

Supporting information

Nitrogen Migration and Transformation during Hydrothermal Liquefaction of Livestock Manures

Jianwen Lu,^{†,§} Hugang Li,^{†,§} Yuanhui Zhang,^{†,‡} Zhidan Liu^{†,}*

[†]Laboratory of Environment-Enhancing Energy (E2E), and Key Laboratory of Agricultural Engineering in Structure and Environment, Ministry of Agriculture, College of Water Resources and Civil Engineering China Agricultural University, Qinghua Donglu 17, Beijing 100083, China

[‡]Department of Agricultural and Biological Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

[§]These authors contributed equally.

*Corresponding author: Dr. Zhidan Liu

Fax: +86-10-62737329; Tel.: +86-10-62737329.

E-mail address: zdliu@cau.edu.cn

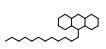
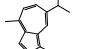
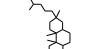
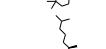
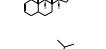
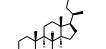
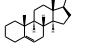
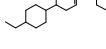
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Table S1 Characterization of HTL products from different livestock manures

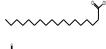
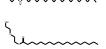
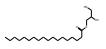
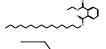
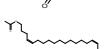
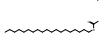
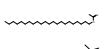
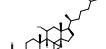
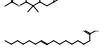
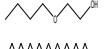
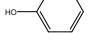
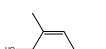
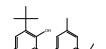
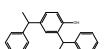
Feedstock	Temperatures (°C)	Biocrude oil					Solid residue				Aqueous phase				Gases		
		C (%)	H (%)	N (%)	O (%)	HHV (MJ/kg)	C (%)	H (%)	N (%)	Ash (%)	TN (mg/L)	TC (mg/L)	TOC (mg/L)	COD (mg/L)	CO ₂ (%)	CH ₄ (%)	H ₂ (%)
Swine manure	310	75.02	8.14	4.87	11.97	34.83	35.06	3.64	2.97	56.57	5161	40106	39802	81689	99.26	0.39	0.37
	340	75.62	8.96	4.54	10.88	36.39	33.51	3.37	2.68	60.55	5619	35128	34773	94173	98.52	1.01	0.47
Dairy manure	310	74.33	7.78	3.30	14.59	33.61	11.46	1.17	0.64	67.10	2022	34584	34344	41671	89.91	5.47	4.63
	340	76.80	8.00	3.37	11.83	35.26	16.16	1.36	0.88	68.69	2139	30948	30684	39995	88.7	5.26	6.05
Beef manure	310	75.42	8.08	3.62	12.89	34.72	31.43	3.01	1.84	53.49	1197	18112	17396	57691	82.81	12.33	4.86
	340	76.84	8.42	3.75	11.00	36.01	32.60	2.76	2.02	53.99	1517	13772	12860	45874	91.19	4.34	4.47
Laying hen manure	310	75.81	8.67	5.36	10.16	36.17	23.15	2.35	1.22	73.86	2682	23316	19760	52843	96.89	ND	3.11
	340	77.25	8.77	5.03	8.95	37.01	21.03	2.19	0.82	74.28	5816	20692	14392	48790	90.92	2.31	6.77
Broiler manure	310	75.77	8.90	5.13	10.21	36.48	18.2	1.86	0.74	70.98	3222	32516	30512	88137	95.29	ND	4.71
	340	76.46	8.88	4.88	9.78	36.76	17.02	1.61	0.86	83.06	2795	25724	22148	67603	90.44	1.40	8.16
Sheep manure	310	75.62	8.11	3.44	12.83	34.83	28.91	2.87	1.5	53.24	1793	19780	18920	63588	95.63	1.90	2.47
	340	74.22	8.35	3.72	13.71	34.55	33.65	3.31	1.59	54.18	2399	16940	16092	47478	94.87	2.51	2.62

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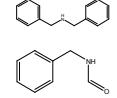
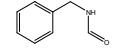
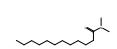
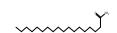
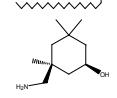
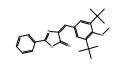
Table S2 Organic compounds in the biocrude oil from HTL of animal manures through GC-MS analysis

