SUPPORTING INFORMATION (S1-S26)

Nitrogen transformation during pyrolysis of various N-containing biowastes with participation of mineral calcium

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Table S1. Differences of previous researches with this study about the nitrogen behavior during biomass pyrolysis.

Study aim	Materials and methods	Main conclusions	Research significance	Source
To investigate influences of mineral matters (K_2CO_3, CaO and Fe_2O_3) on production of NO_x precursors (NH_3 and HCN) during amino acid pyrolysis.	Three amino acids: phenylalanine, aspartic acid and leucine. Only HCN and NH_3 were detected by FTIR, no other instruments were used. Pyrolysis: gasification at 800°C.	Yields of HCN and NH_3 and nitrogen conversion pathway from amino acid pyrolysis are influenced by the mineral matters, which had catalytic effects on the primary decomposition reaction pathway of amino acid.	This study proved the catalytic effects of minerals on pyrolysis, while no molecular-level of N was detected. It also did not focus on char-N evolution.	(1) 2013
To identify influences of organic fractions (cellulose, hemicellulose and lignin) on production of NO_x precursors (NH_3 and HCN) during amino acid pyrolysis.	Two model amino acids compounds: proline, glutamic acid. Only HCN and NH_3 were detected by FTIR, no other instruments were used. Pyrolysis: gasification at 800°C.	The effects of hemicellulose on NH_3 formation from the two amino acids were similar, hemicellulose inhibited NH_3 conversion and lignin promoted NH_3 formation for the two amino acids.	This study reported the influences of organic fractions (as main components of biomass) on production of NH_3 and HCN, while no molecular-level of N was detected. A controversy was that cellulose and lignin contained N themselves, while this paper did not distinct the N source.	(2) 2013
To control the formation of HCN and NH_3 derived from sewage sludge by exploring the nitrogen distributions and evolution of nitrogen functionalities in the char, tar, and gas fraction.	Dewatered sewage sludge. Microwave pyrolysis: 100–800°C. Instruments: TGA, XPS, GC-MS.	Thermal cracking of protein produced amine-N, heterocyclic-N, and nitrile-N; Deamination of amine-N compounds resulted from labile proteins cracking led to the formation of NH_3; Cracking of nitrile-N and heterocyclic-N in the tars generated HCN.	This study first clarified N species from molecular level, and authors proposed that the role of inorganic mineral matters in the emission of N_2 should be investigated in the future.	(3) 2013
To investigate the nitrogen transformations with attention to NH_3 and HCN during microwave pyrolysis of a protein model compound.	Dewatered sewage sludge. Microwave pyrolysis: 300–800°C. Instruments: XPS, GC-MS.	The NH_3 and HCN formed at 300–500°C was mainly via deamination and dehydrogenation of amine-N from protein cracking, while those formed at 500-800°C was derived from cracking of nitrile-N and heterocyclic-N compounds.	This study suggested that HCN and NH_3 emissions could be reduced through controlling the intermediates production at temperatures of 500–800°C.	(4) 2013

To investigate the evolution of N-containing organic compounds during sewage sludge pyrolysis under different heating rates.	Dewatered sewage sludge. No pyrolysis equipment was used, and only TG-FTIR-MS analysis was employed to study the pyrolysis behavior. Char-N was not characterized.	Heterocyclic-N, amine-N and nitrile-N were detected in bio-oil, and the heating rates significantly changed the species of liquid organic compounds, but they did not alter the gaseous species produced.	This study shows that a higher heating rate (200 $K \cdot min^{-1}$) and medium temperature (400–550°C) were favorable for complete decomposition of sludge and production of large quantities of liquid compounds.	(5) 2014
To study the pyrolytic N transformation from different types of sewage sludge derived from 3 sewage treatment processes, and at different temperatures.	Dewatered sewage sludge from three municipal wastewater plants. Pyrolysis at 500−800°C. Instruments: XPS.	Rising temperature from 500 to 800°C increased formation of gas-N (HCN and NH_3); Sludge produced from anaerobic process of wastewater treatment tended to be converted to more HCN.	The contribution of this study was that it compared N transformation in sludge derived from different stages of sewage treatment. It did not report N species in bio-oil.	(6) 2015
To investigate the properties of tobacco waste pyrolysis products and the N distribution/forms over the 250−950°C range for determining the optimum operating temperature.	Tobacco waste. Pyrolysis at 250−950°C. Instruments: FTIR, GC-MS, XPS.	The three types of N-containing species in char were pyridinic N, pyrrolic/pyridine N, and quaternary N; NH_3 and HCN escaped from chars with temperature increasing and are primarily found in liquid oil below 550°C and gas above 650°C.	Many characterizations were conducted for the tobacco waste pyrolysis products including physical structures of char and N species in the char, oil and gas to give an understanding of pyrolytic utility this waste.	(7) 2016
To explore N distribution and transformation mechanisms during algae pyrolysis.	Nannochloropsis sp. (NS) was purchased from a biology technology Co., Ltd., while Spirulina platensis (SP) and Enteromorpha prolifera (EP) were provided by a university. Fast pyrolysis: 400−800°C. Instruments: GC-MS, XPS.	The protein-N in algae cracked and formed pyridinic-N, pyrrolic-N, and quaternary-N in char; Amides in bio-oil were formed through NH_3 reacting with fatty acids, while N-heterocyclic compounds mainly came from pyrifinic-N, pyrrolic-N, and quaternary-N decomposition; NH_3 resulted from ammonia-N, labile amino acids and amides decomposition, while HCN came from nitrile decomposition.	A mechanism of N transformation during algae pyrolysis was proposed based on amino acids decomposition. It suggested that combustion and gasification are not suitable for algae, as algae would release large amounts of N-containing gas products at higher temperature (>600°C).	(8) 2017

To give an insight into the evolution of fuel-N to NO_x precursors during pyrolysis of N-rich non-lignocellulosic biomass.	Two target categories of N-rich nonlignocellulosic biomass: chlorella microalgae and penicillin mycelia waste. Fast pyrolysis: 200−800°C. Instruments: FTIR, XPS, GC-MS.	Around 80% of NH_3-N yield was produced at devolatilisation stage, which was attributed to cyclization of more stable amino-N into pyridinic-N/pyrrolic-N in chars; More than 90% of HCN-N yield was generated at secondary reaction stage due to a basically equal contribution from char-N and tar-N. The relevant pathways were ring scission of pyrrolic-N while ring-opening of heterocyclic-N and dehydrogenation of amines.	These detailed evolution pathways and characteristics of fuel-N to NO_x precursors were adequately applicable for N-rich non-lignocellulosic biomass with similar fuel-N types, and this was also helpful to control the emission of N-containing pollution during their energy utilization.	(9) 2018
To investigate the conversion of nitrogen bound in biomass fuel (abbreviated to fuel-N) during biomass pyrolysis.	Wheat straw, rice straw, spent coffee grounds, palm kernel cake. Fast pyrolysis: 500−900°C. Instruments: FTIR, XPS.	After pyrolysis, amide-N was completely vanished in the char, and minor of it was decomposed into NH_3, while most of it was converted to the other gas-N (HCN, HNCO, etc.). As temperature increased, a small amount of pyrrolic/pyridinic-N was converted to more stable quaternary-N and N-oxides structures.	This study reported that the conversion of fuel-N was highly reliant on temperature and fuel-N content. An unexpected founding was that amide-N was also the main contributor to formation of HCN, while the contribution of heterocyclic-N was less important.	(10) 2019
To elucidate molecular N transformation and distribution in char-tar-gas phases with interferences of minerals and organic matrix in context of environmental/industrial/agricultural influences of products.	Four solid biowastes: sewage sludge, algae, shrimp shell, and bone dreg. Doping exogenous Ca. Slow pyrolysis: 500°C. Continuous dynamic monitoring. Instruments: XPS, FTIR, XRD, TG-FTIR-GCMS*.	Conversion of protein-N into char-N, tar-N, and gas-N was of same tendency for these biowastes, while N-conversion ratios varied widely; Doping Ca didn't alter char-N yield, while it decreased percentages of protein/pyridine-N, and increased pyrrole/quaternary-N content; Ca catalyzed cracking of N macromolecules in tar, especially amine, drove their migration from tar to gas.	This study depicted molecular N profile in pyrolysis of several biowastes with different minerals and organic matrix, and firstly clarified Ca- catalytic N transformation pathways. It could guild pyrolytic production and subsequent application of biochar and biofuel, as well as exhaust gas collection in regards to N recovery and pollution control.	**This study** 2020

*TG-FTIR-GCMS: Thermogravimetric analyzer-fourier transform infrared spectrometer-gas chromatography mass spectrometer

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Table S2. Major elements content in the raw biowastes and the $CaCl_2$ treated biowastes.

