Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.

Enhancing energy recovery of wastewater treatment plants through hydrothermal liquefaction

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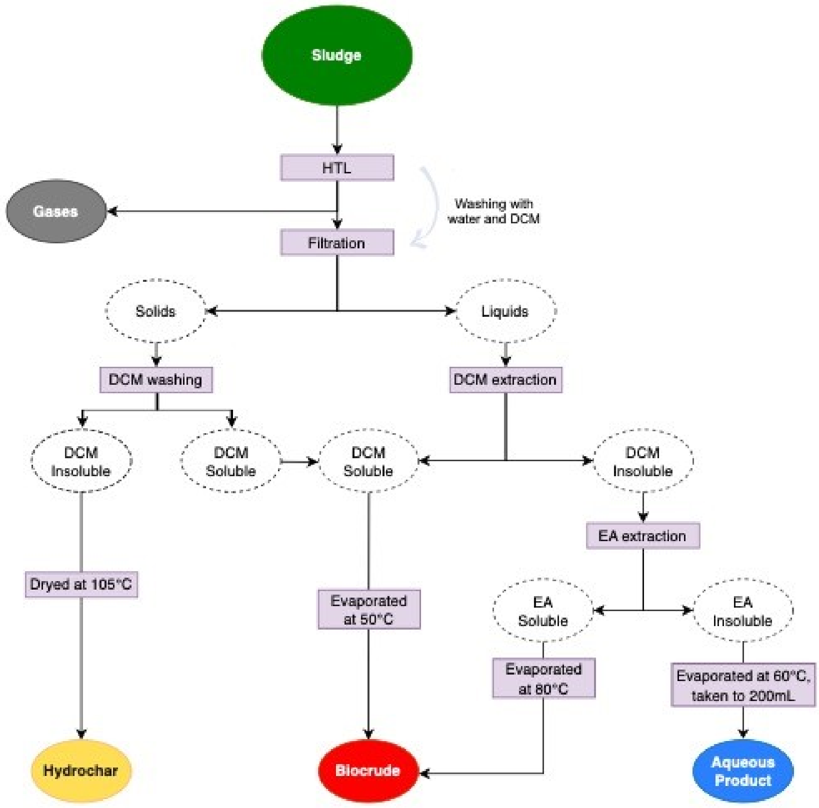

Figure S1. Diagram of the HTL products separation.

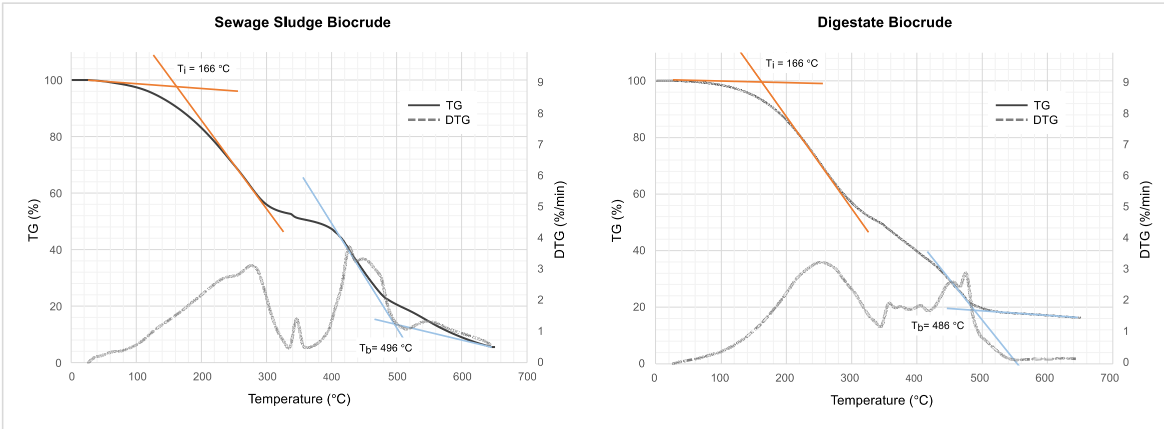

Figure S2. Thermogravimetric (TG) and Derivative Thermogravimetric (DTG) curves for sewage sludge and digestate biocrudes. T_i = ignition temperature; T_b = burnout temperature.

