Supplementary material

Catalytic fast pyrolysis of sewage sludge over HZSM-5: a study of light aromatics, coke and nitrogen migration under different atmospheres

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Schematic diagram of the reactor

Different CFP atmospheres were provided by the gas supply sector. Ar and H_2 atmospheres can be provided directly. In the steam cases, Ar was first injected to the reactor. Then the deionized water delivered by peristaltic pump was heated to generate water vapor, and subsequently the water vapor was carried by Ar to the reactor to create steam atmosphere. The reaction tube can be heated by the heating section and the reaction temperature can be controlled accurately. Bio-oil from CFP process was collected by condensing sector, and the non-condensable gases were collected by gas bag. As shown in the schematic diagram of the reactor, the CFP experiments were carried out in a quartz tube. A quartz plate was placed at the bottom of the tube to hold the catalysts. A piece of quartz wool was placed above the catalyst bed. The SS sample was placed in the feed bottle before feeding, and then the sample was fed into the tube after the heating was completed. The sample was rapidly pyrolyzed by the high temperature and the volatile was carried by carrier gas to contact with catalyst. Therefore, the SS sample and the catalyst did not directly contacted each other in our study, and this was facilitated the separate collection of solids. The char was retained on the quartz wool and the spent catalysts were hold on the quartz plate.

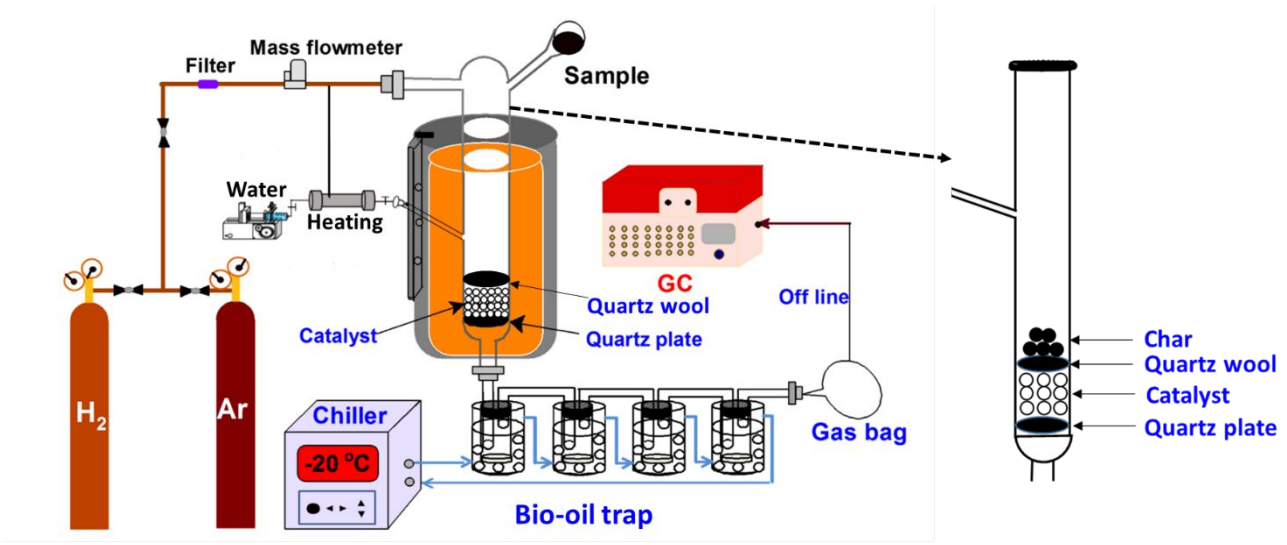

Fig. S1. Schematic diagram of the reactor.

Instruments specification and test program

The solid-state ^{13}C CPMAS NMR analysis were conducted on an Agilent DD2 500 MHz instrument (B0=11.7T) using a 4 mm probe. The resonance frequency was 125.69 MHz. The relaxation time was 4 s and the rotation speed was 8 KHz. The number of sampling times was 1800-3600 times, and the pulse width was 2.5 μs (π/4).