Biomass	Ash content (%)	Elemental content							
		C(%)	H(%)	N(%)	S(%)	Ca($g \cdot kg^{-1}$)	Mg($g \cdot kg^{-1}$)	Fe($g \cdot kg^{-1}$)	Al($g \cdot kg^{-1}$)
SS	23.2±0.15	34.8±0.32	5.10±0.71	5.88±0.29	0.94±0.23	6.47±0.79	4.41±0.18	24.8±0.23	9.34±0.34
A	34.3±1.22	30.3±0.19	5.07±0.12	2.92±0.12	0.37±0.06	12.7±0.51	4.24±0.03	6.97±1.08	6.68±0.10
ShS	18.3±0.18	36.8±0.19	6.23±0.23	10.4±0.22	1.00±0.21	14.2±1.53	3.66±0.36	0.23±0.02	0.11±0.01
BD	22.0±1.10	29.3±0.14	5.01±0.29	4.88±0.17	0.34±0.22	77.5±3.63	4.17±0.00	5.41±0.71	0.37±0.00
SS-Ca	28.5±0.26	29.2±0.28	5.67±0.10	5.57±0.23	0.84±0.06	48.8±2.07	3.19±0.48	17.5±3.13	6.33±1.31
A-Ca	41.3±0.73	25.3±0.12	5.30±0.21	2.38±0.17	0.97±0.04	48.9±15.5	4.01±0.08	5.72±0.49	6.13±0.83
ShS-Ca	36.7±1.33	31.0±0.17	5.29±0.17	8.68±0.27	0.97±0.00	50.2±1.31	3.54±0.12	0.20±0.02	0.07±0.08
BD-Ca	46.5±1.92	24.0±0.04	5.12±0.23	4.08±0.11	0.32±0.21	91.8±8.28	3.59±0.17	1.37±0.86	0.35±0.04

Table S3. Relative percentage of N-containing species.

Biomass	Protein-N / %	Inorganic-N / %
Sewage Sludge	81.92	18.08
Algae	93.91	6.095
Shrimp Shell	84.83	15.17
Bone Dreg	71.82	28.18

Values were calculated based on the XPS spectra.

Table S4. Absolute contents of N-containing species in biochar along biowaste pyrolysis.

Biowaste	SS	SS-Ca	A	A-Ca	ShS	ShS-Ca	BD	BD-Ca
Biomass weight /g	5.00	6.00	5.00	6.00	5.00	6.00	5.00	6.00
N in Biomass/g	0.29	0.33	0.15	0.14	0.52	0.52	0.24	0.24
Biochar weight /g	2.14	2.99	2.34	3.27	1.95	2.90	2.58	3.52
N in Biochar/g	0.10	0.11	0.05	0.05	0.13	0.13	0.07	0.07
Biochar								
Protein-N/mg	16.9	33.8	10.8	7.85	24.2	18.6	13.6	9.22
Pyridine-N/mg	31.2	24.0	16.8	14.1	45.3	40.6	23.3	20.3
Pyrrole-N/mg	29.9	40.4	16.1	19.8	40.7	45.3	24.2	26.5
Quaternary-N/mg	14.6	15.6	6.89	11.9	10.2	21.4	6.91	10.9
Nitrogen oxides/mg	5.21	0	4.41	0	5.59	0	0	0

The addition ratio of Ca/biowaste was 7% (w/w, dry basis) (SS: sewage sludge; SS-Ca: sewage sludge+$CaCl_2$; A: algae; A-Ca: algae+$CaCl_2$; ShS: shrimp shell; ShS-Ca: shrimp shell+$CaCl_2$; BD: bone dreg; BD-Ca: bone dreg+$CaCl_2$).

Table S5. N-containing compounds in bio-oil derived from sewage sludge (SS) and Ca-doping SS pyrolysis.

N-containing compounds	Relative content (area%)	
	SS	SS-Ca
Total N-containing compounds	**34.75**	**30.16**
Amines and amides	**13.47**	**11.39**
Ammonium acetate	**3.73**	**5.03**
Acetamide	0.65	**2.85**
Acetamide, N-octyl-		0.33
Pentanamide, 4-methyl-	0.36	0.26
N,N-Dimethylacetamide		0.33
N-Acetyl-2-ethylbutan-1-amine		0.16
3-Amino-4-methylbenzyl alcohol	0.38	
Non-7-ynamide		0.64
Bicyclo[4.2.0]octa-1,3,5-triene, 7-methyl-		0.17
Glycine, N-isobutoxycarbonyl-, isohexyl ester	**3.46**	
4-Cyanobenzoic acid, tridecyl ester	0.66	
Phenylacetamide, N-hexyl-		0.22
4-(Aminomethyl)-N,N-dimethyloxan-4-amine		0.38
2-Furaldehyde chloroacetylhydrazone	0.24	
Dodecanamide	2.03	
Hexadecanamide	0.9	
9-Octadecenamide, (Z)-	0.52	
Octadecanamide	0.54	0.51
Cyclohexanamine, N-cyclohexylidene-		0.41
Acetic acid, 2-((2-[(1,1-dimethylbutoxycarbonyl)amino]propanyl)amino		0.1
Nitriles	**7.10**	**10.85**
1-Hydroxy-4,4-dimethylcyclohexanecarbonitrile	0.17	
Benzyl nitrile	0.47	0.45
Octanenitrile	0.49	
Isoamyl cyanide		0.67
Nonanenitrile		0.57
Pentadecanenitrile		**1.08**
2-Isobutylideneamino-3-methylbutyronitrile		0.39
1,1-Cyclopropanedicarbonitrile, 2-methyl-2-pentyl-		0.23
Hexamethyleneiminoacetonitrile		**1.17**
Benzenepropanenitrile	0.97	0.76
Decanenitrile	0.23	
Nonadecanenitrile	0.16	
Heptadecanenitrile		0.62
2,6-Dimethyltridecanenitrile		0.74
Oleanitrile	0.69	**1.16**
Tetradecanenitrile	**3.92**	**3.01**
N-heterocyclic compounds	**14.18**	**7.92**
Pyridine, 2-methyl-	0.41	0.1
Pyridine, 2,3-dimethyl-	0.35	
Pyridine, 2,5-dimethyl-		0.38
1H-Pyrrole, 2,5-dihydro-1-nitroso-	1.11	
Pyrazine, 2-ethyl-5-methyl-		0.18
2-Amino-5,6-dihydro-4,4,6-trimethyl-4H-1,3-oxazine		0.53
1H-Pyrrole, 2,5-dimethyl-	0.12	
Pyrrole		0.98
Pyrimidine-4,6-dione, hexahydro-4-(3-phenyl-2-propenyl)-2-thioxo-	0.23	
4-Amino-N-(tert-butylimino)-2-methyl-1-oxo-1,2,3-triazol-5-imine oxide		1.02
1-Azabicyclo[3.2.1]octan-6-ol,	0.52	
Aziridine, 2-isopropyl-1,3-dimethyl-, trans-	1.27	

2-Piperidinone	0.64	
1H-Pyrrole-2,5-dione, 3-ethyl-4-methyl-	0.37	
3-Methyl-2-pyrrolidinone	0.36	
Indole	3.52	1.16
1H-Indole, 2,3-dimethyl-		0.29
Pyrazol-3-one, 5-amino-1-(1-ethylpropyl)-1,2-dihydro-	0.65	
1-Isopropyl-1H-indole	0.31	0.1
2,5-Piperazinedione, 3-methyl-6-(1-methylethyl)-	0.13	
Piperidine-4,4-diol		0.56
Pyrazine, 2-methoxy-3-(1-methylpropyl)-	0.16	
3-Methyl-1,4-diazabicyclo[4.3.0]nonan-2,5-dione, N-acetyl-	1.00	
Piperazine-3,5-dione, 1-tetradecanoyl-	0.45	0.92
Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-	0.32	0.83
Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-	0.39	
5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo[1,2-a:1',2'-d]pyrazine	1.87	
morpholine, 4-[2-(1H-1,2,4-triazol-5-ylthio)ethyl]-		0.26
2-Oxo-1-methyl-3-isopropylpyrazine		0.35
1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone		0.14
Benzofuro[3.2-d]pyrimidin-4(3H)-one		0.12

Table S6. N-containing compounds in bio-oil derived from Algae (A) and Ca-doping A pyrolysis.