Compounds	Formula	Peak areas of compounds in the biocrude oil from HTL of different livestock manures (%)						Structure
		Swine manure	Dairy manure	Beef manure	Laying hen manure	Broiler manure	Sheep manure	
Hydrogen carbons								
Anthracene, 9-dodecyltetradecahydro-	C ₂₆ H ₄₈			0.72	1.51*			
Azulene, 1,4-dimethyl-7-(1-methylethyl)-	C ₁₅ H ₁₈		2.13*	2.35*	2.12*	2.31*	1.89*	
Baccharane	C ₃₀ H ₅₄							
Cholest-2-ene	C ₂₇ H ₄₆	3.77*						
Cholest-4-ene	C ₂₇ H ₄₆	3.17						
Cholest-5-ene	C ₂₇ H ₄₆	0.71*						
Cyclohexene, 4-(4-ethylcyclohexyl)-1-pentyl-	C ₁₉ H ₃₄			0.66				
Eicosane	C ₂₀ H ₄₂			0.49				
Ethylbenzene	C ₈ H ₁₀	1.37		0.68	1.13	1.06	1.29	
Toluene	C ₇ H ₈	2.17	0.83	0.93	1.28	1.24	1.50	

1-Pentadecene	C ₁₅ H ₃₀	0.77						
1,3,5,7-Cyclooctatetraene	C ₈ H ₈	0.97	0.59		1.04	0.87	0.91	
2-Hexadecene, 3,7,11,15-tetramethyl-, [R-[R*,R*-(E)]]-	C ₂₀ H ₄₀					1.15		
Total		12.93	3.55	5.83	7.08	6.63	5.59	
Acids and esters								
Acetic acid n-octadecyl ester	C ₂₀ H ₄₀ O ₂		1.42					
Butanoic acid	C ₄ H ₈ O ₂	1.31						
Cholestan-3-ol, (3.alpha.,5.beta.)-	C ₂₇ H ₄₈ O					2.22		
cis-Vaccenic acid	C ₁₈ H ₃₄ O ₂	8.91			11.49			
cis-9,cis-12-Octadecadienoic acid	C ₁₈ H ₃₂ O ₂					0.78*		
cis-10-Nonadecenoic acid	C ₁₉ H ₃₆ O ₂	3.48						
Heptadecyl acetate	C ₁₉ H ₃₈ O ₂			1.65	1.16	19.94	1.89	
Hexadecanoic acid, methyl ester	C ₁₇ H ₃₄ O ₂			0.74		0.80	1.53	
Hexadecanoic acid, 2-hydroxyethyl ester	C ₁₈ H ₃₆ O ₃						1.30	
Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester	C ₁₉ H ₃₈ O ₄	16.08	22.84	20.26	11.59	7.12	2.17	
n-Hexadecanoic acid	C ₁₆ H ₃₂ O ₂	4.62		0.65	2.74	2.97	1.26	
Oleic Acid	C ₁₈ H ₃₄ O ₂							

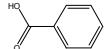
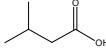
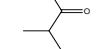
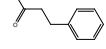
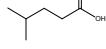
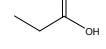
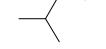
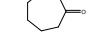
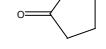
Octadecanoic acid	C ₁₈ H ₃₆ O ₂	9.60						
Octadecanoic acid, methyl ester	C ₁₉ H ₃₈ O ₂						0.97	
Octadecanoic acid, 2-hydroxyethyl ester	C ₂₀ H ₄₀ O ₃							
Octadecanoic acid, 2-(2-hydroxyethoxy)ethyl ester	C ₂₂ H ₄₄ O ₄					0.78*		
Octadecanoic acid, 2,3-dihydroxypropyl ester	C ₂₁ H ₄₂ O ₄	8.74	13.49	12.18	7.09	4.90	1.88*	
Phthalic acid, ethyl pentadecyl ester	C ₂₅ H ₄₀ O ₄		0.67*					
sec-Butyl acetate	C ₆ H ₁₂ O ₂	1.37				1.08		
Z,Z-4,16-Octadecadien-1-ol acetate	C ₂₀ H ₃₆ O ₂						1.03	
1-Acetoxy nonadecane	C ₂₁ H ₄₂ O ₂			0.93				
1-Docosanol, acetate	C ₂₄ H ₄₈ O ₂						1.38	
7,8-Epoxy lanostan-11-ol, 3-acetoxy-	C ₃₂ H ₅₄ O ₄		0.83*					
9-Hexadecenoic acid	C ₁₆ H ₃₀ O ₂					10.47	0.93	
Total		54.11	39.25	36.41	34.07	48.84	16.56	
Alcohols and phenols								
Ethanol, 2-butoxy-	C ₆ H ₁₄ O ₂	5.43	4.30					
n-Octadecanol	C ₁₈ H ₃₈ O						1.37	
Phenol	C ₆ H ₆ O	2.74		1.44	2.30	1.47	4.28	
Phenol, 2-methyl-	C ₇ H ₈ O						0.96	
Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-]	C ₂₃ H ₃₂ O ₂	0.74	18.10	24.66	16.00	2.68	31.91	
Phenol, 2,4-bis(1-phenylethyl)-	C ₂₂ H ₂₂ O		12.20*	9.80	11.54	17.12	9.40*	

