



Effect of biochar addition on H₂S production in an anaerobic digester

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Biogas Constituents

Compound	Chemical	Range %
Methane	CH ₄	50-75
Carbon Dioxide	CO_2	25-50
Nitrogen	N_2	0-10
Hydrogen	H_2	0.01-5
Oxygen	O_2	0.1-2
Water Vapor	H_2O	0-10
Hydrogen Sulfide	H_2S	10-30,000 ppm
Ammonia	NH_3	$0.01 - 2.5 \text{ mg/m}^3$



Formation of H₂S and its effects

- ♦ Reduction of sulfur-containing compounds under anaerobic conditions by sulfate reducing bacteria (SRB) → H₂S production
- ♦ H₂S is corrosive and damages pipelines, compressors, engine generator sets (EGS) and gas storage tanks



Corroded engine generator at a dairy farm



Corrosion after-effects



H₂S generated from sulfates in waste water



Hydrogen Sulfide Limits and Control Technologies

Technologies	Hydrogen Sulfide Limits (ppm)	
Heating (Boilers) and Stirling	< 1,000	
Engines		
Internal	< 500 (depending	
Combustion	on the engine type,	
Engines	it can be < 50 ppm)	
Fuel Cells	< 1	
Natural Gas	< 4 (variations	
Upgrade	among countries)	

- 1. Biological Desulfurization
- 2. Iron Oxide Scrubbing
- 3. Activated Carbon Adsorption
- 4. Air Injection/Microaeration
- 5. Chemical Addition to the digester



Iron Oxide Scrubber



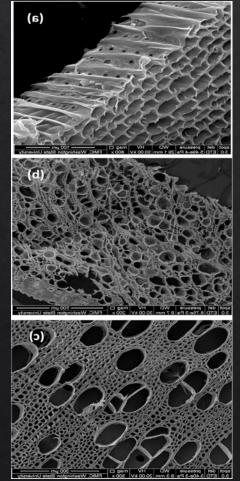
Biological Scrubber



Activated Carbon



Biochar as an additive for H₂S reduction



SEM images of Douglas fir wood, bark and poplar wood. Suliman et al. (2016)

- ♦ Managing and operating external scrubbing systems require technical expertise and manpower that may be unavailable on smaller-scale farms.
- ♦ Biochar could be a possible low-cost and less labor intensive solution for H₂S removal, if added directly into a digester
- ♦ Previous work on direct biochar addition has shown some positive effects on CH₄ production and CO₂ sequestration in waste water sludge digesters
- ♦ Biochar has also been shown to be comparable or even better than activated carbon at H₂S adsorption from a biogas stream in an external scrubber





Objectives

♦ Investigate the effect of direct addition of two types of biochar on CH₄ and H₂S production in lab-scale anaerobic digestion systems

Research Questions

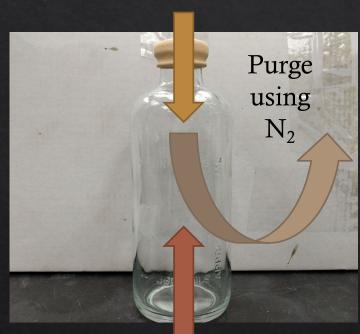
- ♦ Does increasing the concentration of biochar lower the volume of H₂S produced in an anaerobic digestion system?
- ♦ Does the biochar type, mineral composition, and pH affect the H₂S production?