N-containing compounds	Relative content (area%)	
	A	A-Ca
Total N-containing compounds	**28.53**	**7.12**
Amines and amides	**17.88**	**1.63**
2-Isopropoxyethylamine	12.98	
Ammonium acetate	2.85	
Acetamide	0.38	0.14
Hexanamide	0.12	
Benzenepropanoic acid, .alpha.-(hydroxyimino)-	0.12	
4-Aminooxane-4-carboxylic acid		0.1
Carbonic acid, monoamide, N-3-methylbutyl-, menthyl ester		0.08
Phenol, 2-(1-methylethyl)-, methylcarbamate		0.19
5-Nitrothiophene-2-carboxylic acid n-nonyl ester		0.08
4-Cyanobenzoic acid, 6-ethyl-3-octyl ester		0.21
5-Nitrothiophene-2-carboxylic acid, N-tetradecanyl ester	0.17	
1,2-Diphenyl-1-isocyanoethane	0.33	
Propane-1,2,3-trione, 1-(2-furyl)-, 2-(4-methoxyphenyl)hydrazone		0.17
1,2-Diphenyl-1-isocyanoethane		0.3
Tetradecanamide	0.03	
Hexadecanamide	0.79	
Nonadecanamide	0.11	
Octadecanamide		0.36
Nitriles	**4.35**	**2.89**
Benzenepropanenitrile	0.53	0.34
9-Octadecynenitrile	0.18	
Tetradecanenitrile	2.74	
Oleanitrile	0.31	
Pentadecanenitrile	0.59	
5-Cyanomethylene-2,3,3-trimethylpyrrolidine-2-carbonitrile		0.08
Nonadecanenitrile		1.92
Hexadecanenitrile		0.28
Benzonitrile, m-phenethyl-		0.27
N-heterocyclic compounds	**6.30**	**2.60**
Pyrrole		0.27
Pyridine, 2-methyl-	0.08	0.21
1-Amino-4-methylpiperazine	0.28	
Glutarimide	0.38	
1H-Pyrrole-2,5-dione, 3-ethyl-4-methyl-	0.22	
Piperidine-4,4-diol	0.17	
2,4-Dimethyl-2-thiazoline		0.06
Glutarimide		0.23
4,6-Dimethyltetrahydro-1,3-oxazine-2-thione		0.19
1H-Pyrrole-2,5-dione, 3-ethyl-4-methyl-		0.09
1H-Imidazole-2-methanol, 1-butyl-		0.03
2-Benzyl-5-([(3-methoxyphenyl)amino]methyl)-2,3-dihydro-1H-1,2,4-triazol-3-one	0.26	
Indole	1.32	0.83
Benzhydrazide, 2-hydroxy-N2-(2,2,6,6-tetramethyl-4-piperidinylideno)-	0.46	
Tetrahydrofurfuryl N-(4-pyridyl)carbamate		0.1
2-Imidazolidinone, 1,3-diethenyl-	0.34	
Pyrimido[1,2-a]azepine, 2,3,4,6,7,8,9,10-octahydro-	0.31	
5H-Cyclopentapyrazine, 6,7-dihydro-2,5-dimethyl-		0.29
N-Methyl-1H-benzimidazol-2-amine	0.23	
3-(1-Methylethyl)(1H)pyrazolo[3,4-b]pyrazine		0.07
6,6-Dimethyl-1,3-diazaadamantane	0.31	

1-(5,6-Dimethyl-2-pyrazinyl)-3-methyl-1-butanol	0.18	
3-Ethyl-5-methylindolizidine	0.34	0.06
Piperidine, 1-(cyanoacetyl)-	0.89	
5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo[1,2-a:1',2'-d]pyrazine	0.5	
Pyrrolidine, 1-(12-methyl-1-oxotetradecyl)-	0.03	
Propane-1,2,3-trione, 1-(2-furyl)-, 2-(4-methoxyphenyl)hydrazone		0.17

Table S7. N-containing compounds in bio-oil derived from shrimp shell (ShS) and Ca-doping ShS pyrolysis.

N-containing compounds	Relative content (area%)	
	ShS	ShS-Ca
Total N-containing compounds	**56.23**	**47.19**
Amines and amides	**14.36**	**11.79**
N,N-Dimethylaminoethanol	0.38	0.14
2-Isopropoxyethylamine		3.88
Pentanamide, 4-methyl-	1.26	0.94
Acetamide, N-methyl-		0.13
DL-Asparagine	0.53	
Propanamide, 2-methyl-	0.12	
Butanamide, 3-methyl-	1.81	
dl-Alanyl-l-leucine		0.24
p-Isopropoxyaniline	0.28	
Benzenamine, N-ethyl-N-methyl-		0.11
1,2-Benzenediamine, N-methyl-		0.14
2-Propenal, 3-(dimethylamino)-	0.9	
3-[(4-Aminobenzoyl)hydrazono]-N-(2,4,6-trimethylphenyl)butyramide	0.17	
Phenol, 3-methyl-5-(1-methylethyl)-, methylcarbamate	0.25	
Hex-5-enamide, N-(2-phenylethyl)-		0.22
Acetamide, N-(2,4-dihydroxyphenyl)-	0.4	
4-Fluoro-5-amino veratrole		0.38
Benzaldehyde, oxime		0.29
Octadecane, 1-isocyanato-	1.34	
Di(pent-4-enyl)amine		0.11
Phenylpropanamide	0.71	0.78
Propanamide, 3-cyclopentyl-N-methyl-		0.02
Acetamide, 2,2-diphenyl-N-(3,3,5-trimethylcyclohexyl)-	0.28	
Acetamide, N-(3-amino-2,4,6-trimethylphenyl)-	0.19	
2-Amino-4-nitrophenol, N,N-dimethyl-, methyl ether		0.16
N-[4-(2-Hydroxyethyl)phenyl]acetamide		0.07
6-Aminocaproic acid, N-(6-aminocapryloyl)-N'-propoxycarbonyl-, propyl ester	0.17	
Glycine, N-isobutoxycarbonyl-, isohexyl ester		1.35
5-Acetamido-2-methylphenyl acetate	0.58	
dl-Alanyl-l-leucine	0.63	
Ethane-1,2-diamine, N,N'-bis(4-methyl-2-oxocyclohexylidenomethyl)-	0.58	
Cyclohexanamine, N-cycloheptylidene-	0.29	
Benzeneethanamine, N-(2-phenylethyl)-		0.1
6-Aminocaproic acid, N-neopentyloxycarbonyl-, isobutyl ester	0.15	
Dodecanamide	0.52	0.4
l-Allylglycine, N-propargyloxycarbonyl-, pentadecyl ester		0.43
Octadecanamide	0.17	
N,N-Dimethyldodecanamide	0.22	0.29
2-Nonadecanone, O-methyloxime	0.13	
9-Octadecenamide, (Z)-	0.66	0.27
Hexadecanamide	1.50	0.5
Myristamide, N-methyl-	0.14	0.21
Benzenesulfonamide, N-[1,1'-biphenyl]-4-yl-4-ethyl-		0.43
Propylamine, N,N-di(pentyl)-		0.2
Nitriles	**11.7**	**9.88**
Cyanamide, dimethyl-		0.28
Isoamyl cyanide	0.85	0.79
Propanenitrile, 3-(dimethylamino)-		0.45
Hexanenitrile, 5-methyl-		0.19
2-Dimethylamino-4-methyl-pent-4-enenitrile	0.58	1.04