BANTE 931 ion meter is equipped with the NH_4-US NH_4^+ and CN-US CN^- electrodes. The NH_4^+ electrode is a PVC membrane ion-selective electrode. The CN^- electrode is a solid membrane ion-selective electrode. The detection method is the external standard method. A series of standard solutions with different concentrations were used to calibrate the electrode. Each sample reading was compared with the calibration reading to obtain the sample concentration.

The collected liquid product was identified by Agilent 7890/5797 GC-MS and quantified by Shimadzu GC-2014 GC-FID. External standards were prepared for the major aromatics such as benzene, toluene, xylene (*o*-xylene, *m*-xylene, *p*-xylene), alkylbenzene, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, alkylnaphthalene, fluorine, anthracene, phenanthrene, and pyrene.

Determination of gas-C, coke-C, char-C and oil-C

The C-containing gases including hydrocarbons (C_1-C_4) were analyzed by Shimadzu GC-2014 gas chromatograph equipped with a flame ionization detector (FID). Total carbon contents in char and coke were determined with the Elementar vario MACRO cube CHNS elemental determinator. And the oil-C was calculated by difference.

The calculation of carbon yields of LAs

$$\text{Carbon yields of LAs (\%)} = \frac{\text{Moles of carbon in LAs}}{\text{Moles of carbon in feed}} \times 100\%$$