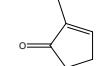
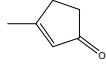
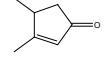
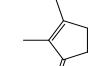
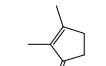
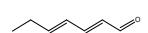
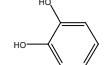
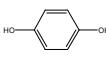
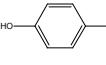
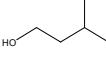
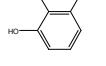
Phenol, 4-ethyl-	C ₈ H ₁₀ O	0.89	1.06	1.08	0.84	1.89		
p-Cresol	C ₇ H ₈ O	1.91				1.04		
1,2-Benzenediol	C ₆ H ₆ O ₂					1.93		
1,2-Benzenediol, 4-methyl-	C ₇ H ₈ O ₂					2.40		
3-Hexadecanol	C ₁₆ H ₃₄ O					1.42		
3-Oxetanol, 2,2,3-trimethyl-	C ₆ H ₁₂ O ₂	0.75						
Total		11.71	36.41	36.98	30.68	21.27	56.60	
Ketones and aldehyde								
2-Pentanone, 4-hydroxy-	C ₅ H ₁₀ O ₂	2.49	1.40	1.31	2.81	1.85		
2-Pentanone, 4-hydroxy-4-methyl-	C ₆ H ₁₂ O ₂				1.16	2.16		
3-Penten-2-one, (E)-	C ₅ H ₈ O		1.76					
3-Penten-2-one, 4-methyl-	C ₆ H ₁₀ O	2.66	1.06	0.98	1.37	1.37	2.79	
9-Undecen-2-one, 6,10-dimethyl-	C ₁₃ H ₂₄ O				1.31*			
Total		5.15	4.22	2.29	6.65	3.22	4.95	
Nitrogen-containing compounds								
Bis(dodecanamido)methane	C ₄₅ H ₉₀ N ₂ O ₂				1.45			

Dibenzylamine	C ₁₄ H ₁₅ N	0.81	1.26	1.22	0.86	1.99		
N-Benzylformamide	C ₈ H ₉ NO		0.62					
N,N-Dimethyldodecanamide	C ₁₄ H ₂₉ NO		4.27	2.30	5.26	7.32		
Octadecanamide	C ₁₈ H ₃₇ NO	6.08						
Tetradecanamide	C ₁₄ H ₂₉ NO				1.28			
3-Aminomethyl-3,5,5-trimethylcyclohexanol , trans-	C ₁₀ H ₂₁ NO			0.85				
(4E)-4-(3,5-Ditert-butyl-4-methoxybenzylidene)-2-phenyl-1,3-oxazol-5(4H)-one	C ₂₅ H ₂₉ NO ₃		6.35	9.24	6.04	5.20		
9-Octadecenamide	C ₁₈ H ₃₅ NO				0.73			
9-Octadecenamide, (Z)-	C ₁₈ H ₃₅ NO	4.09			1.64			
Total		10.17	0.81	12.50	16.70	14.17	14.51	

*Similarity index with NIST mass spectral database is less than 80%

Table S3 Organic compounds in the aqueous phase from HTL of livestock manures through GC-MS analysis

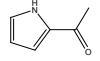
Compounds	Formula	Peak areas of compounds in the aqueous from HTL of different livestock manures (%)						Structure
		Swine manure	Diary manure	Beef manure	Laying manure	hen	Broiler manure	
Acids								
Benzoic acid	C ₇ H ₆ O ₂	0.92		10.57				
Butanoic acid, 3-methyl-	C ₅ H ₁₀ O ₂			1.60				
Butanoic acid, 2-methyl-	C ₅ H ₁₀ O ₂			2.01				
Hydrocinnamic acid	C ₉ H ₁₀ O ₂		1.26					
Pentanoic acid, 4-methyl-	C ₆ H ₁₂ O ₂	1.57		1.00			0.4	
Propanoic acid	C ₃ H ₆ O ₂			1.32				
Propanoic acid, 2-methyl-	C ₄ H ₈ O ₂			2.08				
2-Oxepanone, 7-methyl-	C ₇ H ₁₂ O ₂			4.09				
Total		3.75	22.67	0	0		0.4	0
Ketones and aldehyde								
Cyclopentanone	C ₅ H ₈ O			2.01	1.28		1.19	

