Supplemental Information for:

Pressurized Solvent Extraction of Secondary Char from Hydrothermal Carbonization: Sample Preparation and Analytical Strategy Shape GC-MS Results

James L. Adair[1^], Matteo Pecchi[1,2^], Jillian L. Goldfarb[1,2 *]
[1]Biological and Environmental Engineering, Cornell University, Ithaca NY 14850 USA
[2] Smith School of Chemical and Biomolecular Engineering, Cornell University, Ithaca NY 14850 USA

Table S1. Composition of representative retail-level food waste used in this study, reproduced from Pecchi, M., Baratieri, M., Maag, A. R., & Goldfarb, J. L. (2023). *Waste Management*, *168*, 281-289.

Food Waste Category	Composition [wt %]	Products used (equal quantities, by mass, of each item were used for each category)
Grain products	16.7	Rice, dry pasta, bread, biscuits, harvest wheat crackers, plain bagels
Fresh fruit	10.2	Banana, apples, tangerines, strawberries, grapes
Processed fruit	3.7	Raspberry jam, applesauce, seedless raisins
Fresh vegetables	12.1	Iceberg lettuce, baking potatoes, carrots, bell pepper, broccoli
Processed vegetables	4.2	Canned sweet peas, corn, kidney beans, tomato sauce
Milk	15.1	2% milk
Dairy (not milk)	6.5	Plain low-fat yogurt, cheddar cheese, small curd cottage cheese
Meat	3.3	Ground beef, uncured bacon
Poultry	2.1	Chicken (whole rotisserie), breaded chicken nuggets
Fish and seafood	0.9	Canned tuna, fresh salmon, raw shrimp, pre-frozen tilapia
Eggs	1.6	Grade AA large eggs
Nuts	0.5	Lightly salted dry roasted peanuts
Sweeteners	10.5	Pepsi, Hostess cupcakes, candy (KitKat), raw sugar cookie dough
Fats and oils	12.6	Beef tallow, all-vegetable shortening, canola oil
Total	100.0	

[^] Co-first authors (equal contribution)
[*] To whom correspondence should be addressed: goldfarb@cornell.edu, 607.255.5789

Feedstock, HC, PC, and SC characterization and yields are provided in Table S2. These results reflect the compositional differences among feedstocks.

Table S2: Proximate analysis and yields for feedstock, HC, PC, and SC reported as average ± standard deviation of triplicates on a dry feedstock basis [wt%]. Y_x (x is HC, PC, or SC), Y_{liquid}, and Y_{gas} indicate the wt% yield of the correspondent phase. Y_{liquid} includes losses. The deviation of Y_{PC} and Y_{SC} are assessed based on the deviation of PSE of CLS that was performed 4 times and by error propagation from the Y_{HC}. HTC of MIS was not replicated.

|		VM [wt%]	FC [wt%]	Ash [wt%]	Y_x [wt%]	Y_{liqid} [wt%]	Y_{gas} [wt%]
CLS	Raw	92.9 ± 0.6	6.88 ± 0.4	0.2 ± 0.3	n.a.		
	HC	59.6 ± 0.5	40.3 ± 0.5	0.1 ± 0.0	50 ± 1	45 ± 1	5 ± 0
	PC	47.2 ± 0.2	50.8 ± 0.2	0.0 ± 0.0	43 ± 1		
	SC	70.3 ± 1.0	29.7 ± 1.0	0.0 ± 0.0	7 ± 1		
AP	Raw	77.8 ± 1.2	21.6 ± 0.4	0.6 ± 1.0	n.a.		
	HC	53.3 ± 0.2	46.5 ± 0.1	0.2 ± 0.1	39 ± 2	60 ± 4	1 ± 0
	PC	45.0 ± 0.1	55.0 ± 0.1	0.0 ± 0.0	34 ± 2		
	SC	80.3 ± 3.0	19.7 ± 3.0	0.0 ± 0.0	5 ± 2		
MIS	Raw	80.7 ± 0.8	15.6 ± 0.5	3.7 ± 1.3	n.a.		
	HC	55.1 ± 0.3	40.2 ± 0.9	4.6 ± 0.9	49	42	9
	PC	51.6 ± 0.2	48.4 ± .2	0.0 ± 0.0	33		
	SC	73.4 ± 0.8	26.6 ± 0.8	0.0 ± 0.0	16		
FW	Raw	86.8 ± 0.2	12.0 ± 0.2	1.3 ± 0.0	n.a.		
	HC	81.5 ± 0.8	17.7 ± 0.8	0.8 ± 0.1	55 ± 1	41 ± 1	4 ± 0
	PC	47.3 ± 0.4	52.7 ± 0.4	0.0 ± 0.0	15 ± 1		
	SC	97.3 ± 0.3	2.7 ± 0.3	0.0 ± 0.0	40 ± 1		