Azeleonitrile	0.15	
Dodecanenitrile		0.2
8-Nonene-1-nitrile		0.25
2-Dimethylamino-4-methyl-pent-4-enenitrile	0.44	
Dicyclopropylmethanimine, N-cyano-	0.12	
3-Furonitrile, 2-amino-4,5-dimethyl-		0.47
Benzyl nitrile	0.79	
1-Azido-4-dimethylaminobenzene		0.32
Benzenepropanenitrile	3.34	1.57
Benzenebutanenitrile		0.41
Undecanenitrile	0.66	
3-(4-Hydroxyphenyl)propionitrile	0.42	
2,4,6-Trimethylbenzonitrile		0.37
2,3,5,6-Tetramethylphenylcyanide		0.41
Pentanenitrile, 5-phenoxy-		0.14
(7-Isopropylidenebicyclo[2.2.1]hept-5-en-2-ylidene)acetonitrile	0.33	
Piperidine, 1-(cyanoacetyl)-	0.7	0.61
Pentadecanenitrile	1.92	1.47
Oleanitrile	0.75	0.32
Hexadecanenitrile	0.53	0.59
Nonadecanenitrile	0.12	
N-heterocyclic compounds	**30.17**	**25.52**
Azetidine, 1,2-dimethyl-	0.1	
Pyridine	0.46	
Pyrrole	0.96	
2-Imidazolidinone, 1,3-diethenyl-		0.48
1H-Pyrrole, 2-methyl-		1.48
1H-Pyrrole, 2-ethyl-4-methyl-		0.8
(S)-(+)-2-Pyrrolidinemethanol		0.28
1H-Pyrazole, 4,5-dihydro-4,5-dimethyl-	0.22	0.17
Pyridine, 2-methyl-	0.64	0.59
Pyridine, 3-methyl-	0.23	
Pyridine, 2,3-dimethyl-		0.64
Pyridine, 2,3-dimethyl-	0.37	0.15
Pyridine, 2-ethyl-6-methyl-	0.24	0.32
Pyridine, 3-ethyl-5-methyl-	0.07	
Pyridine, 2,4-dimethyl-	0.47	
2-Pyridinamine, 3-methyl-	0.23	
2-Pyrimidinamine, 4,6-dimethyl-	0.12	
2-Pyridinamine, 3,6-dimethyl-		0.28
2(1H)-Pyridinone, 1-methyl-	0.1	
2(1H)-Pyridinone, 1,6-dimethyl-	0.21	
4(H)-Pyridine, N-acetyl-		0.26
1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone		0.52
4-Pyrimidinamine, 6-methyl-	0.27	
1H-Pyrrole, 1-ethyl-	0.15	
1H-Pyrrole, 2-methyl-	0.21	
1H-Pyrrole, 2-ethyl-4-methyl-	0.14	
1H-Pyrrole, 2,5-dimethyl-	0.22	0.39
1H-Pyrrole, 3,5-dimethyl-2-phenyl-	0.35	
2,3,7-Trimethylindole		0.18
2-Pyrrolidinone, 4,4-dimethyl-5-methylidene-	0.79	
3,4-Dimethyl-3-pyrrolin-2-one		0.78
2-Hydrazinopyridine	0.52	
Picolinamide		0.32
2-(2H-1,2,4-Triazol-3-yl)ethanamine	0.14	
Dimethyl-(1H-pyrrol-3-ylmethyl)-amine	0.26	

3,4-Dimethyl-3-pyrrolin-2-one	0.48	
5,6-Dihydro-6-methyluracil		0.74
7-Azabicyclo[4.1.0]heptane, 1-methyl-	0.07	
2H-Azepin-2-one, hexahydro-3-methyl-	0.21	
Pyrrolidine, 1-acetyl-	0.45	
3-Pyridinecarbonitrile, 1,4-dihydro-1-methyl-4-oxo-	0.11	
2-Amino-5,6-dihydro-4,4,6-trimethyl-4H-1,3-oxazine		0.99
1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone	0.49	0.52
1-Methyl-3-piperidinemethanol		0.38
1-Isopropyl-1H-indole	0.24	
Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-		0.68
2-Isopropylpyrazine	1.47	
4-Isobutylpyrimidine	0.65	
2-Piperidinemethanamine	0.8	
Glutarimide		0.52
Piperidine, 1-(2-methyl-1-propenyl)-	0.46	
4-(2-Hydroxyethyl)-2,2,6,6-tetramethylpiperidine	0.29	
2H-Azepin-2-one, hexahydro-3-methyl-		0.27
2-Methyl-6-propylpyridine		0.2
2-Oxo-1-methyl-3-isopropylpyrazine	1.03	0.25
Isoquinoline, 5,6,7,8-tetrahydro-3-methyl-		0.62
1,8-Diazabicyclo[5.4.0]undec-7-en-11-one	0.65	
Tetrazolo[1,5-a]pyridin-7-ol, 5-methyl-	0.35	
Benzoic acid, 3-amino-6-(1-pyrrolidinyl)-		0.11
Pyridine, 2-phenyl-		0.2
Pyridine, 4-benzyl-		0.22
2,3-Cyclododecenopyridine		0.44
3-Amino-5-cyclopropylpyrazole	0.29	
4-Amino-N-(tert-butylimino)-2-methyl-1-oxo-1,2,3-triazol-5-imine oxide	0.68	
6-Amino-2-(pyrrolidin-1-yl)-3H-pyrimidin-4-one	0.17	
1,1-Dimethyl-3-(3-methyl-1,2,4-oxadiazol-5-yl)guanidine	0.16	
3-Pyridinecarboxamide, N-[2-aminoethyl]-		0.25
2-Pyridinecarbaldehyde 4-allyl(thiosemicarbazone)		0.29
3-Methyl-1,4-diazabicyclo[4.3.0]nonan-2,5-dione, N-acetyl-	0.78	0.65
Indole	3.03	2.34
Indole, 3-methyl-	1.58	
1H-Indole, 2,3-dimethyl-		0.8
3-Ethyl-5-methylindolizidine	1.94	
9-Aza-1-methylbicyclo[3.3.1]nonan-3-one	0.41	
8-Azabicyclo[3.2.1]oct-6-en-3-one, 8-methyl-	0.33	
2,7-Diazaspiro[4.4]nonane, 2-ethyl-	0.75	1.61
4,5-Dihydro-5,5,7-trimethyl-6H-[1,2,5]oxadiazolo[3,4-b][1,4]diazepine	0.17	
3-Indolylacetone	0.14	
Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-	1.08	
6,7,8,9-Tetrahydro-5H-[1,2,4]triazolo[1,5-a]azepin-2-ylamine		0.59
N-[3-[.alpha.-Furylmethylamino]propyl]aziridine	0.22	
2-Aziridinone, 1-(1-adamantyl)-3-(1-methylcyclopentyl)-		0.2
(3Ar)-(+)-8,8-dimethyl-4,5,6,7-tetrahydro-3H-3a,6-methano-2,1-benzisothiazole 2,2-dioxide		0.21
6-Cyano-5,7-dimethyl-1,3-diazaadamantan-6-ol		0.63
Benzofuro[3.2-d]pyrimidin-4(3H)-one	0.28	0.63
5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo[1,2-a:1',2'-d]pyrazine		0.64
Morpholine, 4-(1-cyclopentylpiperidin-4-yl)-	0.84	
Tetrahydropyrrolo[1,2-a] 1,4-diazaspiro[4.5]decan-3-one	0.25	
Acetamide, N-(1,2,3,5,6,7-hexahydro-s-indacen-4-yl)-	0.14	
3-([1,2,4]Triazol-4-ylamino)-3H-isobenzofuran-1-one	0.24	

1,3,5-Triazine, 2-[1-(aminocarbonyl)hydrazino]-4-methoxy-6-(1-pyrrolidinyl)-	0.46	
5,8-Methano-1H-[1,2,4]triazolo[1,2-a]pyridazine-1,3(2H)-dione, 5,6,7,8-tetrahydro-2,5-diphenyl-		0.3
5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo[1,2-a:1',2'-d]pyrazine	1.01	
4(5H)-Thiazolone, 5-[(1,5-dimethyl-1H-pyrazol-4-yl)methylidene]-2-(1-piperidinyl)-		0.44
1-azetidinepropanoic acid, 3,3-dipentyl-, ethyl ester		0.57
1-[3,6-Dimethyl-5-(cis-hex-3-enoxy)-2-pyrazinyl-1-propanone		0.62
Cyclohex-2-enone, 2-butyryl-3-[2-(2-methyl-1H-indol-3-yl)ethylamino]-		0.38
3-Azabicyclo[3.2.2]nonane-3-thiocarboxylic acid, 2-[1-[2-quinolyl]ethylidene]hydrazide		0.59

