Supporting material

Hydrothermal Liquefaction Enhanced by Various Chemicals as a Means of Sustainable Dairy Manure Treatment

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Table S1. Results of one-way ANOVA analysis of liquid yields

Water-only	v.s.	**$NH_3 \cdot H_2O$**				
Difference source	SS	df	MS	F	P-value	F crit
Between groups	249.615	1	249.615	51.733679	0.0019798	7.7086474
Within group	19.3	4	4.825			
Sum	268.915	5				
Water-only	v.s.	**H_3PO_4**				
Difference source	SS	df	MS	F	P-value	F crit
Between groups	57.66	1	57.66	8.7829398	0.0414061	7.7086474
Within group	26.26	4	6.565			
Sum	83.92	5				
Water-only	v.s.	**Glycerol**				
Difference source	SS	df	MS	F	P-value	F crit
Between groups	0.06	1	0.06	0.0146699	0.909437	7.7086474
Within group	16.36	4	4.09			
Sum	16.42	5				

Table S2. GC-MS analysis of liquid products from HTL of dairy manure assisted with various chemicals (% in area)

Chemical names	H_2O	H_3PO_4	NH_3	Glycerol
Cyclopentene			1.26	0.12
Cyclopentyl acetylene	0.80		0.43	0.09
3-Hexanol, 4-methyl-	6.93		3.33	0.03
3-Amino-4,5-dimethyl-2(5H)-furanone				0.38
Benzaldehyde, 2-nitro-, diaminomethylidenhydrazone	0.64			
1,3-Pentadiene, 2-methyl-, (E)-				0.15
Ethyl Acetate				0.28
Monoethylmalonate monoamide	1.56		1.54	
3-Hexyne				0.04
1,4-Cyclooctadiene		0.08		
3-Isoxazolecarboperoxoic acid, 4,5-dihydro-5-phenyl-, 1,1-dimethylethyl ester	0.82			
1,4-Hexadiene		0.01		0.68
Propane, 2,2-dimethoxy-	2.38			
1-[.alpha.-(1-Adamantyl)benzylidene]thiosemicarbazide		0.02		
Benzene	0.56			0.37
3-Methylenecyclopentene		0.02		0.24
Thiophene	0.81			0.26
Acetic acid		7.45		
Hydrazinecarbothioamide	10.74		0.43	
Ethylidenecyclobutane			0.61	0.31
Phenol, 6-methyl-2-[(4-morpholinyl)methyl]-			2.21	
2-Heptanone, 6-methyl-	2.23			0.28
1-Hexanol, 2-ethyl-				0.30
Propanoic acid, 2,3-dihydroxy-				
n-Hexane	2.88			
3,5-Dimethylcyclopentene				0.27
Cyclopentanone, 3-methyl-				0.06
2,4-Hexadiene, 3-methyl-			0.60	0.41
Norbornane				0.18
Butanoic acid, methyl ester	1.32		1.78	0.06
Pyrazine	3.29	2.11		1.17
1,2,4-Triazine-3,5(2H,4H)-dione, 6-benzoylthio-				0.42
2-Pyridinamine, N-(4,5-dihydro-5-methyl-2-thiazolyl)-3-methyl-			0.93	
2,3-Hexadiene, 2-methyl-				0.21
1H-Pyrrole, 1-methyl-			0.88	0.57
Pyridinium, 1-amino-, hydroxide, inner salt				0.14
Pyridine		3.17		0.16
Cyclobutane, (1-methylethylidene)-			0.43	