CLS is chosen as a model feedstock and expectedly its results are in good agreement with the available literature [29,40,41]. By contrast, the other three feedstocks are subject to regional and biological variability, making direct comparison to literature values more difficult. For example, we find approximately 2.5 times as much fixed carbon in our MIS than Mihajlović et al. [22], which is a large discrepancy that can be accounted for by the different environments where the samples were grown or collected—different continents in this case.

For AP [42], measured HC yield (39%) was lower than MIS HC yield (49%) despite them having similar elemental fractions of C, H, N, and O. We attribute this difference to MIS having approx. 90 % lignocellulosic content [25], whereas AP's lignocellulosic content is approx. 40 %, with the rest mainly comprised of fructose, glucose, and sucrose.

For FW [10,11], on both a feedstock basis and HC basis, FW produced far greater SC yield than the other feedstocks, attributed to its high lipid content (29%, [33]) in the form of LCFAs. As the LCFAs were easily extracted with DCM, the resulting FW PC had more fixed carbon than the HC, in line with that of other feedstocks.

HC yields were around 50 % for each feedstock except for AP that produced 39 % HC, consistent with previous works in the literature that hydrothermally carbonized the same feedstocks at similar conditions

[10,29,43,44]. The liquid yields reflect the HC yields, with values around ~45 % except for AP that produced ~60 % liquid. Gas yields were below 10 wt%, in agreement with previous literature values [45].
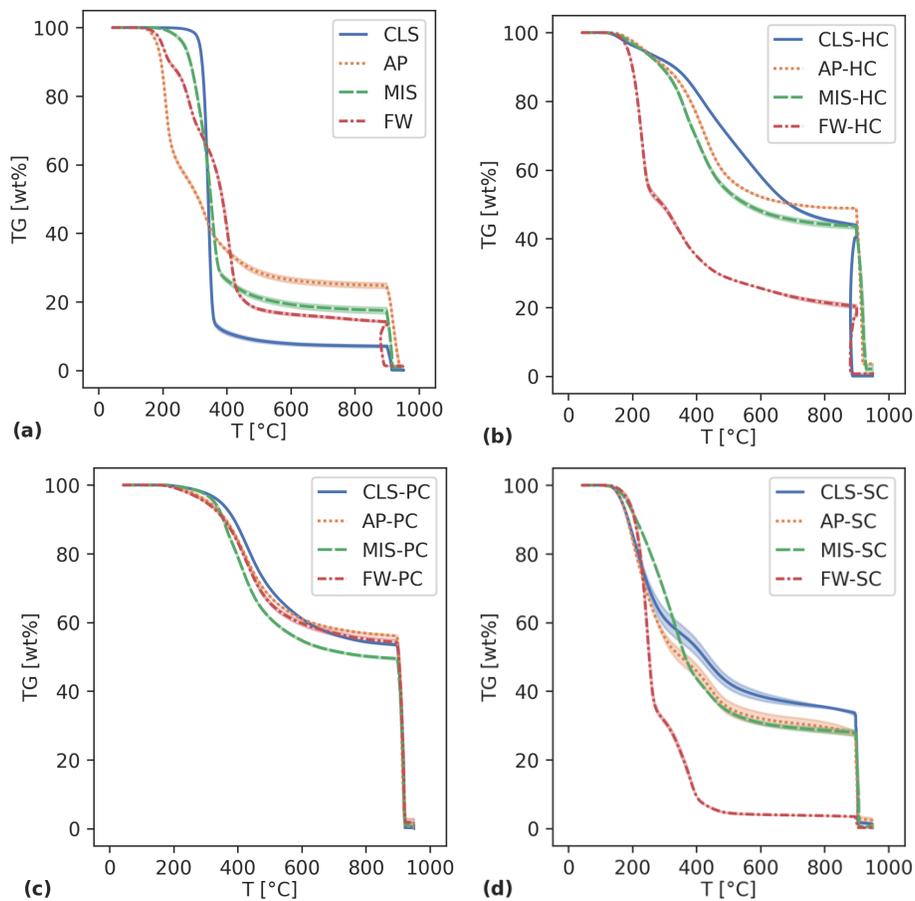
Figure S1: TG curves for raw feedstock, HC, PC, and SC from CLS, AP, MIS, FW.
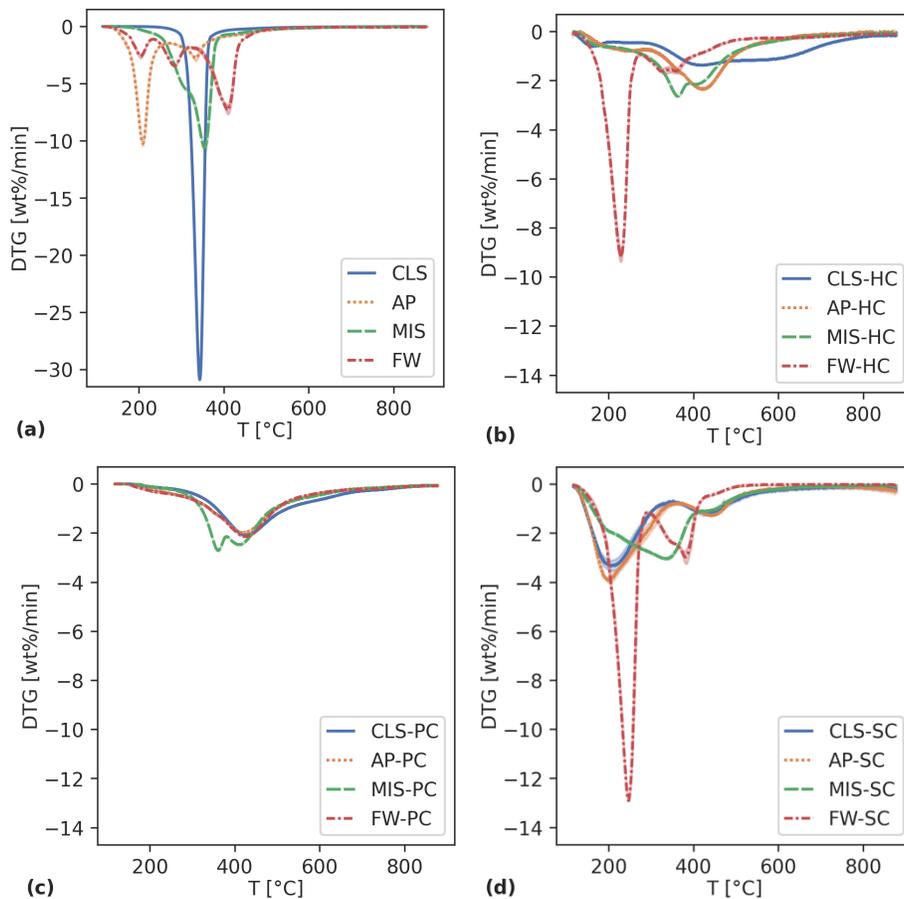
Figure S2: DTG curves for raw feedstock, HC, PC, and SC from CLS, AP, MIS, FW.
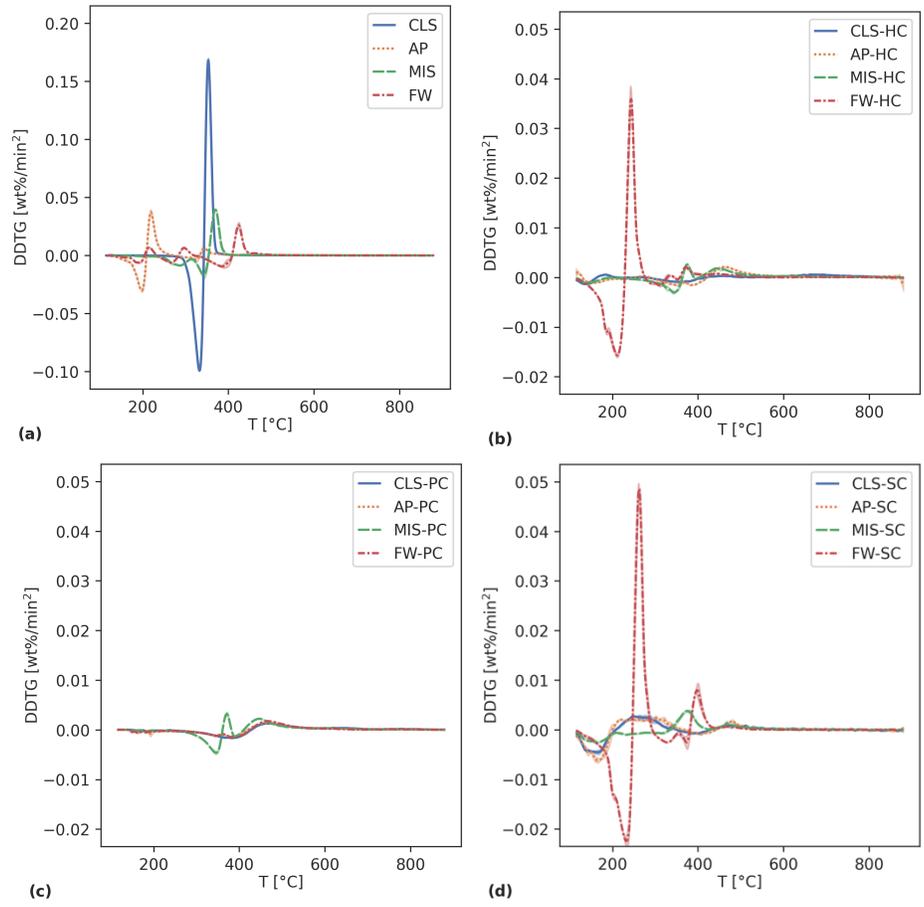
Figure S3: second derivative DDTG curves for raw feedstock, HC, PC, and SC from CLS, AP, MIS, FW.