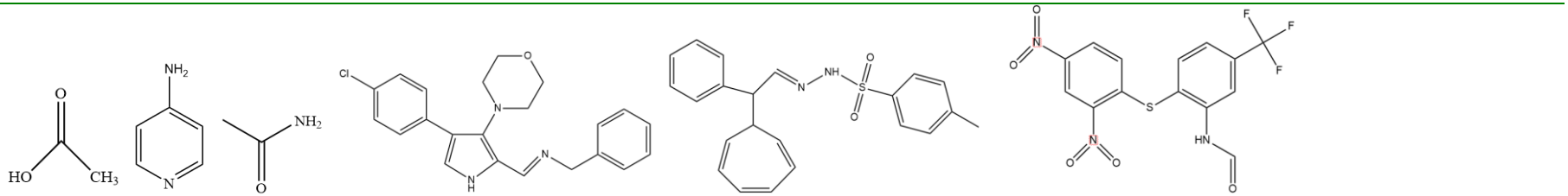
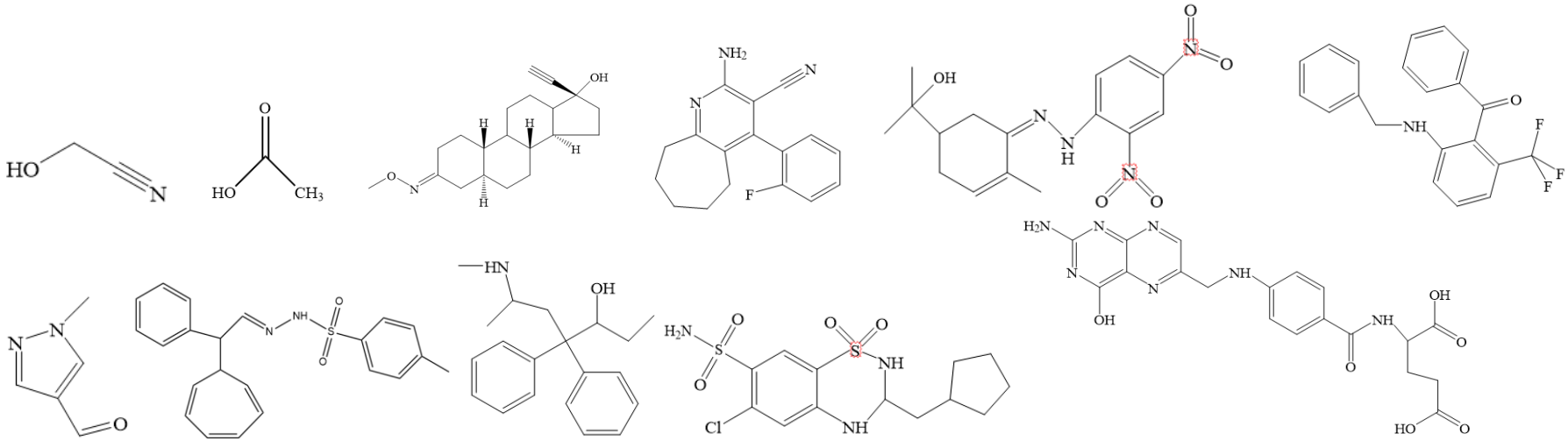
Table S8. N-containing compounds in bio-oil derived from bone dreg (BD) and Ca-doping BD pyrolysis.

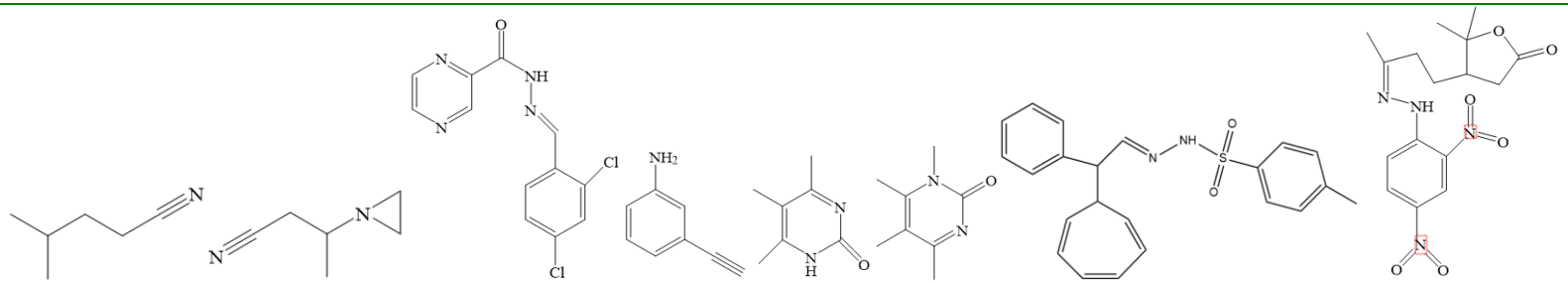
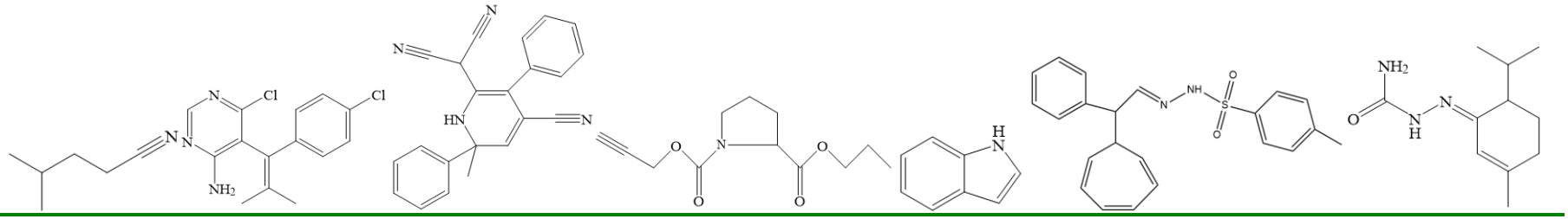
N-containing compounds	Relative content (area%)	
	BD	BD-Ca
Total N-containing compounds	**47.53**	**27.82**
Amines and amides	**11.78**	**5.7**
2-Isopropoxyethylamine	5.05	
Acetamide	0.08	
2-Propanamine, N-methyl-N-nitro-		0.01
p-Aminotoluene	0.02	0.03
Benzenepentanamide	0.17	0.07
2-Hydroxy-2-phenyl-N-(1-phenyl-ethyl)-acetamide	0.17	0.21
Urea, N-(2-methoxyphenyl)-N'-phenyl-		0.03
N-Benzyloxycarbonyl-D-aspartic acid		0.34
1-Cyclohexene-1-carboxaldehyde, oxime	0.13	
Ethene, 1-(N-butyl-N-methylamino)-1-(trifluoromethyl)-	0.11	
Nonadecanamide	0.15	
Acetic acid, (3-methyl-2-nitrophenyl)methyl ester	0.13	0.1
Tyrosine	0.12	
Myristamide, N-methyl-	1.32	0.61
Myristamide, N-(3-methylbutyl)-	0.05	0.05
Myristamide, N-propyl-	0.07	
N-Cyclopropyl-2-methoxybenzenamine	0.24	
Hexadecanamide	1.55	
N-Methyldodecanamide	0.64	0.13
Non-7-enoic acid, dimethylamide	0.16	
N,N-Dimethyldodecanamide	0.21	0.15
2-Nonanone, O-methyloxime		0.01
3-Cyclopentylpropionic acid, 2-dimethylaminoethyl ester	0.09	
Cycloheptanone imine, 2,2,7,7-tetramethyl-	0.04	
Propanamide, 3-cyclopentyl-N-propyl-		0.05
Propanamide, 3-cyclopentyl-N-methyl-		0.06
Propanamide, 3-cyclopentyl-N-isobutyl-		0.01
Hexadecanamide		2.58
Hexanamide, N-allyl-	0.07	
9-Octadecenamide, N-propyl-	0.02	
9-Octadecenamide, (Z)-	0.71	0.72
9-Octadecenamide, N,N-dimethyl-	0.06	0.03
Octadecanamide, N-butyl-	0.32	0.01
Octadecanamide		0.33
Dodecanamide, N-ethyl-	0.06	
Dodecanamide, N-3-methylbutyl-		0.02
S-[2-[N,N-Dimethylamino]ethyl]N,N-dimethylcarbamoyl thiocarbohydroximate	0.04	
Carbonic acid, 2-dimethylaminoethyl ethyl ester		0.02
Acetamide, N-2-norbornen-7-yl-, syn-		0.01
4-Cyanobenzoic acid, undec-2-enyl ester		0.12
Nitriles	**26.33**	**16.8**
Propanenitrile, 3-[(2-methylpropyl)amino]-	0.03	
Isoamyl cyanide		0.18
2-Dimethylamino-4-methyl-pent-4-enenitrile	0.06	
6-Heptene-1-nitrile	0.11	0.24
Heptanonitrile	0.13	0.32
Cyclohexanecarbonitrile	0.08	
7-Octene-1-nitrile	0.07	0.18
Octanenitrile	0.36	0.88
Benzonitrile, 2-methyl-	0.13	0.17