Table S1. Elemental analysis and ash content of biocrude, solids in aqueous product, and hydrochar generated from SS and digestate. Values are in wt% of dry product and represent the mean of three separate experiments ± standard deviation.

	C	H	N	Ash	O	HHV
SS	35.4±0.8	6.3±0.2	6.3±0.1	26.1±1.8	25.9±1.1	16.4±0.7
Biocrude	75.1±0.3	9.9±0.1	3.1±0.1	0.04±0.0	11.8±0.3	37.5±0.3
Aqueous product (db)	10.1±0.1	5.8±0.2	15.9±0.4	46.4±4.7	21.8±0.6	7.8±0.4
Hydrochar	26.7±0.5	1.7±0.1	1.2±0.0	70.6±4.5	0.1±0.2	11.4±0.3
Digestate	30.3±0.7	5.4±0.0	4.8±0.1	35.8±0.6	23.7±0.7	13.7±0.3
Biocrude	77.6±0.1	10.6±0.0	2.5±0.1	3.1±0.0	6.1±0.0	40.3±0.0
Aqueous product (db)	14.1±0.2	5.4±0.1	12.3±0.2	36.3±3.9	31.8±0.1	6.8±0.1
Hydrochar	11.2±1.2	0.9±0.0	0.5±0.1	77.7±2.6	8.1±1.2	3.6±0.6

Table S2. Major compounds identified* in the biocrudes generated from the HTL of sewage sludge and digestate.

Peak	□RT, min	Compound	Sewage sludge (Area, %)	Digestate (Area, %)
1	6,453	Butanoic acid, 3-methyl	4.85	
2	6,703	Butanoic acid, 2-methyl	2.54	
3	9,533	Pentanoic acid, 4-methyl	2.00	
4	10,464	Phenol	6.74	1.64
5	12,198	2(3H)-Furanone, 5-butyldihydro-4-methyl	1.96	
6	13,527	p-cresol	8.20	2.69
7	14,332	Undecane	1.37	
8	14,742	Phenylethyl Alcohol	2.15	
9	16,433	Phenol, 4-ethyl	4.68	3.03
10	19,543	N-2-Hydroxyethyl-succinimide	2.01	
11	27,596	Dodecanoic acid	1.21	1.64
12	13,91	2,5-Pyrrolidinedione, 1-methyl	2.06	
13	21,495	Hydrocinnamic acid	1.40	
14	30,859	1-Hexadecanol		1.47
15	31,66	Benzene, (1-pentylheptyl)		1.34
16	31,765	Benzene, (1-butyloctyl)		1.10
17	32,067	Benzene, (1-propylnonyl)		1.37
18	33,89	Benzene, (1-pentyloctyl)		1.98
19	34,695	2-Nonadecanone	1.01	1.21
20	35,487	Hexadecanenitrile	1.50	
21	35,988	Hexadecanoic acid, methyl ester	1.02	
22	35,113	Heptadecanol-1	3.03	
23	41,073	9-Octadecenamide		2.16
24	46,685	Eicosane	1.61	6.07
25	39,658	1-Eicosanol	1.64	1.36
26	41,051	Tetradecanamide	6.35	
27	44,776	Octadecanamide	2.51	
28	45,001	Octacosane	1.77	
29	48,295	Nonacosane	2.16	
30	49,858	Tetratetracontane		1.54
31	50,476	Cholest-14-ene	1.97	4.29
32	52,15	Cholest-4-ene	15.2	16.07
33	52,344	Cholesta-3,5-diene		1.24
34	54,219	Androstan-17-one, 3-hydroxy	1.88	
35	54,565	13,15-Octacosadiyne	1.99	
36	54,896	Androst-2-en-17-.beta.-ol, 17-methyl	3.81	11.11

