Supplementary material

Hydrothermal conversion of beef-cattle manure can enhance energy recovery in confined feedlots

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1. Temperature profile of the hydrothermal reactions

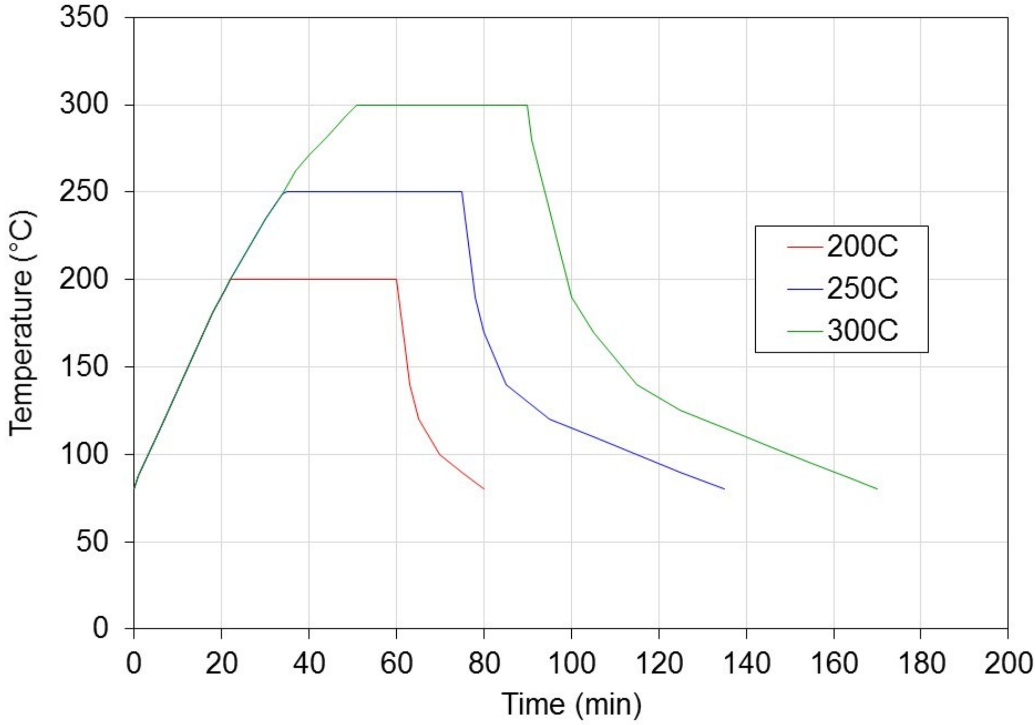

Fig. S1. Representative temperature profiles for the hydrothermal experiments. Time 0 corresponds to the moment when the system reaches 80˚C.

2. Gas chromatography

In addition to the GC-MS profile (**Fig. 4**), a detailed list of compounds in the biocrude oil (for each reaction temperature) with their relative abundance as observed by the qualitative GC-MS analysis is given below.

Table S1. Biocrude oil composition from hydrothermal liquefaction of manure at different reaction temperatures (200, 250 and 300°C). All components were characterized by GC−MS. Values represent % of the total relative peak area.

Retention time	Compound Name	Formula	Relative abundance (%)	CAS#
200°C				
5.2	Pyrazine, 2,6-dimethyl-	C6H8N2	5.8	108-50-9
5.3	Pyrazine, ethyl-	C6H8N2	5.4	13925-00-3
5.3	Pyrazine, 2,3-dimethyl-	C6H8N2	0.7	5910-89-4
6.4	6.56 Furfural<5-methyl->	C6H6O2	1.7	620-02-0
7.1	Phenol	C6H6O	3.2	108-95-2
7.2	Pyrazine, 2-ethyl-6-methyl-	C7H10N2	4.5	13925-03-6
7.3	Pyrazine, 2-ethyl-3-methyl-	C7H10N2	5.8	15707-23-0
8.1	2-Furanmethanol, 5-methyl-	C6H8O2	0.4	3857-25-8
9.4	Pyrazine, 3-ethyl-2,5-dimethyl-	C8H12N2	1.6	13360-65-1
9.8	Phenol, 2-methoxy-	C7H8O2	8.1	90-05-1
9.8	Ethanone, 1-(2-thienyl)-	C6H6OS	1.6	88-15-3
10.7	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	C7H10O2	2.7	21835-01-8
12.5	2-Propionylthiophene	C7H8OS	2.1	13679-75-9
15.1	Phenol, 4-ethyl-2-methoxy-	C9H12O2	3.6	2785-89-9
16.0	2-Penten-4-yn-1-ol, 5-(methylthio)-, (E)-	C6H8OS	5.9	56963-47-4
16.2	2-Methoxy-4-vinylphenol	C9H10O2	1.0	7786-61-0
16.4	Thiobenzoic acid	C7H6OS	0.9	0-00-0