Lab Scale Reactor Tests

Substrate + Biochar



Incubate



Measure



Gas Chromatography

Inoculum

Lab Scale reactor bottle

Full set of experimental units





Experimental Design (effect of biochar concentration)

CONTENTS	Biochar amount added (mg)
Inoculum Control	
Manure Control (DM)	
0.1 g Corn Stover Biochar : 1 g TS of manure (0.1	
CSB)	55
0.5 g Corn Stover Biochar : 1 g TS of manure (0.5	
CSB)	277
1 g Corn Stover Biochar: 1 g TS of manure (1 CSB)	554
1.82 g Corn Stover Biochar: 1 g TS of manure (1.82	
CSB)	1007
0.1 g Maple Biochar : 1 g TS of manure (0.1 MB)	55
0.5 g Maple Biochar : 1 g TS of manure (0.5 MB)	277
1 g Maple Biochar: 1 g TS of manure (1 MB)	554
1.82 g Maple Biochar: 1 g TS of manure (1.82 MB)	1007

- 3 replicates for each treatment
- Total volume of manure and inoculum: 200 mL
- Biochar obtained from ArtiChar prepared at 600 C and a 20 min residence time
- An inoculum: substrate (manure) ratio (ISR) of 2:1 was used on a volatile solids basis.





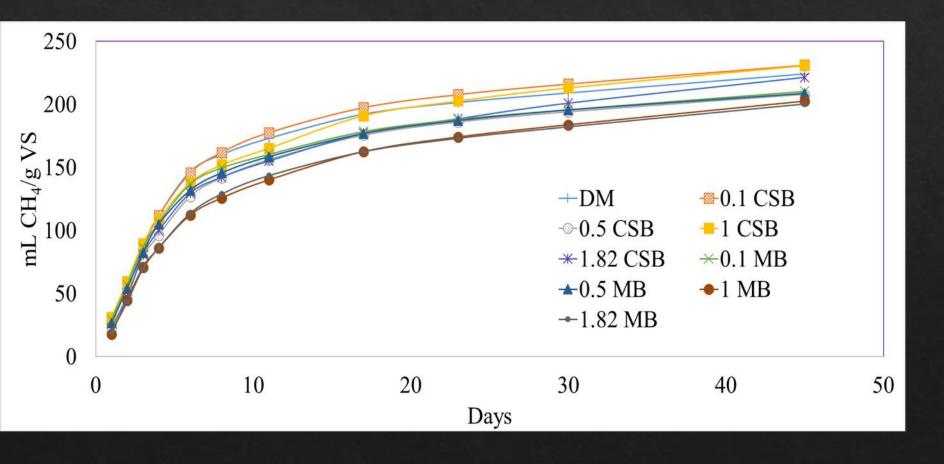
Biochar Mineral Results

	Corn Stover Biochar (CSB)	Maple Biochar (MB)
Total N (%)	1.16	0.79
Phosphorus (% P ₂ O ₅)	0.55	0.19
Potassium (%K ₂ O)	2.98	0.57
Sulfur (%S)	0.04	0.02
Calcium (% Ca)	1.33	1.22
Magnesium (% Mg)	0.33	0.14
Sodium (% Na)	0.04	0.02
Zinc (ppm)	51	67
Iron (ppm)	6194	2659
Moisture (%)	1.67	1.82
рН	10.3	9.6





Results: CH₄ Production

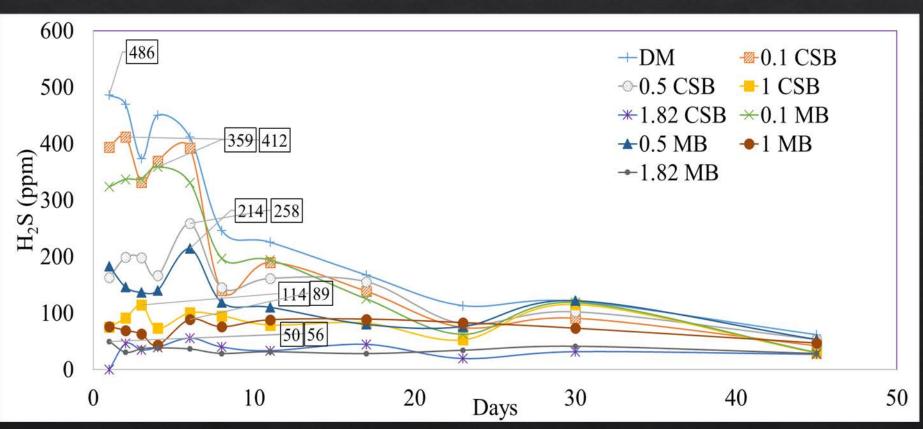


- No significant differences in CH₄ concentration
- Cumulative CH₄ production varied from 200 231 mL/g VS, with 1CSB having the highest and 1MB having the lowest CH₄ volume.