1-Ethylcyclopentene				0.58
Propanoic acid, 3-(butylthio)-	2.67		7.26	
Toluene	0.99		11.43	7.92
2-Ethylacridine			0.52	
Propane, 2,2-diethoxy-	0.20			1.26
Cyclononene				0.13
Thiophene, 3-methyl-	0.35		2.22	0.61
3-Hexanone	0.82			0.45
Cyclopentanone		1.50	0.28	0.76
3-Hexene	9.17			
5,5-Dimethyl-1,3-hexadiene				0.33
(2-Hexyloxy-ethoxy)-acetyl chloride	1.27			
Dichloroacetic acid, nonyl ester				0.11
1-Ethyl-5-methylcyclopentene				0.35
Cyclohexene, 3-ethyl-				0.13
Cyclopentene, 1,2,3-trimethyl-				1.05
Butanoic acid		4.29		
1H-Pyrrole, 1-ethyl-				1.06
Pyridine, 2-methyl-	1.72	3.60		0.08
Cyclopentene, 1-(1-methylethyl)-				0.10
Pyrazine, methyl-	10.00	6.95		0.88
3,5-Octadiene, (Z,Z)-				0.27
2-Cyclopenten-1-one		1.98		
Methyl ethyl cyclopentene				0.83
Cyclopentanone, 2-methyl-				0.60
3-Heptyne				0.11
Cyclopentane, (1-methylethenyl)-				0.55
Hexanoic acid		0.25		
trans-4-(2-(5-Nitro-2-furyl)vinyl)-2-quinolinamine			1.28	
Cyclohexene, 3,3,5-trimethyl-				0.33
1,3-Cyclooctadiene				0.16
2,4-Heptadiene, 2,6-dimethyl-				1.06
Ethylbenzene				4.81
Benzene, 1,3-dimethyl-			12.41	
Pyridine, 3-methyl-		1.61		
Thiophene, 3-ethyl-				0.48
4-Phenyl-3,4-dihydroisoquinoline	2.06			
Benzene, 1,3-dimethyl-		0.92	1.72	2.04
1-Methyl-2-methylenecyclohexane				0.22
2-Pyrazoline, 1,3,4-trimethyl-				1.05
Cyclohexene, 3,3,5-trimethyl-				0.07
2-Ethylacridine	0.87			
Ethyl 3-cyclohexenecarboxylate				0.23
Butanoic acid		0.36		0.12
Thiophene, 2,3-dimethyl-				0.57

Styrene			1.69	1.11
o-Xylene		0.54	0.87	0.39
N-(2-Acetylcyclopentylidene)cyclohexylamine	1.15			
2(1H)-Pyridinone, 3-methyl-				0.61
1,3-Hexadiene, 3-ethyl-2-methyl-, (Z)-			0.23	0.27
Thiophene, 2,4-dimethyl-			0.24	0.28
1,3-Hexadiene, 3-ethyl-2-methyl-, (Z)-				0.30
2-Cyclopenten-1-one, 2-methyl-	3.79	9.80		0.48
2-Octyn-1-ol			0.65	
Pyrazine, 2,6-dimethyl-		2.80		
Pyrazine, ethyl-	2.46	1.60		0.20
Pyrazine, 2,3-dimethyl-		1.19		0.23
3-Cyclohexene-1-carboxaldehyde, 1-methyl-			0.27	0.93
Cyclohexane, (1-methylethylidene)-				0.33
Pentanoic acid		0.98		
Pyridine, 3,5-dimethyl-		0.42		
(2S,4R)-p-Mentha-[1(7),8]-diene 2-hydroperoxide	1.97			1.40
N-Methyl-1-adamantaneacetamide			1.02	
Longipinane, (E)-			0.32	0.37
1H-Pyrrole, 1-butyl-		0.57		0.92
Cyclohexane, 2,4-diethenyl-1-methyl-		0.35		0.49
Benzene, propyl-			0.98	0.71
2-Ethylacridine	0.70		0.26	
.alpha.-Aminooxy-propionic acid, ethyl ester		0.44		
3-Hexyne			0.95	1.56
2-Cyclopenten-1-one, 3-methyl-		7.90		0.63
3-Hexyne				1.56
Pyridine, 1,2,3,6-tetrahydro-1-methyl-4-[4-chlorophenyl]-	1.34			
Alantolactone, 4.alpha.,4A.alpha.-epoxy-				0.63
1,1,3-Trimethyl-1-silacyclo-3-pentene				0.64
1-Hydroxymethyl-2-methyl-1-cyclohexene				0.45
Benzene, 1-ethyl-3-methyl-				0.70
Cyclohexane, 1-methyl-4-(1-methylethenyl)-, trans-				0.75
Phenol	0.90	3.79		
Pyridinium, 1-amino-4-methyl-, hydroxide, inner salt				0.49
2-Cyclopenten-1-one, 3,4-dimethyl-		2.52		1.50
2-Cyclopenten-1-one, 2,3-dimethyl-		1.98		
2,4-Hexadienoic acid, methyl ester				1.24
Pyrazine, 2-ethyl-6-methyl-		0.21		
5,5-Dimethyl-1,3-hexadiene				0.15
Butanoic acid		0.19		
1,3-Cycloheptadiene				0.79
Bicyclo[1.1.1]pentane, 1,3-dipropanoyl-			0.29	
Cyclohexane-1,3-dione, 2-allylaminomethylene-5,5-dimethyl-			0.36	
2-Cyclopenten-1-one, 3,4-dimethyl-		1.97		