17.2	Phenol, 2,6-dimethoxy-	C8H10O3	9.6	91-10-1
18.6	Benzaldehyde, 3-hydroxy-4-methoxy-	C8H8O3	6.8	621-59-0
19.8	Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-	C10H12O2	2.0	5912-86-7
20.9	Apocynin	C9H10O3	4.3	498-02-2
21.7	Benzene, 1,2,3-trimethoxy-5-methyl-	C10H14O3	0.6	6443-69-2
21.7	Benzoic acid, 3-ethyloxy-, ethyl ester	C11H14O3	1.7	2000184-47-7
21.9	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	C10H12O3	7.1	2503-46-0
25.1	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	C9H10O4	2.5	134-96-3
26.0	(E)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol	C11H14O3	2.4	20675-95-0
26.8	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	C10H12O4	5.5	2478-38-8
31.2	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-	C11H18N2O2	4.3	5654-86-4
38.7	2,5-Piperazinedione, 3-(2-methylpropyl)-6-(phenylmethyl)-, (3S-cis)-	C15H20N2O2	1.3	7280-77-5
39.1	2,5-Piperazinedione, 3-(2-methylpropyl)-6-(phenylmethyl)-, (3S-cis)-	C15H20N2O2	1.4	7280-77-5
39.5	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(phenylmethyl)-	C14H16N2O2	1.2	14705-60-3
250°C				
5.1	2-Cyclopenten-1-one, 2-methyl-	C6H8O	2.2	1120-73-6
5.2	Pyrazine, 2,5-dimethyl-	C6H8N2	6.2	123-32-0
5.3	Pyrazine, ethyl-	C6H8N2	2.9	13925-00-3
5.3	Pyrazine, 2,3-dimethyl-	C6H8N2	0.8	5910-89-4
6.4	2-Cyclopenten-1-one, 3-methyl-	C6H8O	0.3	2758-18-1
6.5	2-Isopropylpyrazine	C7H10N2	0.4	29460-90-0
7.2	7.85 Pyrazine<2-ethyl-3-methyl->	C7H10N2	5.1	15707-23-0
7.4	Pyrazine, 2-ethyl-5-methyl-	C7H10N2	4.2	13360-64-0
8.2	2-Cyclopenten-1-one, 2,3-dimethyl-	C7H10O	0.6	1121-05-7

9.3	Pyrazine, 3-ethyl-2,5-dimethyl-	C8H12N2	1.0	13360-65-1
9.9	Phenol, 2-methoxy-	C7H8O2	16.1	90-05-1
9.9	Ethanone, 1-(2-thienyl)-	C6H6OS	0.9	88-15-3
10.3	1,5-Dimethyl-2-pyrrolecarbonitrile	C7H8N2	0.5	56341-36-7
10.7	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	C7H10O2	1.4	21835-01-8
10.8	1H-Pyrrole, 2,3,4,5-tetramethyl-	C8H13N	0.3	1003-90-3
12.3	Phenol, 4-ethyl-	C8H10O	2.3	123-07-9
12.7	Creosol	C8H10O2	0.4	93-51-6
12.8	2-methyl 5H-6,7-dihydrocyclopentapyrazine	C8H10N2	0.9	2000044-83-9
13.8	2-Pyrrolidinone, 4,4-dimethyl-5-methylidene-	C7H11NO	0.3	23461-69-0
14.9	1,2-Benzenediol, 3-methoxy-	C7H8O3	1.0	934-00-9
15.2	Phenol, 4-ethyl-2-methoxy-	C9H12O2	7.2	2785-89-9
15.9	Indole	C8H7N	1.2	120-72-9
16.5	Thiobenzoic acid	C7H6OS	3.2	0-00-0
17.4	Phenol, 2,6-dimethoxy-	C8H10O3	18.0	91-10-1
17.6	23.15 Eugenol <dihydro->	C10H14O2	0.7	2785-87-7
18.6	Vanillin	C8H8O3	0.5	121-33-5
19.7	3,5-Dimethoxy-4-hydroxytoluene	C9H12O3	0.6	1730647
19.9	Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-	C10H12O2	0.4	5912-86-7
20.9	Apocynin	C9H10O3	1.7	498-02-2
21.7	5-tert-Butylpyrogallol	C10H14O3	2.6	20481-17-8
21.9	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	C10H12O3	3.7	2503-46-0
23.8	4 - propyl - syringol	C11H16O3	1.8	2000190-86-2
26.0	(E)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol	C11H14O3	0.5	20675-95-0
26.9	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	C10H12O4	9.0	2478-38-8