37	55,406	Cholestan-3-ol		2.46
38	55,869	Cholestane, 2,3-epoxy-	2.38	13.12
39	56,474	Cholestan-3-one		4.36
40	57,534	Cholest-4-en-3-one		1.55
		Other compounds	**8.12**	**16.00**
Total			**99.12**	**98.8**

* Representing >1% of the GC–MS total ion chromatogram areas. Compounds with match factor scores, between observed and reference mass spectrum, greater than or equal to 75% were assigned as identified compounds.

Table S3. Major compounds identified* in the APs generated from the HTL of sewage sludge and digestate.

Peak	□RT, min	Compound	Sewage sludge (Relative area, %)	Digestate (Relative area, %)
1	6,453	2-Methylpyridine	0,1	
2	6,703	2,6-Dimethylpyridine	0,13	
3	9,533	2-Propanone, 1-hydroxy-	0,09	
4	10,464	Pyridine, 2,4,6-trimethyl-		0,93
5	12,198	Pyridine, 2,4-dimethyl-		0,11
6	13,527	Acetic acid	90,5	17,95
7	14,332	Pyridine, 3-ethyl-2,6-dimethyl-	0,16	
8	14,742	Propanoic acid	0,93	1,07
9	16,433	2-Furancarboxaldehyde, 5-methyl-		0,3
10	19,543	Butanoic acid	0,43	1,15
11	27,596	Butanoic acid, 4-hydroxy-		0,86
12	13,91	Pentanoic acid		0,5
13	21,495	1-Methyl-2-pyrrolidinone		1,73
14	30,859	1-Ethyl-2-pyrrolidinone		0,57
15	31,66	Oxime-, methoxy-phenyl-		14,62
16	31,765	1H-Imidazole, 1-methyl-2-nitro-		0,51
17	32,067	Piperidine, 1-methyl-		0,28
18	33,89	Cinnamonitrile	0,11	
19	34,695	Ethanol, 2,2'-oxybis-		1,69
20	35,487	5-Methyl-2-pyrrolidinone		0,4
21	35,988	2-Pyrrolidinone	0,78	
22	35,113	2-Piperidinone	0,14	8,24
23	41,073	3-Aminopyridine		1,36
24	46,685	Caprolactam		1,29
25	39,658	3,4-dimethyl-1H-pyrrole-2-carboxaldehyde		1,57
26	41,051	2-Ethyl-6-methylpyridin-3-ol		0,89
27	44,776	Phenol, 4-amino-		1,88

28	45,001	2(1H)-Pyridinone, 1,3-dimethyl-	0,29	
29	48,295	2-Ethyl-3-Hydroxypyridine		0,91
30	49,858	Glutarimide		0,54
31	50,476	Phthalic acid, ethyl 2-ethylbutyl ester		0,48
32	52,15	Phenol, o-amino-		5,06
33	52,344	3-Pyridinol, 6-methyl-	0,57	
34	54,219	3-Pyridinol	0,47	8,06
35	54,565	Succinimide	0,44	
36	54,896	2(1H)-Pyridinone, 3-methyl-		0,45
37	55,406	4-Amino-2,3-dimethylbenzaldehyde		0,22
38	55,869	N-(2-Phenylethyl)acetamide		1,34
39	56,474	2-(4-Hydroxyphenyl)ethanol	0,3	
Total			**95.44**	**74.96**

* Compounds with match factor scores, between observed and reference mass spectrum, greater than or equal to 75% were assigned as identified compounds.

