

## ***Supplemental Information***

### **Characterization of products from catalytic hydrothermal carbonization of animal manure**

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#### **Contents:**

Figures S1-S6 shows residual analysis of gas samples by GC-TCD.

Figure S7 shows the analysis of aqueous samples by GC-MS. Tables S1 and S2 give concentrations of peaks shown in those scans.

Tables S3 – S6 show the data used to plot the mass balances presented in Figures 4-7.

Figures S1-S6 show the residual gas analysis results from the hydrothermal treatments of the cow and pig manures. The inset in each plot shows the gases that are also part of the larger peak but are at much lower levels. For example, in Figure S1, the inset shows H<sub>2</sub>S as the predominant gas but it is present at only about 0.1% of the volume of the N<sub>2</sub> and CO<sub>2</sub> shown in the main plot. These levels are very low but due to the toxic nature of these gases, they need to be considered. Despite the fact that these results are only semiquantitative and only collected on a limited number of samples, the impact of the acid catalysis is evident. In each manure, hydrothermal treatment in water gave H<sub>2</sub>S as the largest minor gas. Strong acid treatment reduced the amount of this gas formed but this increased the amount of NO<sub>2</sub> formed. This same change is observed with the pig manure but more of the minor gases was formed in these runs.

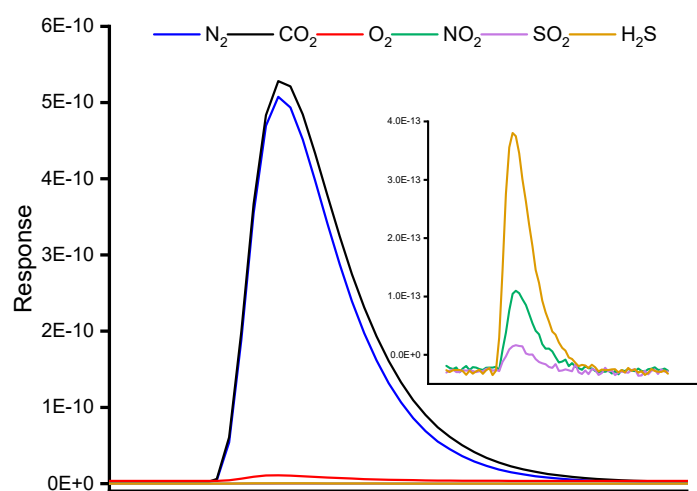


Figure S1. Residual gas analysis of CM-DIW

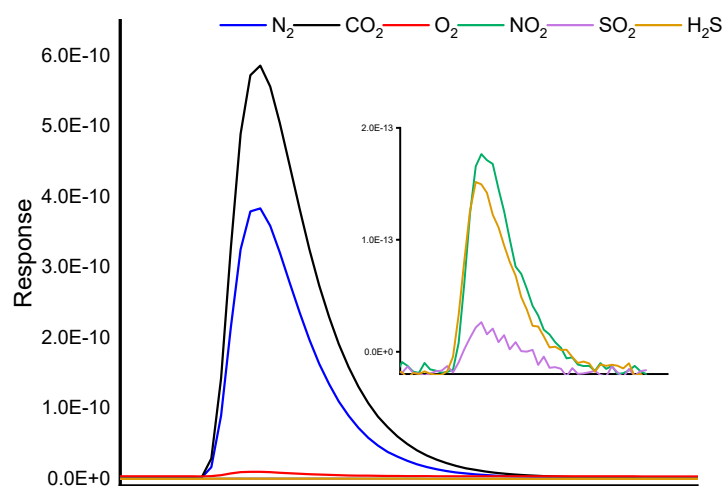


Figure S2. Residual gas analysis of CM-SA.

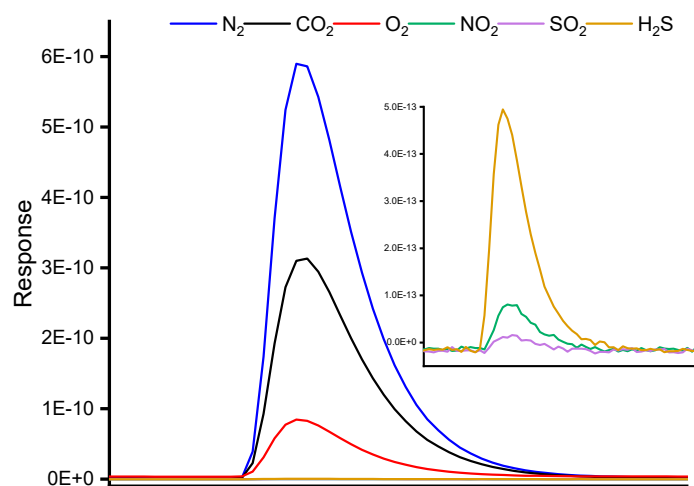


Figure S3. Residual gas analysis of CM-AA.