39.4	2,5-Piperazinedione, 3-(2-methylpropyl)-6-(phenylmethyl)-, (3S-cis)-	C15H20N2O2	1.2	7280-77-5
300°C				
5.1	2-Cyclopenten-1-one, 2-methyl-	C6H8O	3.6	1120-73-6
5.2	Pyrazine, 2,5-dimethyl-	C6H8N2	4.4	123-32-0
5.3	Pyrazine, ethyl-	C6H8N2	3.8	13925-00-3
5.3	Pyrazine, 2,3-dimethyl-	C6H8N2	0.3	5910-89-4
5.8	Pyridine, 2,3-dimethyl-	C7H9N	0.1	583-61-9
6.2	3-Ethylcyclopentanone	C7H12O	0.4	10264-55-8
6.4	2-Cyclopenten-1-one, 3-methyl-	C6H8O	1.4	2758-18-1
6.5	2-Isopropylpyrazine	C7H10N2	0.6	29460-90-0
6.8	Aniline	C6H7N	0.5	62-53-3
7.1	2-Cyclopenten-1-one, 3,4-dimethyl-	C7H10O	1.8	30434-64-1
7.4	Pyrazine, 2-ethyl-5-methyl-	C7H10N2	6.0	13360-64-0
7.7	Pyrazine, 2-ethyl-3-methyl-	C7H10N2	0.7	15707-23-0
7.9	2,3,4-Trimethylpyrrole	C7H11N	0.6	3855-78-5
7.9	2-Cyclopenten-1-one, 3,4-dimethyl-	C7H10O	0.8	30434-64-1
8.4	2-Cyclopenten-1-one, 2,3-dimethyl-	C7H10O	6.6	1121-05-7
8.5	2-Cyclopenten-1-one, 2,3-dimethyl-	C7H10O	2.6	1121-05-7
8.9	2-Cyclopenten-1-one, 2,3,4-trimethyl-	C8H12O	0.9	28790-86-5
9.6	4.86 Pyrazine<2-methoxy->	C5H6N2O	1.8	3149-28-8
9.9	Phenol, 2-methoxy-	C7H8O2	4.6	90-05-1
10.0	1,3-Pentadiene, 2,4-dimethyl-	C7H12	1.0	1000-86-8
10.2	5-Ethyl-2-furaldehyde	C7H8O2	1.8	23074-10-4
10.4	1,5-Dimethyl-2-pyrrolecarbonitrile	C7H8N2	0.9	56341-36-7
10.6	Benzeneethanol	C8H10O	2.1	60-12-8
10.9	5-Ethyl-2-furaldehyde	C7H8O2	2.0	23074-10-4
12.3	Phenol, 4-ethyl-	C8H10O	7.5	123-07-9
12.8	2-Cyclopenten-1-one, 2,3,4,5-tetramethyl-	C9H14O	3.5	54458-61-6
12.9	2-methyl 5H-6,7-	C8H10N2	1.1	2000044-83-

	dihydrocyclopentapyrazine			9
15.0	1,2-Benzenediol, 3-methoxy-	C7H8O3	0.8	934-00-9
15.0	2H-Pyran-3(6H)-one, 6-methoxy-5-(1-methylethyl)-, (.+-.)-	C9H14O3	4.2	131262-54-9
15.2	Guaiacol, 4-ethyl-	C9H12O2	12.0	2785-89-9
15.9	Indole	C8H7N	2.9	120-72-9
17.4	Phenol, 2,6-dimethoxy-	C8H10O3	15.9	91-10-1
21.8	5-tert-Butylpyrogallol	C10H14O3	2.8	20481-17-8

3. Energy costs calculation

As a part of the total energy mass balance (Table 2 in the main text), we estimated the energy costs for heat using theoretical calculation. Details are given below.

Table S2. Calculated values of heating demands required for four feedlot sizes (n=100, 500, 1000 or 3000 calves) based on the change of enthalpy for each reaction temperature (200, 250 and 300°C)**.**