Table S3: Calibration of non-derivatized and derivatized compounds for GC-MS analysis

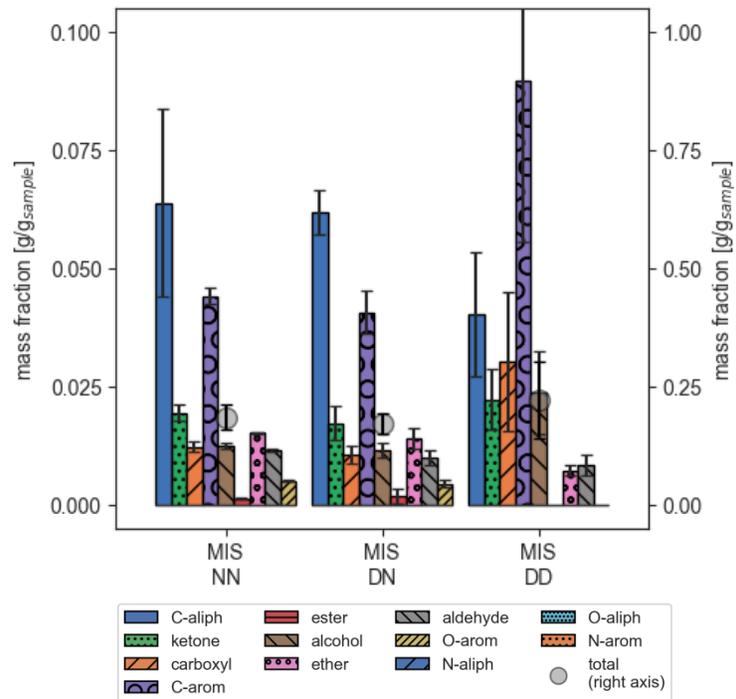| Compound	M.W. (g/mol)	Calibration Solution (S) Concentration (ppm)						Chromatogram Area (TIC)					
		S1	S2	S3	S4	S5	S6	S1	S2	S3	S4	S5	S6
Non-derivatized Compounds													
cyclopent-2-en-1-one	82.10	10	20	30	50			160442	768472	1076720	1925530		
aniline	93.13	5	10	20	50			172962	369352	848808	2161008		
phenol	94.11	5	10	20	50			135884	304546	678618	1866918		
2-methylpyrazine	94.11	5	10	20	50			174299	394074	1195478	3003874		
furan-2-carbaldehyde	96.08	5	10	20	35	50	100	212718	367356	692860	997750	1494740	2697268
2-methylcyclopent-2-en-1-one	96.13	10	20	30	50			175083	759316	1070146	1928385		
2(5H)-Furanone, 3-methyl-	98.10	10	20	30	50			120148	688186	1023230	1814148		
furan-2-ylmethanol	98.10	5	10	20	30	50	100	120772	246548	552986	863881	1420196	2898882
hex-5-en-1-ol	100.16	10	20	30	50			169008	768650	1157626	2030143		
2-methylphenol	108.14	5	10	20	50			381842	799913	1779455	4547240		
4-methylphenol	108.14	5	10	20	30	50		194600	403860	965433	1671459	2591929	
phenylmethanol	108.14	5	10	20	50			127205	324262	766126	1995617		
1-(furan-2-yl)ethanone	110.11	5	10	20	30	50	100	232493	532743	1191584	1867042	3139161	6096503
5-methylfuran-2-carbaldehyde	110.11	10	20	30	50			171774	802556	1210816	2132043		
benzene-1,2-diol	110.11			20	50	100	200			330664	1443845	3062295	6306374
3-methylcyclopentane-1,2-dione	112.13	10	20	30	50			94197	608085	934628	1713053		
4-oxopentanoic acid	116.12			20	50	100	200			298152	1256009	2620022	5331035
benzoic acid	122.12	10	20	35	50	100	300	75192	301818	561536	714761	2790280	8964111
2,4-dimethylphenol	122.16	5	10	20	50			211126	462022	1027635	2858751		
nitrobenzene	123.11	5	10	20	50			115568	287109	635492	1654657		
2-methoxyphenol	124.14	10	20	30	50			242686	1157486	1704355	3006529		
5-(hydroxymethyl)furan-2-carbaldehyde	126.11			20	35	50	100			84249	314383	562952	1662279
3-chloroaniline	127.57	5	10	20	50			145060	397054	859907	2320147		
naphthalene	128.17	5	10	20	50			331622	672230	1442905	3719622		
2-chlorophenol	128.55	5	10	20	50			316535	691566	1511368	3784531		
N,N-dipropylnitrous amide	130.19		10	20	50				294439	698797	1874374		
2-nitroaniline	138.12	5	10	20	50			82068	218051	546364	1576722		
3-nitroaniline	138.12	5	10	20	50			72498	231034	600670	1698204		
4-nitroaniline	138.12	5	10	20	50			58035	172666	557758	1523975		
2-methoxy-4-methylphenol	138.16	5	10	20	30	50	100	186888	436318	987327	1557590	2674614	5074029
3,5,5-trimethylcyclohex-2-en-1-one	138.21	5	10	20	50			184086	446662	974766	2589363		
2-nitrophenol	139.11	5	10	20	50			81605	212846	488343	1377337		
2-methylnaphthalene	142.20	5	10	20	50			730971	1460978	3196417	8180248		
4-chloro-3-methylphenol	142.58	5	10	20	50			153870	353042	842027	2341945		