Table S4. Solids reduction from the HTL of sewage sludge and digestate

Measurement	**Sewage sludge**	**Anaerobic digestate**
Solids in initial sludge feed (g)	2.76±0.004	2.72±0.003
Ash in sludge feed (g)	0.72±0.05	0.98±0.01
Hydrochar (HTL solids) (g)	0.93±0.10	1.19±0.04
Ash in hydrochar (g)	0.66±0.07	0.92±0.03
Recovery of ash in hydrochar (%)	92%	94%
Reduction of initial sludge solids (%)	66%	56%

Table S5. Previous studies on the HTL of sewage sludge and digestate

	Sludge characteristics								HTL operating parameters			Biocrude characteristics							
Author	Sludge	C	H	N	S	O	Ash (%, db)	HHV[a]	Process [b]	T and time	VS (%, db)	Yield (%, daf)	C	H	N	S	O	Ash (%, db)	HHV[a]
[1]	SS	47.4	9.3	8.2		35.1	25.8	23.0	Batch	350C 60’	11.5	25.8							
[2]	PS	46.5	6.1	3.3	0.4	31.2	12.5	18.9	Continuous	350C	3.5	24.5	58.2	6.5	2.4	0.5	5.9	28.4	27.9
[3]	PS	45.3	7.3	2.5	0.3	33.7	13.0	19.7	Continuous	350C	13.9	31.8	72.8	8.9	3.1		12.7	2.0	35.0
[4]	PS	47.8	6.5	3.6	0.5	33.6	7.5	19.4	Continuous	350C 18’	11.0	37.3	76.5	10.1	4.3	0.6	8.1	0.4	38.8
	WAS	43.6	6.5	7.9	0.7	29.0	16.2	18.9	Continuous	350C 19’	8.1	24.8	72.5	8.7	5.1	0.9	6.5	6.3	35.8
	AD	38.7	5.7	4.5	1.6	27.9	28.1	16.2	Continuous	350C 30’	11.5	34.4	78.5	9.5	4.5	1.2	6.2	0.2	39.0
[5]	SS	43.4	6.5	5.0	0.8	27.6	16.7	19.0	Batch	325C 30’	8.3	37.0							39.0
[6]	SS	52.0	7.6	7.5	2.6	30.3	36.7	15.3	Batch	300C 40'	10.5	40.0	66.0	8.5	6.3	1.3	17.9		31.2
[7]	SS	43.4	5.9	3.2		47.5	39.2	14.6	Batch	350C 20’	4.4	39.5	72.5	9.4	7.0		11.1		36.0
[8]	WAS	46.4	7.6	7.4		38.6	23.2	19.7	Batch	350C 15’	16.4	44.5	73.0	10.5	5.2		11.3		37.7
[9]	SS	46.5	7.0	2.1	0.8	33.3	10.3	19.8	Batch	400C 60'	13.5	26.8	72.5	9.4	7.0		11.1		36.1
[10]	PS+ WAS	42.6	7.0	6.8	1.9	19.8	21.8	21.1	Batch	300C 120	10.2	36.9	75.8	10.0	4.5	2.4	7.3		38.8
[11]	WAS	33.8	5.1	5.8	3.2	16.5	35.5	15.8	Batch	350C 10’	6.5	20.0	73.1	9.2	4.4	1.7	11.6		35.8
[12]	WAS	50.9	7.4	6.9		34.8	40.6	21.5	Batch	350C 30’	16.0	40.2	73.7	10.1	5.7		10.5		37.4
[13]	AD						31.0		Batch	300C 30'	13.8	9.4	66.6	9.2	4.3	1.0	18.9		32.3
This study	WAS	35.4	6.3	6.3		25.9	26.1	16.4	Batch	350C 30'	2.0	26.4	75.1	9.9	3.1		11.8	0.0	37.5
	AD	30.3	5.4	4.8		23.7	35.8	13.7	Batch	350C 30'	1.7	15.8	77.6	10.6	2.5		6.1	3.1	40.3

SS: sewage sludge (the source is not known); PS: primary sludge; WAS: waste activated sludge; PS: primary sludge; AD: anaerobic digestate; HHV: higher heating value; T: temperature; COD: chemical oxygen demand.