	200°C				250°C				300°C			
Herd size [-]	100	500	1000	3000	100	500	1000	3000	100	500	1000	3000
Manure/cow [kg/cow/day]	26.7	26.7	26.7	26.7	26.7	26.7	26.7	26.7	26.7	26.7	26.7	26.7
Manure/ day [kg/day]	2670	13350	26700	80100	2670	13350	26700	80100	2670	13350	26700	80100
Water enthalpy @ 25°C [MJ/kg]	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Water enthalpy @ reaction temp. [MJ/kg]	0.85	0.85	0.85	0.85	1.09	1.09	1.09	1.09	1.35	1.35	1.35	1.35
Water enthalpy @ 60°C [MJ/kg]	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Vapor enthalpy @ 60°C [MJ/kg]	2.61	2.61	2.61	2.61	2.61	2.61	2.61	2.61	2.61	2.61	2.61	2.61
Heat efficiency* [-]	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85
Water available for steam [-]	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Steam production [-]	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.5	0.5	0.5	0.5
Steam mass production [kg/day]	340.8	1704.1	3408.3	10224.8	471.6	2358.0	4716.1	14148.3	618.8	3094.1	6188.1	18564.3
Steam heat [MJ/kg]	890	4448	8896	26687	1231	6155	12309	36927	1615	8075	16151	48453
Theoretical heat demand [MJ/day]	2000	10001	20003	60009	2617	13085	26171	78512	3311	16556	33113	99338
Heat demand including heat loss [MJ/day]	2353	11766	23533	70598	3079	15394	30789	92367	3896	19478	38956	116868
Heat demand with heat recovery [MJ/day]	1464	7319	14637	43912	1848	9240	18480	55440	2280	11402	22805	68415

*Heat efficiency was estimated based on the literature (Bauer et al., 2018; Liu et al., 2013)

Table S3. Summary of the overall heating demands (MJ/calf/day) required for reaction at different temperature (200, 250 and 300°C) with and without heat recovery.

	200°C	250°C	300°C
Theoretical heat demand	20.0	26.2	33.1
Heat demand including heat loss	23.5	30.8	39.0
Heat demand with heat recovery	14.6	18.5	22.8

Table S4. Total Energy mass balance simulating four herd differing in size (n=100, 500, 1000 or 3000 calves) and three operating temperatures (200, 250 and 300°C). Conversion yields and energy content of manure, biocrude oil and hydrochar were taken from the experimental data (**Fig. 2 and Table 1**).

Temp.	Herd size	Dry manure production	Manure energy	Biocrude oil production	Biocrude oil energy	Hydrochar production	Hydrochar energy	Total returned energy	Total invested Energy*	Net gained energy	EROI**
		Ton/day	GJ/day	Ton/day	GJ/day	Ton/day	GJ/day	GJ/day	GJ/day	GJ/day	(-)
200	100	0.4	5.7	0.03	1.0	0.2	3.1	4.1	1.5–2.4	1.8–2.7	1.8–2.8
	500	2	28.6	0.2	5.0	0.9	15.6	20.6	7.3–11.8	8.9–13.3	
	1000	4	57.2	0.3	10.1	1.8	31.2	41.3	14.6–23.5	17.8–26.7	
	3000	12	171.6	1.0	30.2	5.4	93.7	123.9	43.9–70.6	53.3–80.0	
250	100	0.4	5.7	0.05	1.8	0.2	2.9	4.6	1.8–3.1	1.5–2.8	1.5–2.5
	500	2	28.6	0.3	8.9	0.8	14.3	23.1	9.2–15.4	7.7–13.9	
	1000	4	57.2	0.5	17.7	1.5	28.6	46.3	18.5–30.8	15.5–27.8	
	3000	12	171.6	1.6	53.1	4.5	85.7	138.9	55.4–92.4	46.5–83.4	
300	100	0.4	5.7	0.1	3.4	0.1	2.0	5.4	2.3–3.9	1.5–3.1	1.4–2.4
	500	2	28.6	0.5	17.2	0.5	9.8	27.0	11.4–19.5	7.7–15.6	
	1000	4	57.2	1.0	34.3	1.0	19.6	54.0	22.8–39.0	15.0–31.2	
	3000	12	171.6	3.0	103.0	2.9	58.9	161.9	68.4–116.9	45.0–93.5	

*Energy costs were estimated based on theoretical calculation given in details at the supporting information.

** EROI Energy returned on investment

Table S5. Parameters used for the sensitivity analysis**.**

		Reference	Best	Worst
T=200°C	Unit			
Daily heat demand [a]	MJ/calf/day	20	15	25
Daily manure production [b]	kg/calf/day	27	32	21
Hydrochar yield [c]	%	45	54	36
Biocrude oil yield [c]	%	8	10	6
T=250°C				
Daily heat demand [a]	MJ/calf/day	26	20	33
Daily manure production [b]	kg/calf/day	27	32	21
Hydrochar yield [c]	%	38	45	30
Biocrude oil yield [c]	%	14	16	11
T=300°C				
Daily heat demand [a]	MJ/calf/day	33	25	41
Daily manure production [b]	kg/calf/day	27	32	21
Hydrochar yield [c]	%	24	29	20
Biocrude oil yield [c]	%	25	30	20

[a] Uncertainty for heat demand was taken from the heat balance calculation (Table S2-3); [b] uncertainty for the daily manure production was taken from the literature (Asher et al., 2018); [c] Uncertainty for the product mass yields were based on our experimental data (Table 1).