1-Azido-4-dimethylaminobenzene	0.1	
8-Nonene-1-nitrile	0.07	0.44
Nonanenitrile	0.37	0.19
Benzenepropanenitrile	0.44	0.48
Benzenebutanenitrile		0.09
9-Decene-1-nitrile	0.14	
Octanedinitrile	0.18	0.56
Decanedinitrile	0.23	0.11
Azeleonitrile	0.39	0.28
9-Octadecynenitrile		0.14
11-Octadecynenitrile		0.07
Hexadecanenitrile	5.60	2.56
10-Undecenenitrile		0.01
Pentadecanenitrile	7.90	4.67
Nonadecanenitrile	0.15	0.08
Oleanitrile	9.79	4.87
Spiro[2.5]octane-1,1-dicarbonitrile, 4-methyl-		0.05
1,1-Cyclopropanedicarbonitrile, 2-methyl-2-pentyl-		0.17
.delta.2,.alpha.-Pyrrolidineacetonitrile, 5-(2-ethoxy-1-pyrrolin-5-yl)-		0.06
N-heterocyclic compounds	**9.06**	**5.91**
Pyrrole	1.01	1.02
1H-Pyrazole, 4,5-dihydro-4,5-dimethyl-	0.03	
Pyridine		0.12
Pyridine, 2-methyl-	0.08	
Pyrimidine, 2-methoxy-		0.08
Pyridine, 3-methyl-	0.05	
Pyridine, 3-ethyl-5-methyl-		0.05
Pyridine, 2,3/4/5-dimethyl-	0.03	0.31
Pyridine, 2-ethyl-6-methyl-	0.03	0.09
1H-Pyrrole, 1-ethyl-		0.09
1H-Pyrrole, 2-methyl-	0.05	
1H-Pyrrole, 2-ethyl-4-methyl-	0.08	0.15
1H-Pyrrole-2-carbonitrile	0.2	
3,4-Dimethyl-3-pyrrolin-2-one	0.13	
Glutarimide	0.2	
2-Methyl-6-propylpyridine	0.16	
1H-Pyrrole-2,5-dione, 3-ethyl-4-methyl-	0.11	
Bis(2,4-dimethylamino)pyrimidine	0.17	
2,5-Dimethyl-3-isopropylpyrazine		0.18
2-Oxo-1-methyl-3-isopropylpyrazine		0.11
Indole	0.54	0.36
1H-Indole, 5,6,7-trimethyl-	0.09	
1-Isopropyl-1H-indole	0.13	0.12
1H-Imidazo(4,5-d)pyridazin-7-ol	0.15	
2H-Azepin-2-one, hexahydro-3-methyl-	0.24	0.25
2-[N-Aziridyl]methylpyrrole	0.02	
N-(2,5-Dicyano-3,4-dihydro-2H-pyrrol-2-yl)-acetamide	0.07	
1H-Pyrazole-1-ethanol, 3,5-dimethyl-	0.04	
1-(6-Methyl-2-pyridyl)propan-2-ol		0.12
2-[(Pyridin-3-ylmethyl)amino]ethanol		0.15
6-Butyloxy-4-methylhexahydropyrimidin-2-thione	0.35	
5-Piperidino-2-pyrrolidone	0.05	
N-[2-Methyl-4-pyridyl]-4-aminophenol	0.28	0.2
Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-	0.93	0.17
Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-	0.76	
2-Methyl-8-nitroisoxazolizidine		0.1
5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo[1,2-a:1',2'-d]pyrazine	0.82	0.48

1H,2H,3H,4H-Pyrido[2,1-b]quinazolin-11-one		0.16
2,5-Dimethyl-1-aza-bicyclo[2.2.1]heptane	0.19	
8-Azabicyclo[3.2.1]oct-6-en-3-one, 8-methyl-		0.26
Cyclohex-2-enone, 3-[2-(1H-indol-3-yl)ethylamino]-5,5-dimethyl-	0.1	
4-Methyl-N-(4-phenyl-piperazin-1-ylmethyl)-benzamide	0.13	
Indoxazen-4-one, 4,5,6,7-tetrahydro-3-undecyl-	0.2	
Benzofuro[3.2-d]pyrimidin-4(3H)-one	0.86	0.51
Tetrazolo[1,5-b]pyridazine, 6-(1-piperidyl)-		0.19
3-Methyl-1,4-diazabicyclo[4.3.0]nonan-2,5-dione, N-acetyl-	0.52	0.3
Phenol, 2-[[[2-(1H-indol-3-yl)ethyl]amino]methyl]-6-methoxy-	0.15	
Cyclohex-3-enecarboxylic acid, 6-[2-(2-methyl-1H-indol-3-yl)ethylcarbamoyl]-		0.1
9-Hexadecenoic acid, pyrrolidide	0.11	
Methanesulfonamide, N-[2-[4-(2,3-dihydroindole-1-sulfonyl)phenoxy]ethyl]-		0.15
Cyclohexanecarboxylic acid, 2-[2-(2-methyl-1H-indol-3-yl)ethylcarbamoyl]-		0.09

Table S9. N-containing substances derived from sewage sludge and shrimp shell with and without the addition of calcium during pyrolysis based on TG-FTIR-MS curves (Note: the N-containing products were obtained at the maximum pyrolysis rate form DTG curves).