[a] Recalculated with Eq. (5)

[b] Values presented in this table correspond to HTL processes without addition of catalyst. For continuous mode, the HTL products were gravimetrically separated. For batch mode, the HTL products were separated using solvents.

Table S6. Parameters used for the Monte Carlo simulations

Parameter	Name	HTL-AD	AD-HTL-AD
COD of SS (kg)	COD_SS	130	130
VS of SS (kg)	VS_SS	100	100
HHV of SS (MJ/kg) [a]	HHV_SS	~ Tri (14, 17, 23)	~ Tri (14, 17, 23)
Biodegradability of SS (fraction) [b]	f_SS	-	~ Tri (0.3, 0.5, 0.7)
Produced methane from AD of SS (L)	CH4_SS	-	COD_SS * f_SS * 350
Recovered energy from AD of SS (fraction)	ER_AD_SS	-	(CH4_SS * 39.74/1000)/ (HHV_SS * VS_SS)
COD of digestate (kg)	COD_D	-	COD_SS * (1 - f_SS)
VS of digestate (kg)	VS_D	-	COD_D / 1.1
HHV of biocrude (MJ/kg) [a]	HHV_oil	~ Tri (28, 37, 39)	~ Tri (32, 37, 40)
Maximum yield of biocrude (fraction)	Max_Yield	0.9 * (HHV_SS)/ (HHV_OIL)	(0.9 - ER_AD_SS) * VS_SS* HHV_SS / (VS_D * HHV_OIL)
Biocrude Yield (fraction) [a]	Yield_oil	~ Tri (a, c, b) a = 0.2 b = min (0.44, Max_Yield) c = min ((a+0.31+b)/3, (a+b)/2)	~ Tri (a, c, b) a = 0.09 b = min (0.34, Max_Yield) c = min ((a+0.16+b)/3, (a+b)/2)
Recovered energy from biocrude (fraction)	ER_oil	(Yield_oil) * (HHV_oil) / (HHV_SS)	Yield_oil * VS_D * HHV_oil / (HHV_SS * VS_SS)
COD of biocrude (kg) [c]	COD_oil	HHV_oil * Yield_oil / 13.9	HHV_oil * Yield_oil / 13.9
COD of AP (kg) [d]	COD_AP	(COD_SS - COD_oil) * 0.5	(COD_D - COD_oil) * 0.5
Biodegradability of AP (fraction) [e]	f_AP	~ Tri (0.4, 0.6, 0.8)	~ Tri (0.3, 0.5, 0.7)
Produced methane from AD of AP (L)	CH4_AP	COD_AP * f_AP * 350	COD_AP * f_AP * 350
Recovered energy from AD of AP (fraction)	ER_AD_AP	CH4_AP *(39.74/1000) / (HHV_SS * VS_SS)	CH4_AP *(39.74/1000) / (HHV_SS * VS_SS)
Total recovered energy (%)	ER	(ER_oil + ER_AD_AP) * 100%	(ER_AD_SS + ER_oil + ER_AD_AP) * 100%

[a] Values based on Table S4
[b] Astals et al.[14]
[c] COD values are converted from a mass to energy basis assuming 13.9 MJ/kg COD as reported by Seiple et al.[15]
[d] From the residual COD, 50% is partitioned to the AP
[e] Posmanik et al.[16] and the present study

Table S7. Main results of the Monte Carlo Simulations (N = 100,000)