TICs and the main compounds of the bio-oils from different conditions

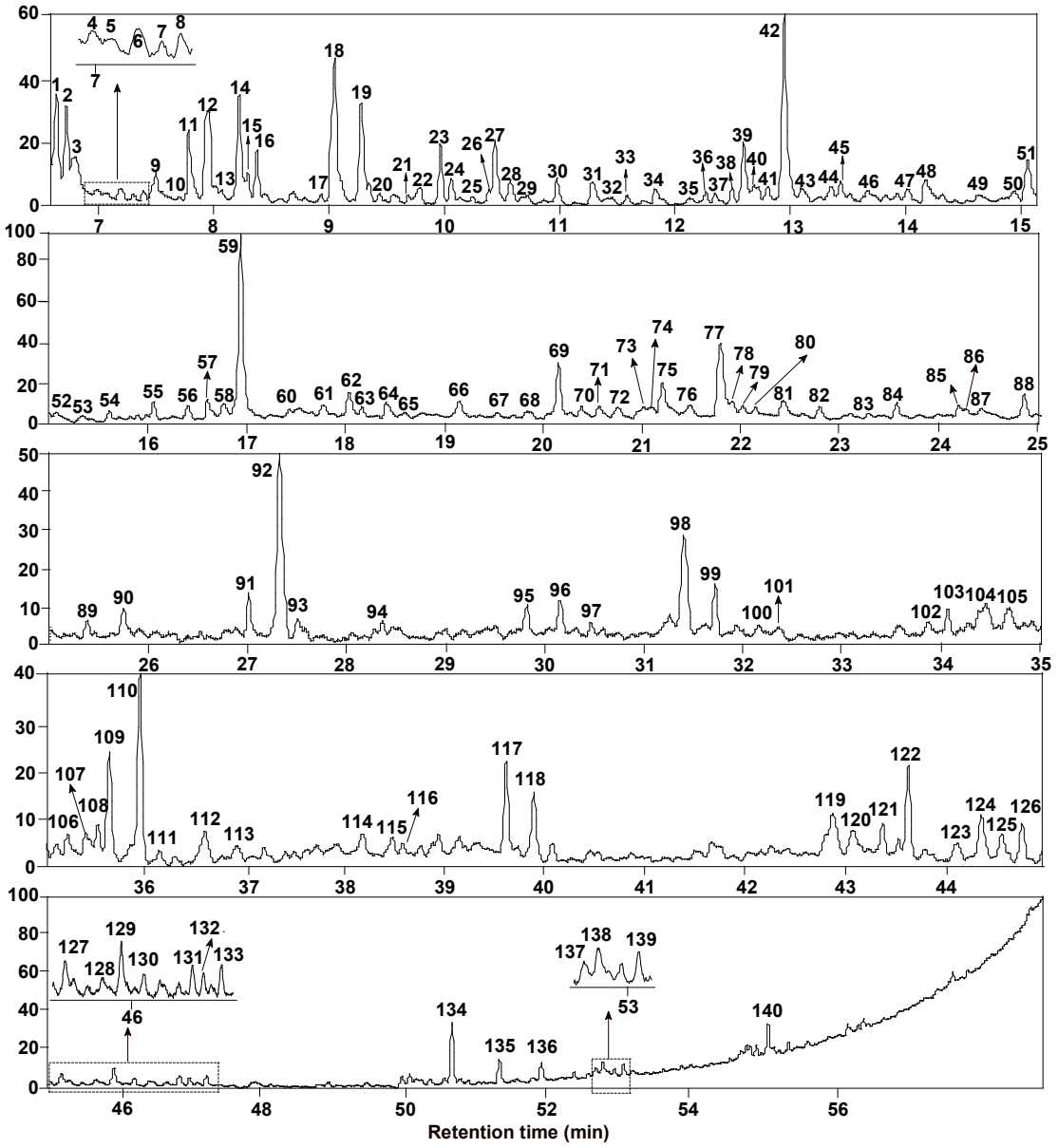

Fig. S2. TICs of the liquid product obtained from non-catalytic pyrolysis of SS under Ar atmosphere at 500 ^{o}C