Results: Daily H₂S Production

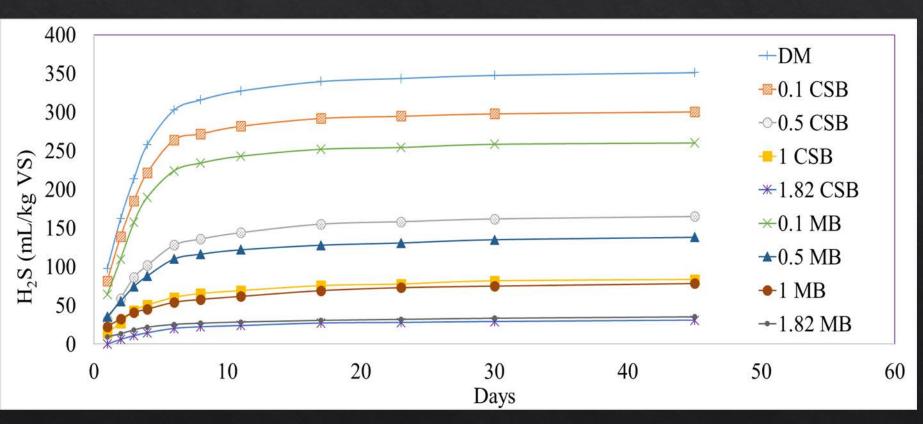


- DM had the highest H₂S concentration during the study period
- Concentration of H₂S gradually decreased as the concentration of biochar increased
- H₂S concentrations at the end of the study were below 100 ppm for all treatments
- The labels denote the maximum H₂S concentration for each treatment





Results: Cumulative H₂S Production



- DM had the highest H₂S volume after the study period (351 ± 9 mL H₂S/kg VS)
- Volume of H₂S generated decreased as the concentration of biochar increased
- At the highest dose of biochar added (1.82 g biochar/g Manure TS), the % reduction in H₂S was 91.1% and 90.0% for CSB and MB, respectively



Results: Biochar Adsorption

	H ₂ S volume reduction* (uL)	Normalized H ₂ S reduction (uL/g biochar)	Adsorption (mg H ₂ S/g biochar)
0.1 CSB	17.87		
0.5 CSB	65.43	236.41	0.33
1 CSB	94.08	169.97	0.24
1.82 CSB	112.62	111.80	0.16
0.1 MB	32.00	578.19	0.81
0.5 MB	74.91	270.66	0.38
1 MB	95.89	173.25	0.24
1.82 MB	111.02	110.21	0.16

^{*}When compared to DM control



Conclusions

- ♦ Biochar was effective in reducing H₂S in biogas and the % reduction increased with increasing amounts of added biochar
- ♦ There were no significant differences in % CH₄ between treatments
- ♦ H₂S adsorption capacity decreased as the amount of added biochar increased
- ♦ H₂S reduction efficiency increased to >90% for each biochar type (CSB and MB) at the highest dosage (1.82 g biochar/g manure TS)
- ♦ There were no significant differences in H₂S reduction between the two biochar types at higher doses





Current Projects and Research Questions

- ♦ How does particle size of the biochar affect the sorption of H₂S onto the biochar surface?
- ♦ Can a surface modified biochar increase the amount of H₂S adsorbed?
- ♦ Can biochar be used for N and P adsorption from dairy manure along with H₂S reduction in biogas?
- ♦ Is it better to add biochar directly into a digester or should it be used in an external gas filter column for H₂S removal?



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Thank You