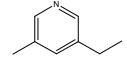
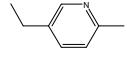
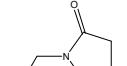
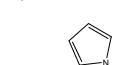
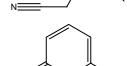
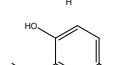
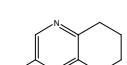
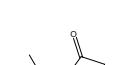
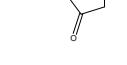
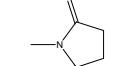
2-Cyclopenten-1-one, 2-methyl-	C ₆ H ₈ O	1.22	4.12	4.26	2.94	2.15	3.67	
2-Cyclopenten-1-one, 3-methyl-	C ₆ H ₈ O	0.68	1.62	2.94	1.32		2.18	
2-Cyclopenten-1-one, 3,4-dimethyl-	C ₇ H ₁₀ O			1.42	1.24		1.19	
2-Cyclopenten-1-one, 2,3-dimethyl-	C ₇ H ₁₀ O	1.72	1.83	2.92			3.21	
2-Propanone, 1-(1,3-dioxolan-2-yl)-	C ₆ H ₁₀ O ₃	0.78						
2,4-Heptadienal, (E,E)-	C ₇ H ₁₀ O							
Total		4.40	7.57	13.55	6.78	2.15	11.44	
Alcohols and phenols								
Catechol	C ₆ H ₆ O ₂			10.42			5.35	
Hydroquinone	C ₆ H ₆ O ₂		1.35					
p-Cresol	C ₇ H ₈ O	0.80	2.09				2.88	
1-Butanol, 3-methyl-	C ₅ H ₁₂ O						1.19	
1,2-Benzenediol, 3-methoxy-	C ₇ H ₈ O ₃		1.91					

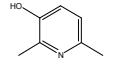
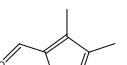
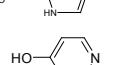
1,2-Propanediol, 3-methoxy-	C ₄ H ₁₀ O ₃	10.35						
2,3-Butanediol, [R-(R*,R*)]-	C ₄ H ₁₀ O ₂	5.71						
Phenol	C ₆ H ₆ O	1.98	9.03	9.79	2.62	2.77	11.51	
Phenol, 2-methyl-	C ₇ H ₈ O						1.64	
Phenol, 2-methoxy-	C ₇ H ₈ O ₂		6.98	10.7	2.64*		4.29	
Phenol, 2,6-dimethoxy-	C ₈ H ₁₀ O ₃		1.80	1.53				
Phenol, 3-amino-4-methyl-		1.01						
Phenol, 4-ethyl-	C ₈ H ₁₀ O			1.74				
Phenol, 4-ethyl-2-methoxy-	C ₉ H ₁₂ O ₂		1.24					
Total		19.85	24.40	34.18	5.26	2.77	26.86	

Nitrogen-containing compounds

Acetamide, N-(2-hydroxyethyl)-	C ₄ H ₉ NO ₂	7.65*			
Dexrazoxane	C ₁₁ H ₁₆ N ₄ O ₄	0.57			

Ethanone, 1-(1H-pyrrol-2-yl)-	C ₆ H ₇ NO		0.51					
Pyrazine	C ₄ H ₄ N ₂				3.78			
Pyrazine, methyl-	C ₅ H ₆ N ₂	5.49		8.13	21.7	22.53	11.24	
Pyrazine, ethyl-	C ₆ H ₈ N ₂	2.52	1.54	4.54	5.96	6.32	5.4	
Pyrazine, trimethyl-	C ₇ H ₁₀ N ₂	2.52		1.37	4.09		3.05	
Pyrazine, (1-methylethenyl)-	C ₇ H ₈ N ₂				2.61			
Pyrazine, 2-ethyl-3,5-dimethyl-	C ₈ H ₁₂ N ₂	1.09*						
Pyrazine, 2-ethyl-6-methyl-	C ₇ H ₁₀ N ₂	3.96		3.55	3.28	5.9	5.85	
Pyrazine, 2-methyl-5-(1-propenyl)-, (E)-	C ₈ H ₁₀ N ₂	0.94*				1.92		
Pyrazine, 2,3-dimethyl-	C ₆ H ₈ N ₂	1.12			3.01	2.94	1.83	
Pyrazine, 2,5-dimethyl-	C ₆ H ₈ N ₂	6.41	1.65	4.14	11.85	12.54	8.02	
Pyrazine, 2,6-dimethyl-	C ₆ H ₈ N ₂							
Pyrazine, 3-ethyl-2,5-dimethyl-	C ₈ H ₁₂ N ₂	0.50						