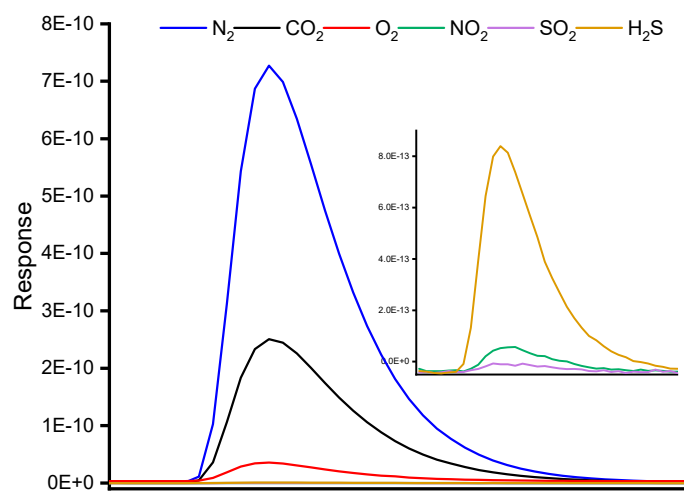


Figure S4. Residual gas analysis for PM-DIW.

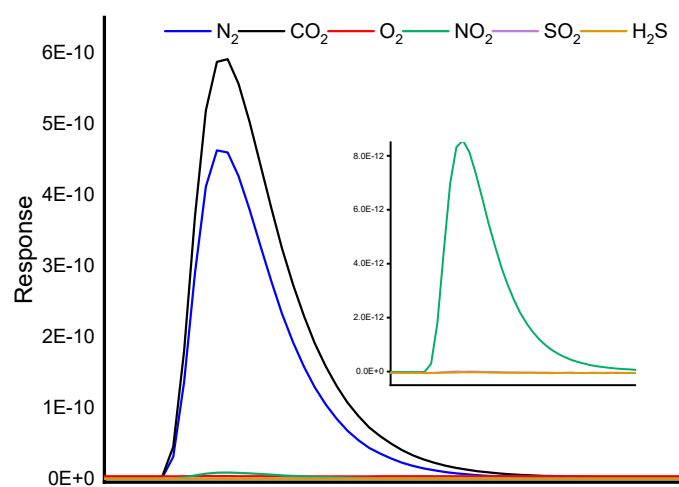


Figure S5. Residual gas analysis for PM-SA

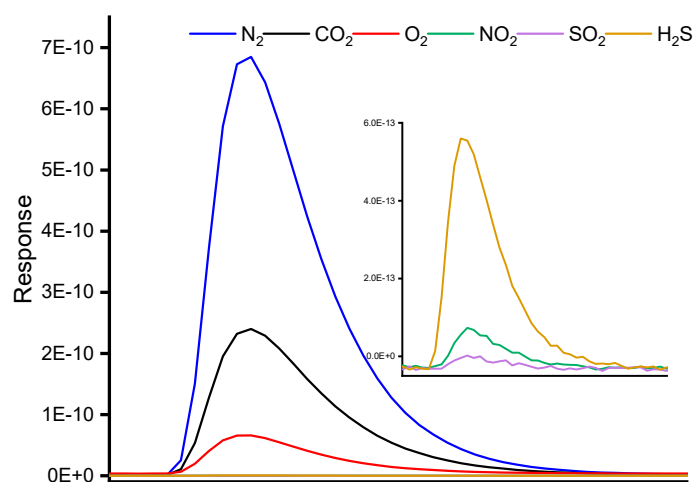


Figure S6. Residual gas analysis for PM-AA

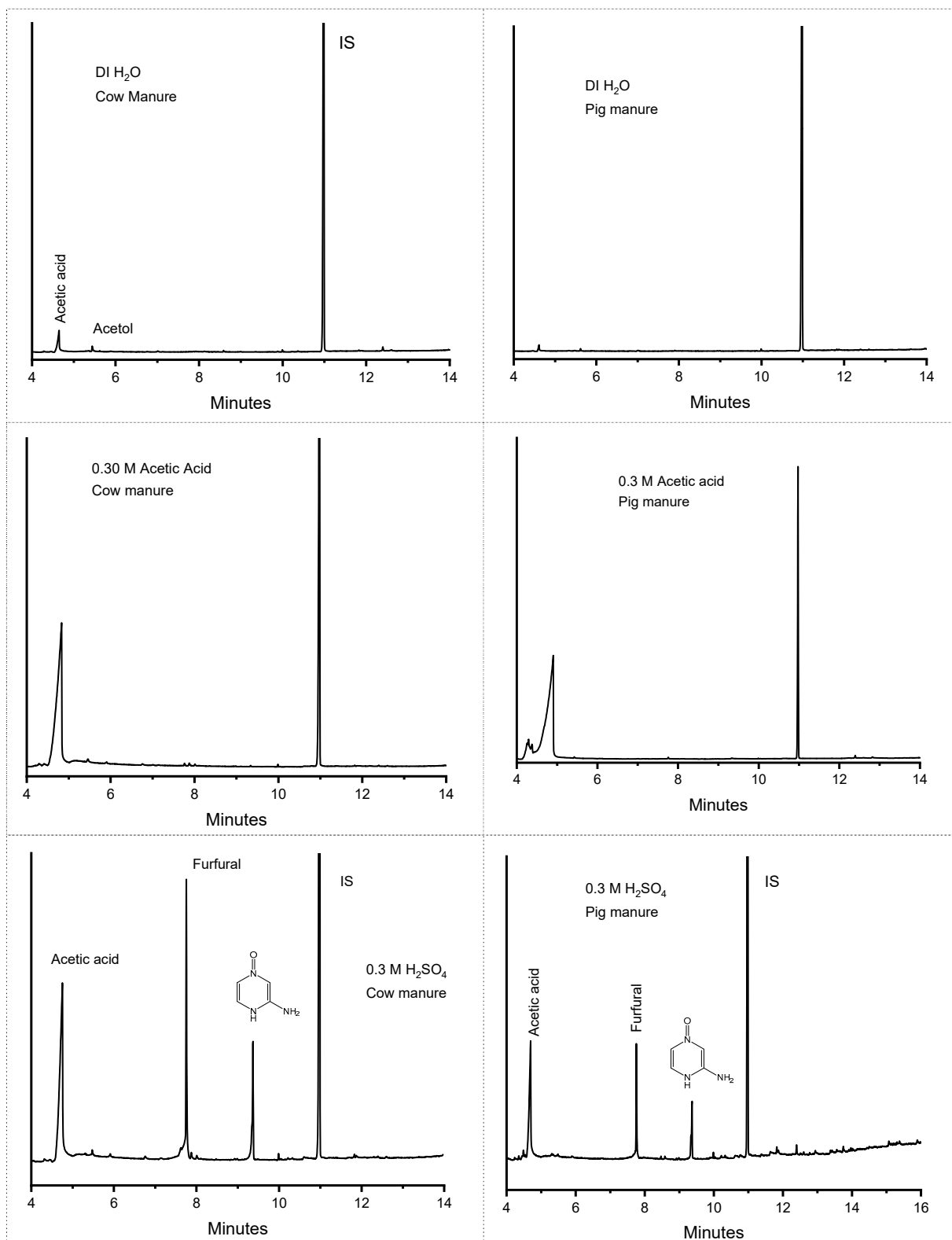


Figure S7. GC MS analyses of aqueous products.

Table S1. Integrator area %s for the compounds found in the samples treated with 0.3 M H<sub>2</sub>SO<sub>4</sub> (Figure S7).

	Cow manure	Pig manure
Acetic acid	64.3	62.2
Furfural	23.5	21.0
3-aminopyrazine 1-oxide	12.2	16.7

Table S2. Concentrations of acetic acid in six samples (Figure S7).

Sample	[Acetic acid], mg/ml
DI water cow manure	0.9
Acetic acid cow manure	9.8
Sulfuric acid cow manure	5.1
DI water pig manure	<0.2
Acetic acid pig manure	22.2
Sulfuric acid pig manure	1.70

Table S3. Mass balance of carbon in solid, aqueous, and gas phases. Data are presented without normalization, i.e., the totals are not normalized to 100%. Data are presented on the basis of mass of carbon present in manure prior to HTC.

	C [wt%] Solid	C [wt%] Liquid	C [wt%] Gas
CM-DIW	87.3	12.4	0.9
CM-SA	71.4	21.8	1.5