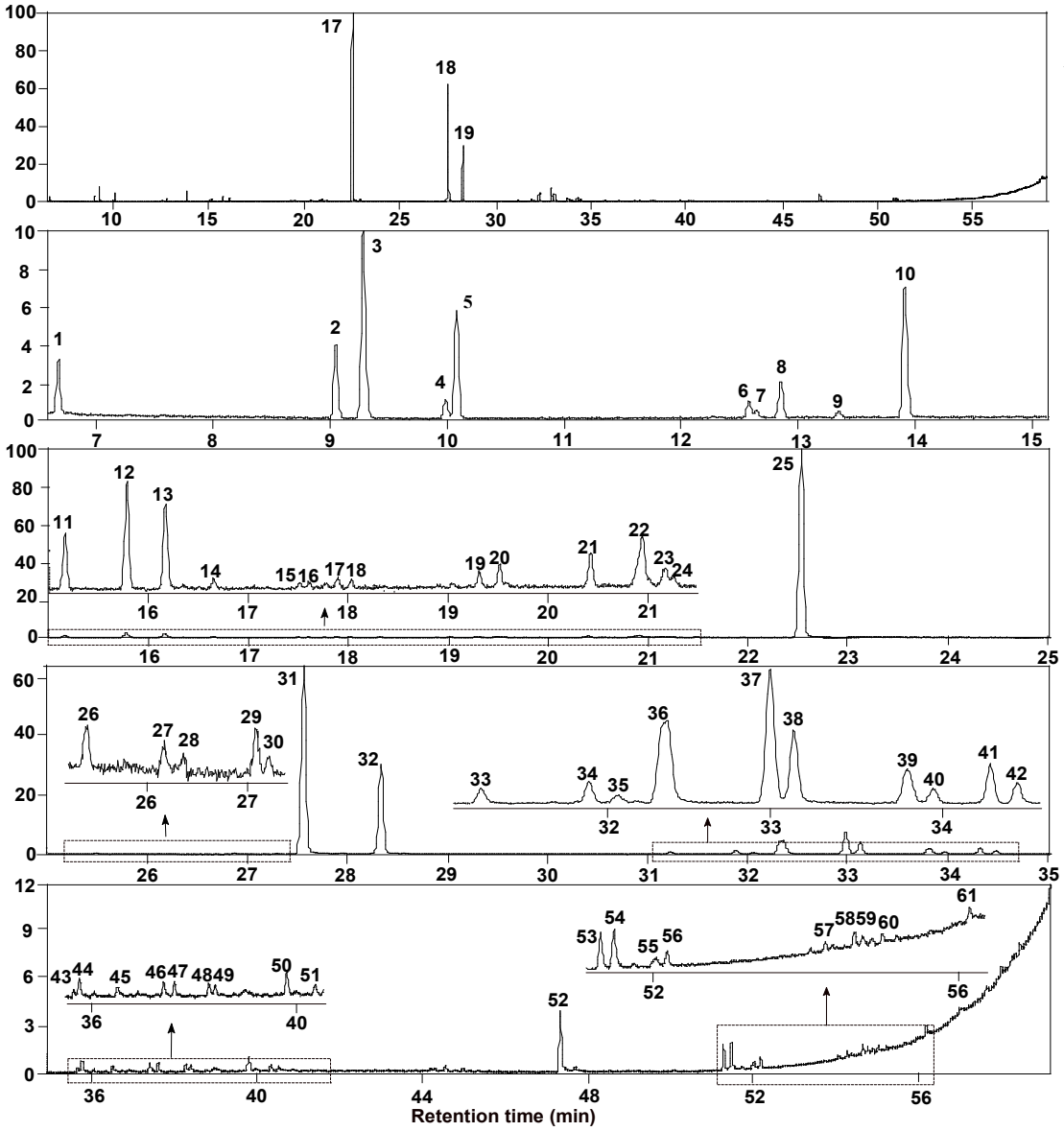

Fig. S3. TICs of the liquid product obtained from CFP of SS over HZ under Ar atmosphere at 500 ^{o}C

Table S1. The main compounds identified by GC-MS of the bio-oil obtained from non-catalytic pyrolysis of SS under Ar at 500 °C.

Peak	Compound	Peak	Compound
1	Butanoic acid	71	4-Aminophenol
2	Toluene	72	3-Methyl-1*H*-indene
3	Methyl isovalerate	73	Pentyl-benzene
4	2-Methylenebutanenitrile	74	3-Pentenenitrile
5	2-Methyl-3-butenenitrile	75	4-Ethyl-phenol
6	2-Hexene	76	1-Acetylpyrrolidine
7	Hexanal	77	2-Piperidinone
8	*N*,*N*-dimethylacetamide	78	Methyl 2-phenylacetate
9	Crotonic acid	79	Glutarimide
10	3-Ethyl-1*H*-pyrrole	80	1-Piperidineethanol
11	2-Methylpyridine	81	1-Nonene
12	3-Methylbutanoic acid	82	Undecane
13	Methyl 2-oxobutanoate	83	2*H*-Pyrano[*3*,*2*-*b*]pyridine
14	2-Cyclopenten-1-one	84	2,3-Dihydro-benzofuran
15	2-Propen-1-amine	85	3-Acetamidofuran
16	Isoamyl cyanide	86	Ethylidenecyclopropane
17	2-Ethyl-4-hexene-1-ol	87	Methyl ethylcarbamate
18	Ethylbenzene	88	Benzenepropanenitrile
19	1,3-Dimethylbenzene	89	3-Methyl-1-hexene
20	Hexanenitrile	90	Hexylbenzene
21	2,3-Dimethyl-pyridine	91	(*Z*)-6-Tridecene
22	2-Hexanol acetate	92	Indole
23	Styrene	93	1-Methyl-naphthalene
24	Ethylbenzene	94	4,5-Dimethyloxazole
25	2-Methylpropanamide	95	4-(1-Aziridinyl)-3-buten-2-one
26	2-Ethylpyridine	96	Eicosane
27	2-Methyl-2-cyclopenten-1-one	97	Octadecane
28	1-(2-Furanyl)-ethanone	98	6-Methyl-1*H*-indole