Pyridine	C ₅ H ₅ N	0.82					
Pyridine, 3-ethyl-5-methyl-	C ₈ H ₁₁ N	1.37*					
Pyridine, 5-ethyl-2-methyl-	C ₈ H ₁₁ N		1.03				
1-Ethyl-2-pyrrolidinone	C ₆ H ₁₁ NO	0.77					
1H-Pyrrole-2-acetonitrile, 1-methyl-	C ₇ H ₈ N ₂	1.01					
2(1H)-Pyridone, 6-methyl-	C ₆ H ₇ NO	1.44	2.02	2.15	1.57	2.12	
2-Ethyl-6-methyl-pyridin-3-ol	C ₈ H ₁₁ NO	0.53					
2-Methyl-5,6,7,8-tetrahydroquinoxaline	C ₉ H ₁₂ N ₂	0.50					
2,5-Pyrrolidinedione, 1-ethyl-	C ₆ H ₉ NO ₂	1.32					
2,5-Pyrrolidinedione, 1-methyl-	C ₅ H ₇ NO ₂	0.89*					
3-Pyridinol, 6-methyl-	C ₆ H ₇ NO	1.04	1.43	1.1	1.19	1.42	

3-Pyridinol, 2,6-dimethyl-	C ₇ H ₉ NO	0.68						
3,4-dimethyl-1H-pyrrole-2-carbo xaldehyde	C ₇ H ₉ NO	0.57	1.44			1.4		
4-Pyridinol	C ₅ H ₅ NO	2.89	4.38	5.16		6.59	2.81	
Total		34.66	16.66	30.34	56.26	66.68	42.77	