Benzene, 1-ethyl-3-methyl-			1.13	1.41
o-Cymene			2.40	3.96
Diborane(6), 1,1:2,2-di-1,5-cyclooctylene-			0.26	
Benzeneethanol, .beta.-ethenyl-			0.74	
2-Cyclopenten-1-one, 2,3-dimethyl-	1.16	8.10		
4,7-Methano-1H-indene, octahydro-			1.24	
2-Pyrrolidinone, 1-methyl-		1.17	0.47	
Bicyclo[5.1.0]octane, 8-methylene-				0.47
2-Myristynoyl-glycinamide			0.53	
1H-Pyrrole, 1-pentyl-				0.45
Phenol, 2-methyl-		0.85	0.28	
Bicyclo[2.2.1]heptan-2-ol, 1,3,3-trimethyl-				1.00
o-Veratramide			0.36	
2-Cyclopenten-1-one, 3,4,4-trimethyl-		1.05	0.51	
3-Methylpyridazine			1.13	
2-Cyclopenten-1-one, 3-ethyl-		3.41		
Cyclopentasiloxane, decamethyl-			1.36	
1H-Imidazole, 1,2-dimethyl-		0.91		
Benzene, 2-butenyl-				0.51
Phenol, 2-methoxy-		6.63	0.65	1.60
Phenylethylene, 3'-methoxy-2,2'-dinitro-			0.77	
5-Ethyl-2-furaldehyde		0.70	0.35	
1-Isopropylcyclohex-1-ene		0.87		
1,3,5-Triazin-2(1H)-one, 4,6-diamino-		0.67		
.beta.,.beta.-Galactonic phenylhydrazide			0.43	
Bicyclo[5.2.0]non-1-ene			0.85	
1,4-Pentadiene, 2,3,4-trimethyl-		0.35		
1,3-Heptadiene, 5,5-dimethyl-		1.15	0.78	
Benzene, 2-butenyl-				1.56
1-(3-n-Propoxyphenyl)-2-propanone oxime			0.51	
Phenol, 2,3-dimethyl-/Phenol, 2-ethyl-			1.09	0.63
1,7-Dimethylpentacyclo[5.5.0(4,11).0(5,9).0(8,12)]dodecane-2,6-dione			0.57	
6-(3,5-Dimethyl-1H-pyrazol-1-yl)-N-benzyl-1,2,4,5-tetrazine-3-amine			1.28	
Pyrazine, 2-methoxy-3-(1-methylethyl)-		0.53		
1-Tridecene				0.91
Indolizine, 2-methyl-			2.08	
1-Pentadecene				1.57
1H-Indole, 2,3-dimethyl-				2.32
1,11,11-Trimethyl-3-azatricyclo[6.2.1.0(2,7)]undeca-2,4,6-triene				1.20
2,6,10-Dodecatrien-1-ol, 3,7,11-trimethyl-, (Z,E)-				1.89

Blank: not detectable

Table S3. *p*-values of ANOVA analysis of biochar samples, comparing to dry dairy manure and water-only HTL (Data in Table 4)

Sample	**BET surface area**	**Pore volumes**	**Average pore diameter**	**BET surface area**	**Pore volumes**	**Average pore diameter**
	Compared to dry dairy manure			Compared to water-only HTL		
Biochar-water	4.3E-06	6.03E-05	**0.16**	-	-	-
Biochar-$NH_3 \cdot H_2O$	2.2E-06	5.1E-06	0.00013	2.94E-06	5.79E-07	1.85E-06
Biochar-H_3PO_4	0.00016	0.0001	0.008	0.0021	**0.085**	0.00073
Biochar-Glycerol	5.0E-07	0.000014	0.0007	0.0014	**0.52**	0.00038