	AD	HTL-AD			AD-HTL-AD			
	ER from AD of SS (%)	ER from biocrude (%)	ER from AP (%)	Total ER (%)	ER from AD of SS (%)	ER from biocrude (%)	ER from AP (%)	Total ER (%)
Mean	50.7	60.9	12.2	73.1	50.8	23.0	6.9	80.6
SD	9.8	10.9	3.8	9.6	9.8	7.2	2.4	8.4
Min	25.1	28.2	1.9	42.7	24.9	6.4	0.9	49.2
2.5%	33.2	40.4	5.5	54.6	33.1	11.2	2.9	63.5
97.5%	71.1	82.1	20.1	91.2	71.0	39.0	12.2	94.7

References

1. Inoue, S., Sawayama, S., Dote, Y. & Ogi, T. Behaviour of nitrogen during liquefaction of dewatered sewage sludge. *Biomass and Bioenergy* **12**, 473–475 (1997).
2. Anastasakis, K., Biller, P., Madsen, R. B., Glasius, M. & Johannsen, I. Continuous Hydrothermal Liquefaction of Biomass in a Novel Pilot Plant with Heat Recovery and Hydraulic Oscillation. *Energies* **11**, 1–24 (2018).
3. Silva Thomsen, L. B. *et al.* Hydrothermal liquefaction of sewage sludge; energy considerations and fate of micropollutants during pilot scale processing. *Water Res.* **183**, 116101 (2020).
4. Marrone, P. A. *et al.* Bench-Scale Evaluation of Hydrothermal Processing Technology for Conversion of Wastewater Solids to Fuels. *Water Environ. Res.* **90**, 329–342 (2018).
5. Prestigiacomo, C. *et al.* Catalytic hydrothermal liquefaction of municipal sludge assisted by formic acid for the production of next-generation fuels. *Energy* **232**, 121086 (2021).
6. Malins, K. *et al.* Bio-oil from thermo-chemical hydro-liquefaction of wet sewage sludge. *Bioresour. Technol.* **187**, 23–29 (2015).
7. Huang, H. jun *et al.* Comparative studies of thermochemical liquefaction characteristics of microalgae, lignocellulosic biomass and sewage sludge. *Energy* **56**, 52–60 (2013).
8. Conti, F. *et al.* Valorization of animal and human wastes through hydrothermal liquefaction for biocrude production and simultaneous recovery of nutrients. *Energy Convers. Manag.* **216**, 112925 (2020).
9. Qian, L., Wang, S. & Savage, P. E. Hydrothermal liquefaction of sewage sludge under isothermal and fast conditions. *Bioresour. Technol.* **232**, 27–34 (2017).
10. Zhang, W. & Liang, Y. Hydrothermal liquefaction of sewage sludge – effect of four reagents on relevant parameters related to biocrude and PFAS. *J. Environ. Chem. Eng.* **10**, 107092 (2022).
11. Xu, D. *et al.* Comprehensive evaluation on product characteristics of fast hydrothermal liquefaction of sewage sludge at different temperatures. *Energy* **159**, 686–695 (2018).
12. Shah, A. A., Toor, S. S., Conti, F., Nielsen, A. H. & Rosendahl, L. A. Hydrothermal liquefaction of high ash containing sewage sludge at sub and supercritical conditions. *Biomass and Bioenergy* **135**, (2020).
13. Vardon, D. R. *et al.* Chemical properties of biocrude oil from the hydrothermal liquefaction of Spirulina algae, swine manure, and digested anaerobic sludge. *Bioresour. Technol.* **102**, 8295–8303 (2011).
14. Astals, S. *et al.* Anaerobic digestion of seven different sewage sludges: A biodegradability and modelling study. *Water Res.* **47**, 6033–6043 (2013).
15. Seiple, T. E., Skaggs, R. L., Fillmore, L. & Coleman, A. M. Municipal wastewater sludge as a renewable, cost-effective feedstock for transportation biofuels using hydrothermal liquefaction. *J. Environ. Manage.* **270**, 110852 (2020).
16. Posmanik, R. *et al.* Coupling hydrothermal liquefaction and anaerobic digestion for energy valorization from model biomass feedstocks. *Bioresour. Technol.* **233**, 134–143 (2017).