Feedstock	Substances
Sewage sludge	
Sewage sludge-Ca	

Shrimp shell	
Shrimp shell-Ca	

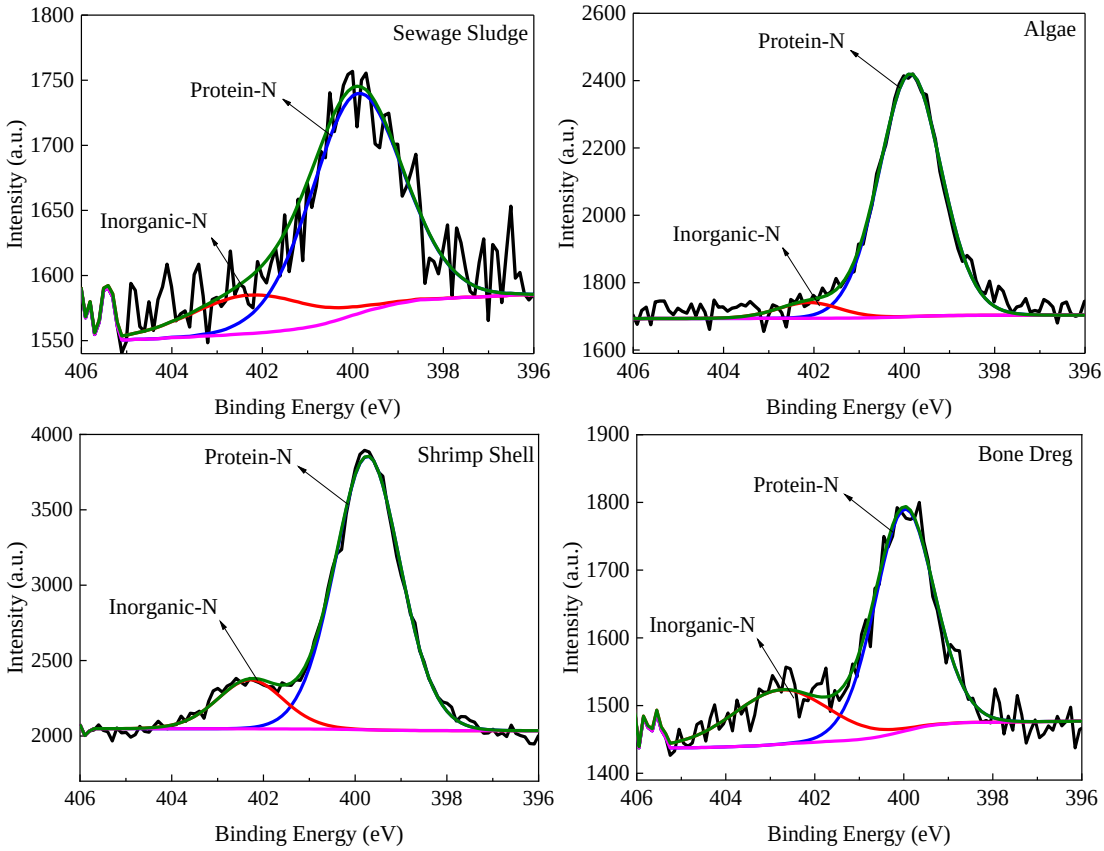


Figure S1. N1s peaks for the raw sewage sludge, algae, shrimp shell, and bone dreg.

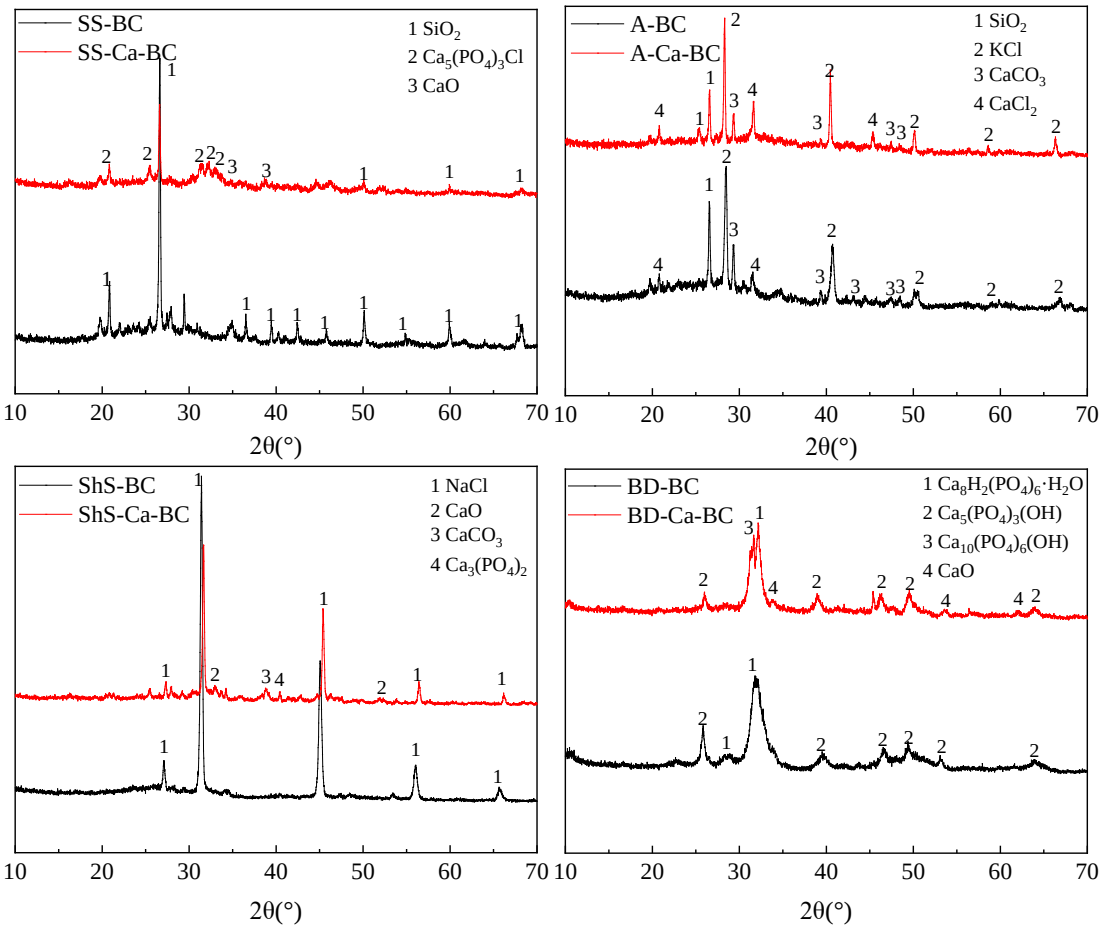


Figure S2. XRD patterns of the biochars produced by pyrolysis of different biowastes with and without calcium at 500°C (SS: sewage sludge; SS-Ca: sewage sludge+$CaCl_2$; A: algae; A-Ca: algae+$CaCl_2$; ShS: shrimp shell; ShS+Ca: shrimp shell+$CaCl_2$; BD: bone dreg; BD-Ca: bone dreg+$CaCl_2$).

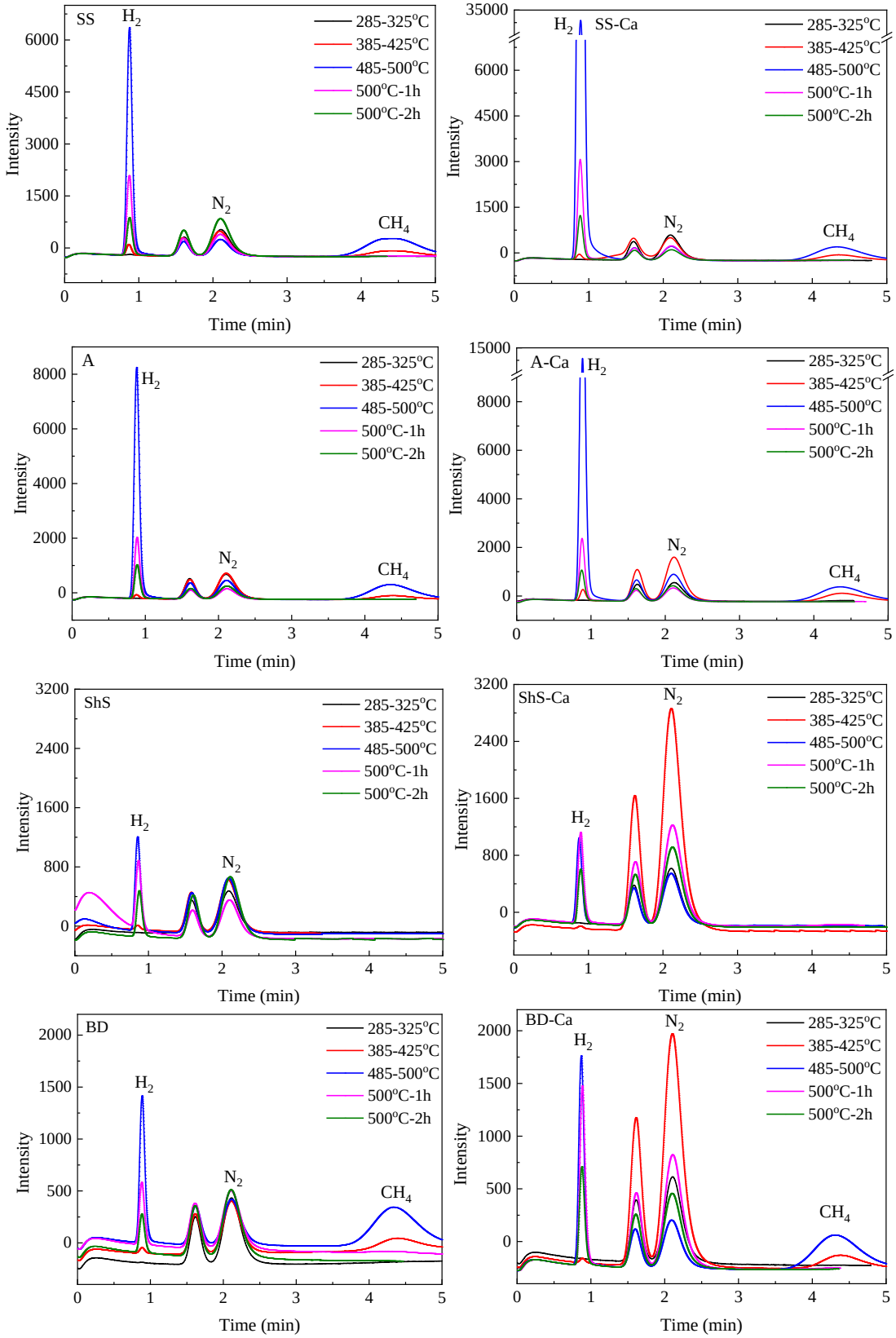


Figure S3. Gas-release (H_2, N_2, and CH_4) from the four types of biowaste pyrolysis at different time. (SS: sewage sludge; SS-Ca: sewage sludge+$CaCl_2$; A: algae; A-Ca: algae+$CaCl_2$; ShS: shrimp shell; ShS+Ca: shrimp shell+$CaCl_2$; BD: bone dreg; BD-Ca: bone dreg+$CaCl_2$).