Table S4. *p*-values of ANOVA analysis of biochar samples, comparing to dry dairy manure and water-only HTL (Data in Table 5)

Composition	**Biochar (compared to dairy manure)**				**Biochar (compared to water-only HTL)**		
	Water	$NH_3 \cdot H_2O$	H_3PO_4	Glycerol	$NH_3 \cdot H_2O$	H_3PO_4	Glycerol
C	9.62E-07	0.0012	0.0001	1.6E-05	0.015	0.0016	0.037
H	**0.12**	0.007	0.0004	0.002	0.024	0.00026	0.0034
N	5.89E-06	1.44E-05	2.64E-06	8.55E-07	0.00043	**0.67**	**0.43**
S	0.0047	0.0042	0.0034	0.0032	**0.94**	**0.97**	**0.95**
Volatile content	1.41E-05	2.75E-05	0.000178	6E-06	0.00019	9.3E-06	**0.065**
Ash content	7.69E-05	2.01E-05	3.22E-06	0.0038	0.0063	0.0005	0.013
HHV	2.82E-05	3.13E-06	3.48E-07	0.0001	**0.68**	8.62E-05	**0.62**

Table S5. *p*-values of ANOVA analysis of gases produced during HTL, comparing to water-only HTL (Data in Table 6)

Concentration of gases	**Water-only**	**$NH_3 \cdot H_2O$**	**H_3PO_4**	**Glycerol**
H_2	-	**0.076**	**0.063**	**0.59**
CO	-	**0.93**	**0.57**	0.001
CH_4	-	**1.5**	**1.4**	**1.1**
CO_2	-	**0.31**	**0.59**	**0.47**
Ethane	-	**0.32**	**0.42**	**0.07**

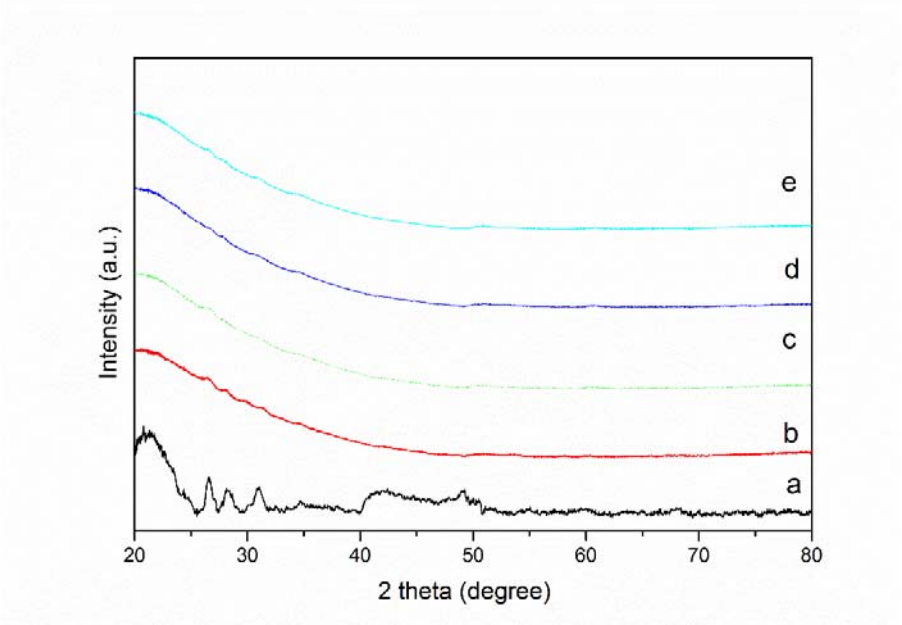

Figure S1. XRD curves of raw dairy manure and biochar produced by the HTL of dairy manure assisted with various chemicals (a. Dry dairy manure, b. Biochar- Glycerol, c. Biochar- H_3PO_4, d. Biochar-Water, e. Biochar- $NH_3 \cdot H_2O$)