29	Methallyl cyanide	99	Tetradecane
30	3-Buten-2-ol	100	2-Butenenitrile
31	2,4-Dimethylpyridine	101	2-Cyclohexen-1-one
32	2-Ethenylpyridine	102	(1*H*-Pyrrol-3-yl)acetic acid
33	4,4-Dimethyl-2-pentene	103	cis-2-Methyl-7-octadecene
34	2,3-Dimethylpyridine	104	*N*-4-pyridinyl-acetamide
35	Dihydro-5-methyl-2(3*H*)-furanone	105	Octylbenzene
36	4-Methyl-1-pentyne	106	Cyclopentadecane
37	3-Ethylpyridine	107	Cetene
38	Benzaldehyde	108	1-Ethyl-1*H*-indole
39	3-Methyl-2-cyclopenten-1-one	109	1-Pentadecene
40	Methyl 2-oxohexanoate	110	Pentadecane
41	1-Propoxy-2-butene,	111	(*Z*)-5-Tridecene
42	Phenol	112	*N*-(2-phenylethyl)-acetamide
43	2,3-Dimethylpyridine	113	2-Methyl-1*H*-benzimidazole
44	Methyl 4-oxopentanoate	114	1-Ethenylcyclohexanol
45	Benzonitrile	115	2,6-Dimethylpiperazine
46	3-Methyl-butanamide	116	2-Propylphenol
47	2-Methylene-4-pentenal	117	(*E*)-9-Octadecene
48	3-Aminopyridine	118	Tridecane
49	5,6,7,8-Tetrahydroindolizine	119	(2-Methylbutyl)-benzene
50	2-(1-Methylethyl)-pyridine	120	*E*-14-Hexadecenal
51	2-Methyl-1,3-cyclopentanedione	121	(*E*)-5-Eicosene
52	1-Ethenyl-4-methyl-benzene	122	Heptadecane
53	1-(2-Pyridinyl)-ethanone	123	3-Pyrrolidin-2-yl-propionic acid
54	2,3-Dimethyl-2-cyclopenten-1-one	124	Thiazolo[5,4-f]quinoline
55	*p*-Cresol	125	Methyl undecanoate
56	1-(1*H*-Pyrrol-2-yl)-ethanone	126	3,7,11-Trimethyl-1-dodecanol
57	2-Pyrrolidinone	127	cis-2-Methyl-7-octadecene
58	2-Pyridinecarbonitrile	128	Hexahydro-pyrrolo[1,2-a]pyrazine-1,4-dione
59	*p*-Cresol	129	Tetradecanenitrile

60	1-(2-Furanyl)-ethanone	130	Heptadecanenitrile
61	1-Methyl-2,5-pyrrolidinedione	131	Methyl 13-methyltetradecanoate
62	4(1*H*)-Pyridone	132	1-Dodecanol
63	Undecane	133	Octadecane
64	3-Aminopyridine	134	Undecanenitrile
65	3,5-Dimethylphenol	135	Methyl palmitate
66	Succinimide	136	Ethoxyacetonitrile
67	2,4-Dimethylstyrene	137	1-Methyl-9*H*-Pyrido[3,4-*b*]indole
68	N-ethyl-cyclohexylamine	138	9*H*-Pyrido[3,4-*b*]indole
69	Benzyl nitrile	139	Eicosane
70	2,5-Dimethylphenol	140	Heptadecanenitrile

Table S2. The main compounds identified by GC-MS of the bio-oil obtained from CFP of SS over HZ under Ar at 500 °C.