*Similarity index with NIST mass spectral database is less than 80%

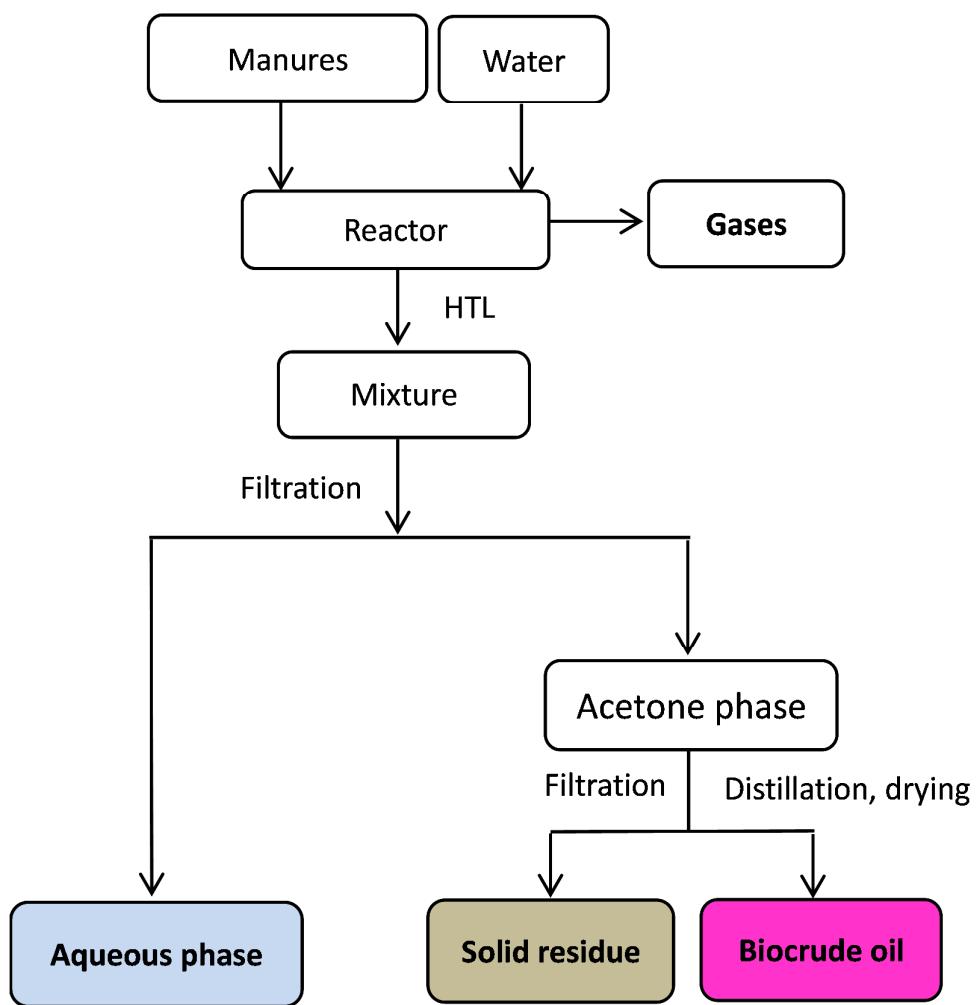


Fig. S1 The separation procedure of the HTL products

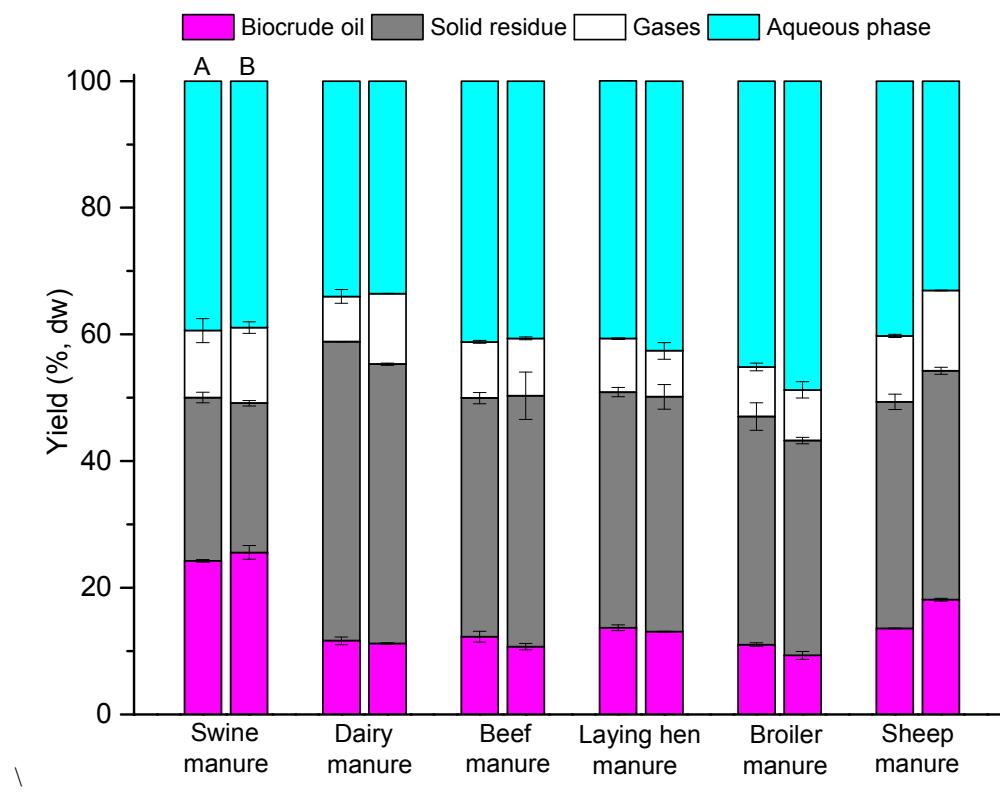


Fig. S2 The yield of HTL products from different manures based on the dry weight of the feedstock, the yield of aqueous phase was calculated by difference (A: at 310°C; B: at 340°C)