1,2-dichlorobenzene	147.00	5			50			431092			6928686		
1,4-dichlorobenzene	147.00	5	10	20				215697	1292160	1853892			
acenaphthylene	152.19	5	10	20	50			428370	1016794	2227212	5677929		
4-ethyl-2-methoxyphenol	152.19	5	10	20	30	50	100	220083	551222	1259250	2062635	3472260	6678602
2,6-dimethoxyphenol	154.16	10	20	30	50			101974	717078	1107224	2098739		
1,2-dihydroacenaphthylene	154.21	5	10	20	50			408361	881029	1789699	4397178		
1-chloronaphthalene	162.61	5	10	20	50			301446	636726	1377182	3524448		
2,4-dichlorophenol	163.00	5	10	20	50			129614	332017	830143	2259600		
9H-fluorene	166.22	5	10	20	50			655144	1370820	2917517	7341601		
9H-carbazole	167.21	5	10	20	50			304281	721404	1548416	3918317		
1,2-dinitrobenzene	168.11	5	10	20	50			79345	205815	415659	1122729		
1,3-dinitrobenzene	168.11	5	10	20	50			44943	152162	390905	1116604		
dibenzofuran	168.19	5	10	20	50			331158	699261	1462773	3740800		
1-methyl-2-phenylbenzene	168.23			20	50					46914	102278		
N-phenylaniline	169.22	5	10	20	50			336331	753485	1659622	4204173		
dodecane	170.33	5	10	20	30	50	100	294190	574014	1230336	1855129	3065785	5581739
1-chloro-3-(3-chloropropoxy)propane	171.06			20	50					23468	52269		
1-chloro-2-(2-chloroethoxymethoxy)ethane	173.03	5	10	20	50			181549	412410	891927	2265597		
phenanthrene	178.23	5	10	20	50			416174	1755400	3776327	9516737		
1,2,4-trichlorobenzene	181.40	5	10	20	50			244879	494944	1056261	2795944		
1-methyl-2,4-dinitrobenzene	182.13	5	10	20	50			125695	339652	1005171	2792336		
diphenyldiazene	182.22	5	10	20	50			298458	580126	1262381	3205840		
2,4-dinitrophenol	184.11		10	20	50				48785	177420	585235		
dimethyl benzene-1,2-dicarboxylate	194.18	5	10	20	50			317507	708801	1582315	4044177		
(E)-tetradec-7-ene	196.37	5	10	20	30	50	100	240968	558410	1308611	2047259	3477068	6695304
2,3,6-trichlorophenol	197.40	5	10	20	50			167502	369463	862297	2371298		
2,4,5-trichlorophenol	197.40	5	10	20	50			155710	343277	805095	2302730		
2-methyl-4,6-dinitrophenol	198.13	5	10	20	50			36098	134262	422118	1143383		
pyrene	202.25	5	10	20	50			871403	1925182	4161597	10282063		
1-chloro-3-phenoxybenzene	204.65	5	10	20	50			310332	641404	1431640	3559154		
triphenylene	228.30	5	10	20	50			872292	2001022	4390166	11153284		
tetradecanoic acid	228.37	10	20	35	50	100	300	70675	203215	500430	469543	2957268	11730886
5-bromoacenaphthylene	231.09			20	50					15445	110776		
2,3,5,6-tetrachlorophenol	231.90	5	10	20	50			306091	760383	1746658	4751171		
1,1,1,2,2,2-hexachloroethane	236.70		10	20	50				392476	809999	2023497		
1-bromo-4-phenoxybenzene	249.10	5	10	20	50			247830	541262	1150464	3020197		
benzo[e]pyrene	252.30	5	10	20	50			758106	2773332	6276379	15208049		
hexadecanoic acid	256.42	10	20	35	50	100	300	51545	130834	361070	430809	3164919	12451729
1,1,2,3,4,4-hexachlorobuta-1,3-diene	260.80	5	10	20	50			216656	428030	901970	2448764		
2,3,4,5,6-pentachlorophenol	266.30	5	10	20	50			51162	189554	563590	1624381		