Peak	Compound	Peak	Compound
1	Toluene	32	2-Methylnaphthalene,
2	Ethylbenzene	33	Biphenyl
3	*p*-Xylene	34	1-Ethylnaphthalene,
4	Styrene	35	2-Ethylnaphthalene,
5	*o*-Xylene	36	Dimethylnaphthalene,
6	Ethylmethylbenzene	37	Dimethylnaphthalene,
7	Ethylmethylbenzene	38	Dimethylnaphthalene,
8	Trimethylbenzene	39	Dimethylnaphthalene,
9	Ethylmethylbenzene	40	Dimethylnaphthalene,
10	Mesitylen	41	Hexamethyl-benzene,
11	Trimethylbenzene	42	Dimethylnaphthalene
12	Indane	43	Diphenylmethane
13	Indene	44	Acenaphthene
14	Ethyldimethylbenzene	45	Trimethylnaphthalene
15	Ethyldimethylbenzene	46	Trimethylnaphthalene
16	Ethyldimethylbenzene	47	Trimethylnaphthalene
17	Ethyldimethylbenzene	48	Trimethylnaphthalene
18	1-Methylindan	49	Trimethylnaphthalene
19	Tetramethylbenzene	50	Fluorene
20	Tetramethylbenzene	51	3-Methyl-1,1'-biphenyl
21	1-Ethenyl-4-ethylbenzene	52	Anthracene
22	2-Ethenyl-1,4-dimethylbenzene	53	1-Methylanthracene
23	1,4-Dihydronaphthalene	54	2-Methylanthracene
24	1-Methyl-1*H*-indene	55	9-Methylanthracene
25	Naphthalene	56	1-Methylphenanthrene
26	2,3-Dihydro-4,7-dimethyl-1*H*-indene	57	Dimethylphenanthrene
27	(1,2-Dimethyl-1-propenyl)-benzene	58	Dimethylphenanthrene
28	1-Phenyl-1-pentyne	59	Dimethylphenanthrene

29	Pentamethylbenzene	60	Dimethylphenanthrene
30	2,3-Dihydro-1,3-dimethyl-1*H*-indene	61	Pyrene
31	1-Methylnaphthalene		

The absolute amount of LAs (mg/g SS, daf) obtained from CFP under different conditions

Table S3. Absolute amount of LAs obtained from CFP of SS under different conditions.

Atmosphere	PT (°C)	Catalyst	Gaseous products yields (mg/g SS, daf)						
			B	T	E	X	N	M-N	Total LAs
Ar	400	HZ	3.5	8.2	0.4	5.3	1.2	2.1	20.6
	500	HZ	11.4	21.3	0.4	10.4	3.0	3.8	50.3
	600	HZ	18.2	11.7	0.3	6.9	2.7	3.0	42.7
	700	HZ	22.6	7.1	0.2	4.3	1.7	2.4	38.4
	500	0.5Ni-HZ	18.3	25.2	0.4	9.6	3.1	3.4	59.9
	500	0.5Co-HZ	13.3	24.9	0.5	11.9	3.0	3.8	57.3
Steam	400	HZ	3.3	7.8	0.2	4.9	0.9	1.3	18.4
	500	HZ	11.2	17.4	1.7	9.9	2.3	3.5	46.1
	600	HZ	17.1	11.3	1.7	5.5	2.1	2.9	40.5
	700	HZ	21.6	5.7	1.1	2.6	1.6	2.3	34.9
	500	0.5Ni-HZ	16.5	19.4	2.2	9.1	2.8	3.8	53.9
	500	0.5Co-HZ	13.1	20.9	2.1	10.3	2.5	3.9	52.9
H_2	400	HZ	5.1	5.8	2.3	4.6	1.0	2.0	20.9
	500	HZ	13.2	19.4	1.8	10.0	2.9	4.1	51.5
	600	HZ	21.1	11.4	1.4	5.0	3.5	3.4	45.8
	700	HZ	28.6	4.3	1.3	2.8	3.1	2.3	42.4
	500	0.5Ni-HZ	20.5	23.7	1.9	9.4	4.0	4.4	63.8
	500	0.5Co-HZ	18.0	23.8	2.0	11.1	3.9	4.5	63.3