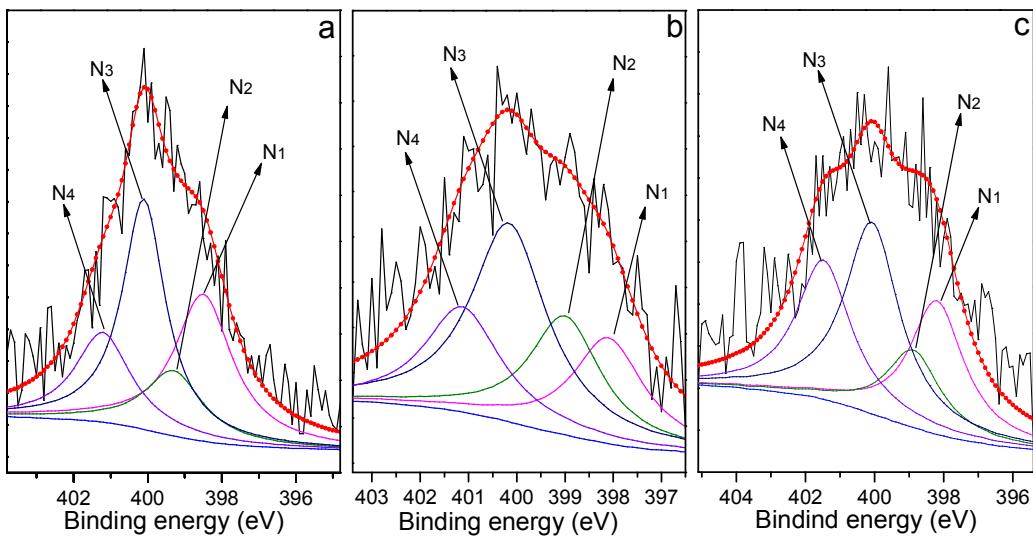


Fig. S3 N 1s spectra of the solid residue from HTL of different manures. The samples with a nitrogen content over 1.5% were selected for determination. N₁: pyridinic-N, N₂: protein-N, N₃: pyrrolic-N, N₄: quaternary-N (a: HTL of swine manure; b: HTL of beef manure; c: HTL of sheep manure).

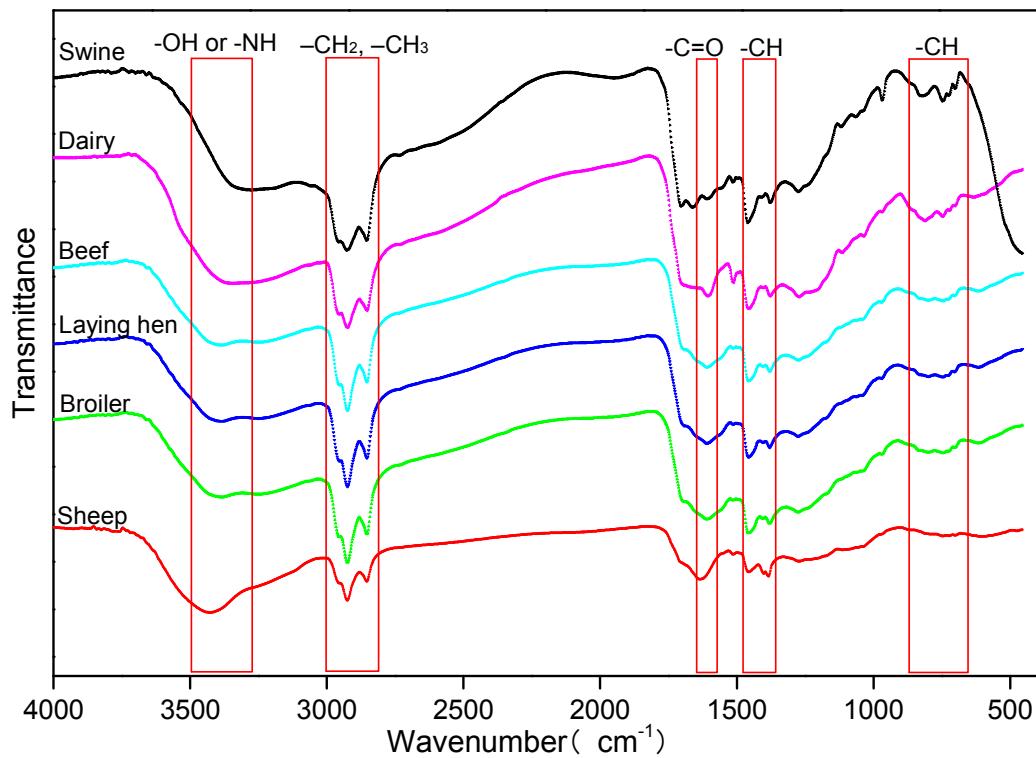


Fig. S4 FT-IR spectra of biocrude oil from HTL of different manures under optimal conditions for biocrude yield.