1,2,3,4,5,5-hexachlorocyclopenta-1,3-diene	272.80	5	10	20	50			62960	213797	553179	1756534		
hexacyclo[12.8.0.02,11.03,8.04,21.017,22]docosa-1(14),2(11),3(8),4,6,9,12,15,17(22),18,20-undecaene	276.30		10	20	50			1544048	2046974	4977215			
hexacyclo[16.3.1.02,7.08,21.011,20.014,19]docosa-1(22),2,4,6,8(21),9,11(20),12,14(19),15,17-undecaene	276.30	5		20	50			661537		1759568	4312637		
naphtho[1,2-b]phenanthrene	278.30	5	10	20	50			426290	868904	2132284	5291672		
dibutyl benzene-1,2-dicarboxylate	278.34	5	10	20	50			252895	578634	1332349	3329162		
(9Z,12Z)-octadeca-9,12-dienoic acid	280.45		20	35		100	300		22338	63841		741540	3975200
9-octadecenoic acid, (E)-	282.46	10	20	35	50	100	300	31509	133847	551470	494928	5345977	19779576
octadecanoic acid	284.48		20	35	50	100	300		77502	222849	265707	2977913	13324128
1,2,3,4,5,6-hexachlorobenzene	284.80	5	10	20	50			288103	604760	1261125	3260598		
methyl octadec-9-enoate	296.49	5	10	20	30	50	100	293301	683264	1755694	2897470	5110192	10246594
2-O-benzyl 1-O-butyl benzene-1,2-dicarboxylate	312.40	5	10	20	50			184645	460136	1188659	3092879		
bis(2-ethylhexyl) hexanedioate	370.60	5	10	20	50			264728	635823	1552007	3973738		
bis(2-ethylhexyl) benzene-1,2-dicarboxylate	390.60	5	10	20	50			269477	638760	1548479	3828878		
dioctyl benzene-1,2-dicarboxylate	390.60	5	10	20	50			221232	549196	1427699	3510829		
Derivatized Compounds													
benzoic acid	122.12					30	50					73458	113812
tetradecanoic acid	228.37	5	10	15	20	30	50	334920	491712	592372	806207	1175238	2071501
hexadecanoic acid	256.42	5	10	15	20	30	50	403058	570479	694901	936570	1474014	2605959
(9Z,12Z)-octadeca-9,12-dienoic acid	280.45	5	10	15	20	30	50	126644	183307	241591	350170	475205	824267
oleic acid	282.46	5	10	15	20	30	50	467088	741971	953554	1408563	2476003	4300414
octadecanoic acid	284.48	5	10	15	20	30	50	295116	501125	630854	891109	1745160	2957950
phenol	94.11			15	20	25	30			17168	21329	21557	71706
4-oxopentanoic acid	116.1	5	10	15	20	25	30	48330	206224	620353	885337	1096645	1394486
benzene-1,2-diol	110.11	5	10	15	20	25	30	184752	729379	1607583	2232039	2972508	3629582
2,4-dimethylphenol	122.16		10	15	20	25	30		29571	400625	612798	1354859	2310288
2-methoxy-4-methylphenol	138.16		10	15	20	25	30		41404	426592	645448	1348333	1995953

Table S4: Information concerning dilution and concentration in each vial to accompany GC-MS analysis (files available at Dataverse link in main article)

Filename	Feedstock	Yield of SC on feedstock basis	Dilution factor	Yield of SC [-]	Extracted HC [mg]	Extraction solvent [mL]	Total sample conc. in vial [mg/L]
CLS-NN_1 CLS-NN_2 CLS-NN_3	CLS250C1h	0.070	1	0.14	500	25	2800
CLS-DN_1 CLS-DN_2 CLS-DN_3			1	0.14	500	25	2800
CLS-DD_1 CLS-DD_2 CLS-DD_3			1	0.14	500	25	2800
AP-NN_1 AP-NN_2 AP-NN_3	AP250C2h	0.065	1	0.2	500	25	4000
AP-DN_1 AP-DN_2 AP-DN_3			1	0.2	500	25	4000
AP-DD_1 AP-DD_2 AP-DD_3			5	0.2	500	25	800
MIS-NN_1 MIS-NN_2 MIS-NN_3	MIS250C1h	0.156	2 1	0.32	500	25	3200 6400
MIS-DN_1 MIS-DN_2 MIS-DN_3			2 1	0.32	500	25	3200 6400
MIS-DD_1 MIS-DD_2 MIS-DD_3			1	0.32	500	25	6400
FW-NN_1 FW-NN_2 FW-NN_3	FW250C1h	0.384	25	0.7	500	25	560
FW-DN_1 FW-DN_2 FW-DN_3			25	0.7	500	25	560
FW-DD_1 FW-DD_2 FW-DD_3			125	0.7	500	25	112
FWd-NN_1 FWd-NN_2 FWd-NN_3			1	0.7	500	25	14000

Figure S4: GC-MS analysis of MIS using a 0.3 Tanimoto Similarity threshold.