CM-AA	71.9	23.8	1.2
PM-DIW	81.5	13.7	0.9
PM-SA	84.9	25.2	1.8
PM-AA	64.4	32.7	0.9

Table S4. Mass balance of nitrogen in solid and aqueous phases. Data are presented without normalization, i.e., the totals are not normalized to 100%. Data are presented on the basis of mass of nitrogen present in manure prior to HTC.

	N [wt%] Solid	N [wt%] Liquid
CM-DIW	57.6	39.1
CM-SA	34.6	74.0
CM-AA	55.9	41.9
PM-DIW	55.1	79.6
PM-SA	42.8	90.2
PM-AA	56.3	53.9

Table S5. Mass balance of phosphorus in solid and aqueous phases. Data are presented without normalization, i.e., the totals are not normalized to 100%. Data are presented on the basis of mass of phosphorus present in manure prior to HTC.

	P [wt%] Solid	P [wt%] Liquid
CM-DIW	85.6	16.9
CM-SA	14.9	90.4
CM-AA	60.2	38.7
PM-DIW	88.1	15.4
PM-SA	14.2	86.4
PM-AA	52.7	49.6

Table S6. Mass balance of potassium in solid and aqueous phases. Data are presented without normalization, i.e., the totals are not normalized to 100%. Data are presented on the basis of mass of potassium present in manure prior to HTC.

	K [wt%] Solid	K [wt%] Liquid
CM-DIW	47.9	85.6
CM-SA	13.8	85.2
CM-AA	16.1	85.3
PM-DIW	28.3	85.8
PM-SA	14.3	86.8
PM-AA	18.2	92.9