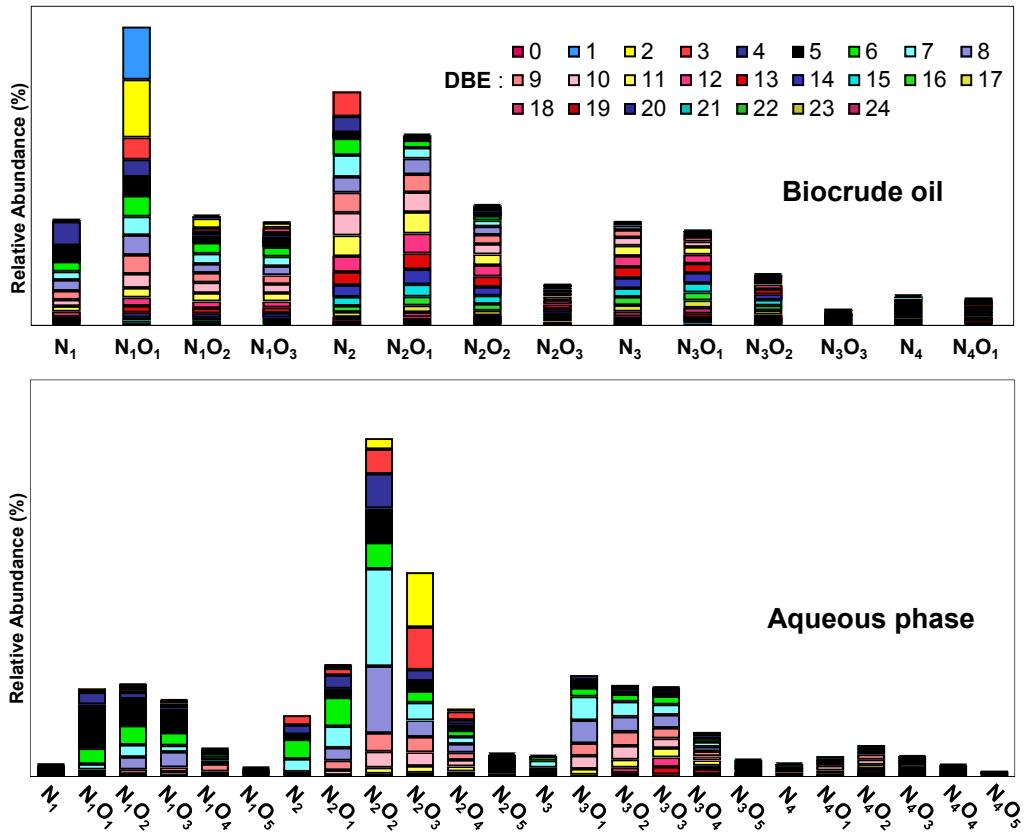


Fig. S5 Heteroatom class distribution of nitrogen species and DBE for N_1O_x , N_2O_x and N_3O_x , N_4O_x ($x=0-5$) species in the biocrude oil and aqueous phase of swine manure identified with positive-ion ESI FT-ICR MS.

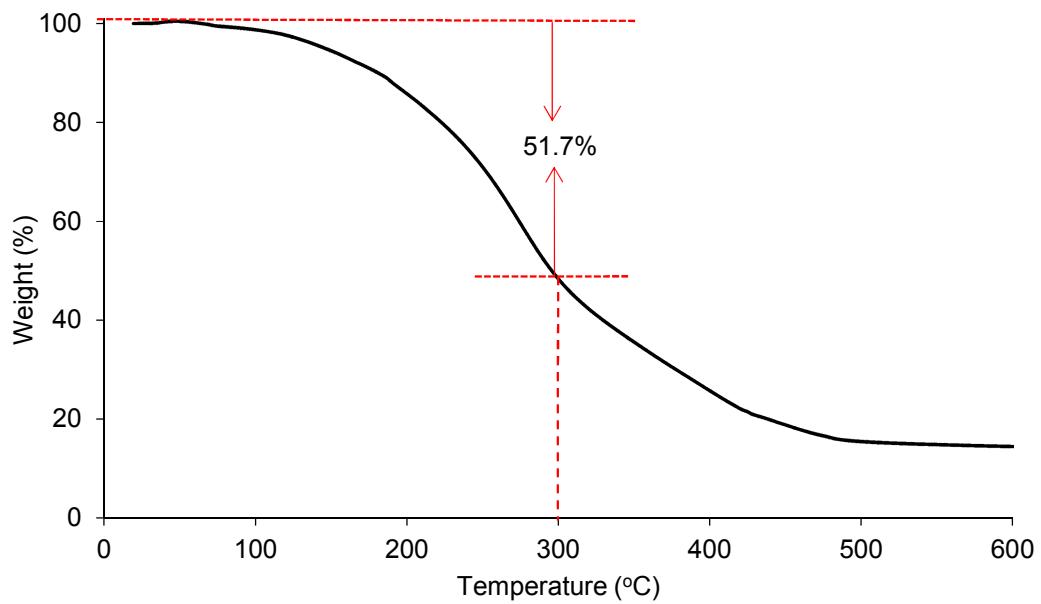


Fig. S6 Thermogravimetry analysis of biocrude oil from HTL of swine manure at 340°C with a retention time of 30 min