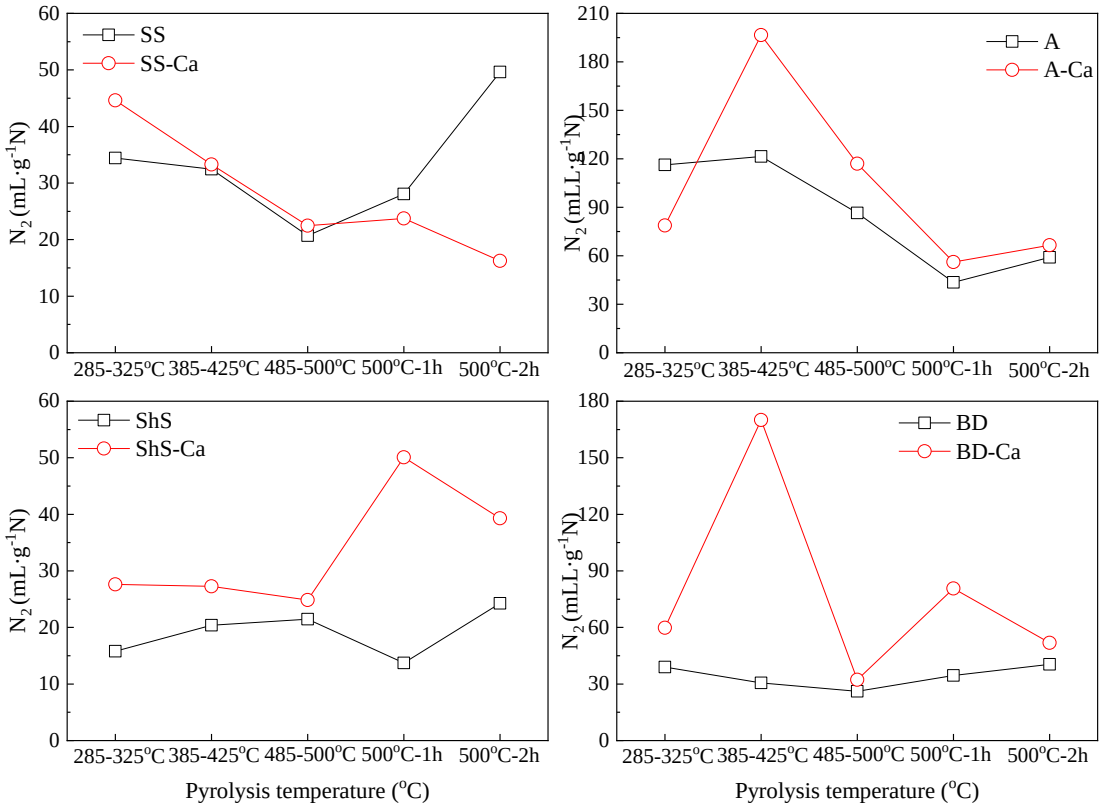


Figure S4. Releasing N_2 yields from the four types of biowaste pyrolysis at different time. (SS: sewage sludge; SS-Ca: sewage sludge+$CaCl_2$; A: algae; A-Ca: algae+$CaCl_2$; ShS: shrimp shell; ShS+Ca: shrimp shell+$CaCl_2$; BD: bone dreg; BD-Ca: bone dreg+$CaCl_2$).

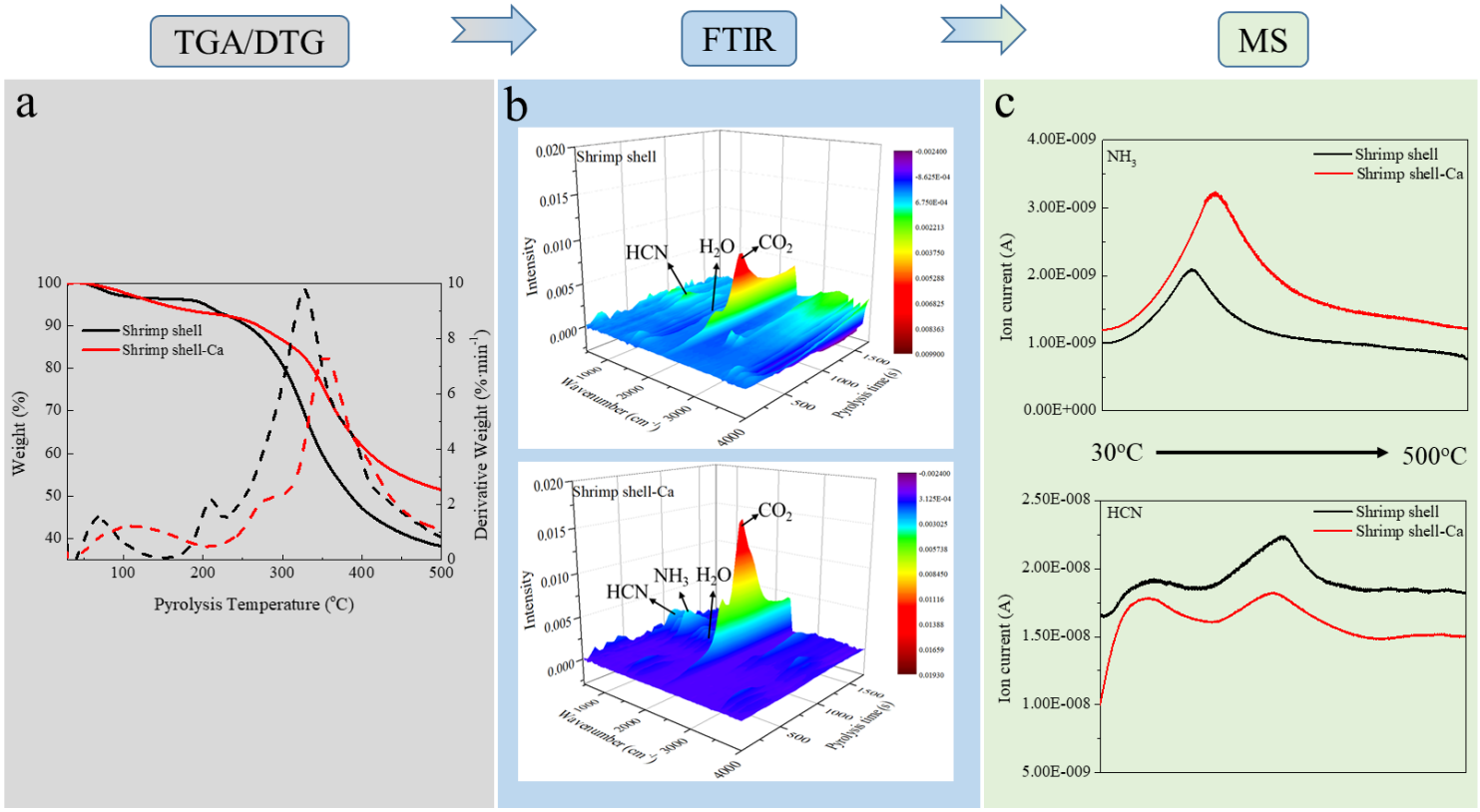


Figure S5. TG-FTIR-MS of shrimp shell with and without the addition of calcium during pyrolysis.