Column (psi)	25	25
Post run (psi)	28	28

2. Method of GC/TOF-MS

Gas chromatography/Time of flight-Mass spectrometry (GC/TOF-MS)			
GC model	Agilent 7890B GC/TOF-MS (ALMSCO, UK)		
Column	DB-5MS (60 m × 0.25 mm × 0.25 μm, Agilent J&W GC Column)		
Injector and Oven setting		Detector setting	
A. Injection	Value	C. Detector	Value
Injector Temp. (°C)	240	Detector (mA)	-2300
Pressure (psi)	19.041	Ion source heating (A)	200
Total flow (ml min-1)	24	Ionisation (mA)	-70
Split ratio	20	Reflector 10 (mA)	3360
B. Temperature control	Value	Reflector 3 (mA)	2146.2
Initial temp. (°C)	35	Trans line heating (A)	200
Hold time (min)	10	Filament voltage (V)	1.72
Ramp 1 at (min)	4	Filament delay (sec)	720
Final temp. (°C)	300		
Hold time (min)	20		
Total time (min)	96.25		
injection volume (μl)	1		

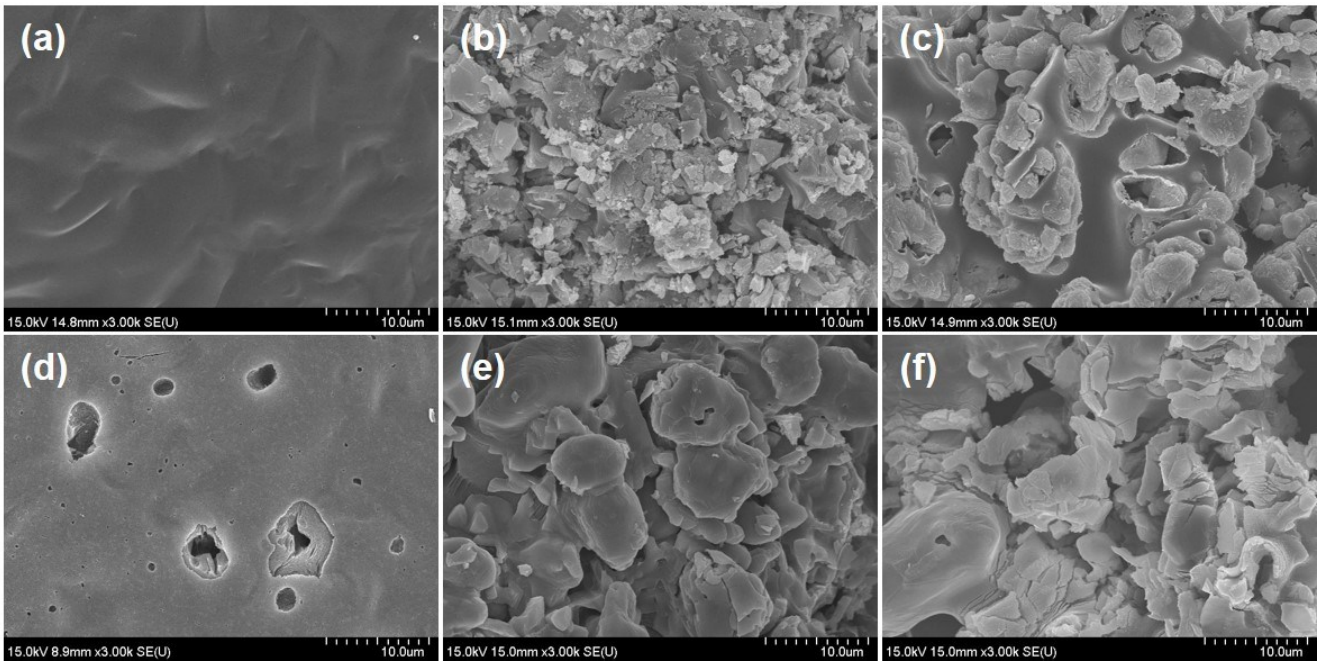

Figure SI-1. SEM images for char at 750 ˚C (a) PVC in N_2, (b) PVC + $CaCO_3$ (10 wt.%) in N_2, (c) PVC + $CaCO_3$ (50 wt.%) in N_2, (d) PVC in CO_2, (e) PVC + $CaCO_3$ (10 wt.%) in CO_2, and (f) PVC + $CaCO_3$ (50 wt.%) in CO_2

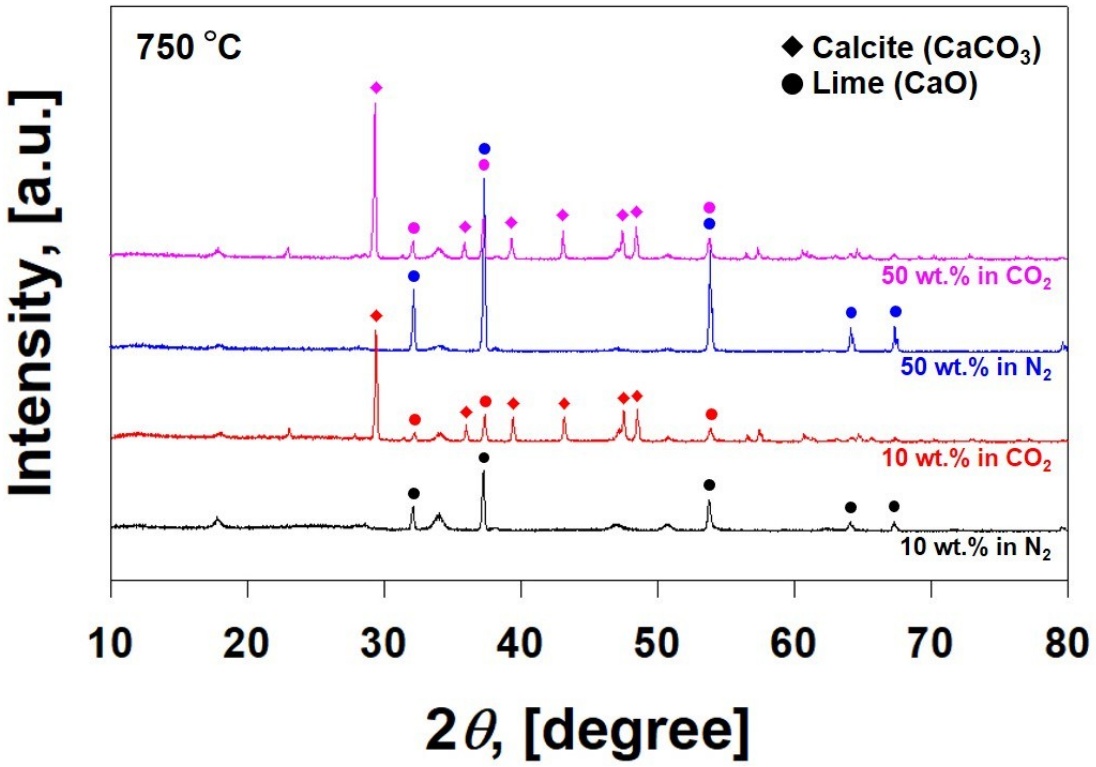

Figure SI-2. XRD spectra for charring compounds from the thermolysis of PVC + $CaCO_3$ (10 and 50 wt.) at 750 ˚C in N_2 and CO_2