

Ammonia Removal and Recovery During Food Waste Anaerobic Digestion Using Selective Membranes

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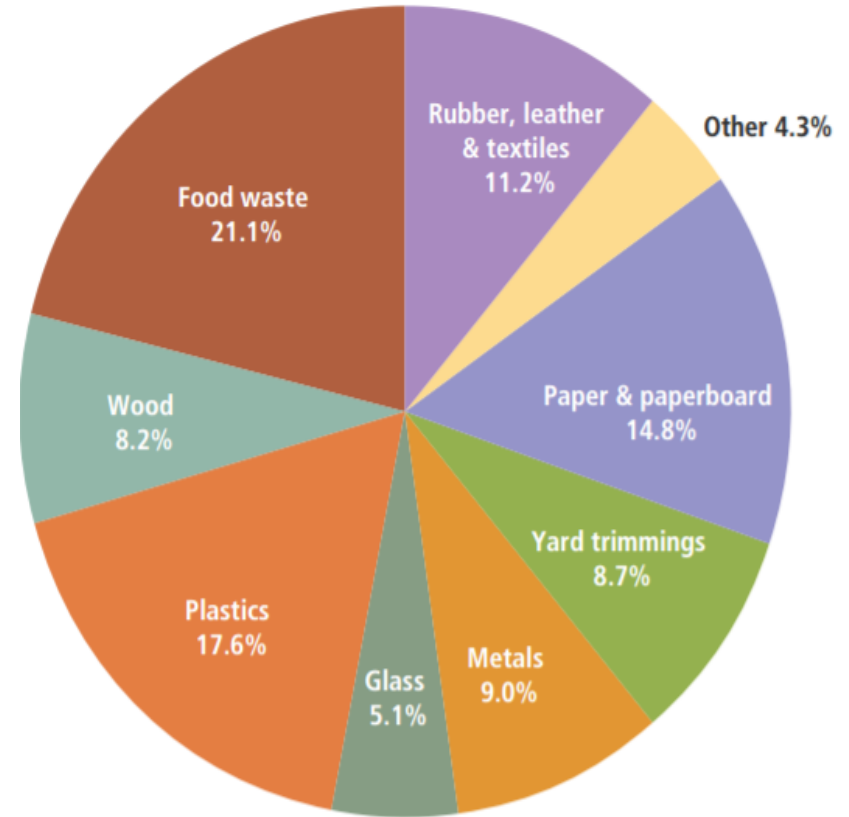
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The Problem

- US: 38 million tons of FW, 5.1% diverted from landfills³
- Worldwide: 1/3 of all food for human consumption is wasted (2011 FAO)³
- With limited oxygen, water, sunlight, and organisms food waste in landfills decomposes very slowly

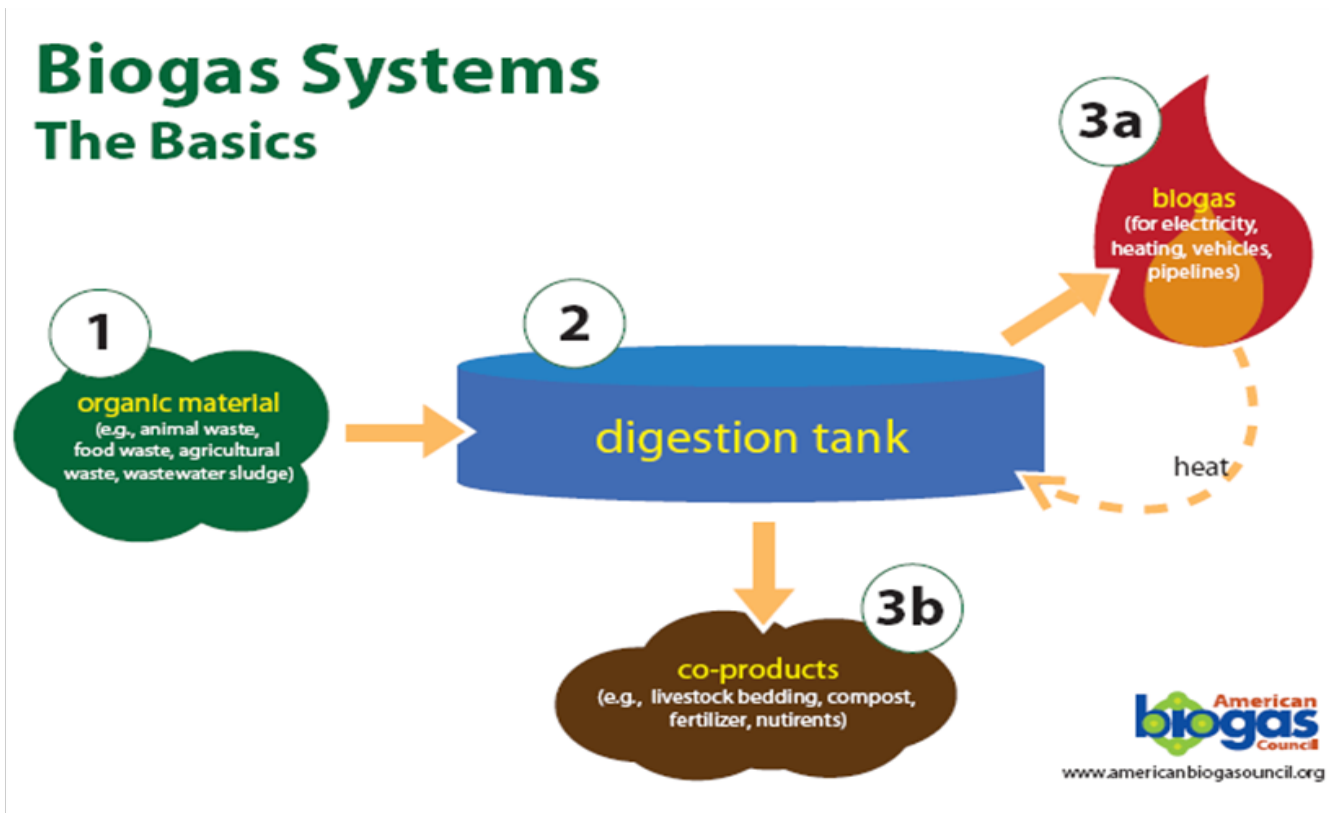


10 year old carrots²



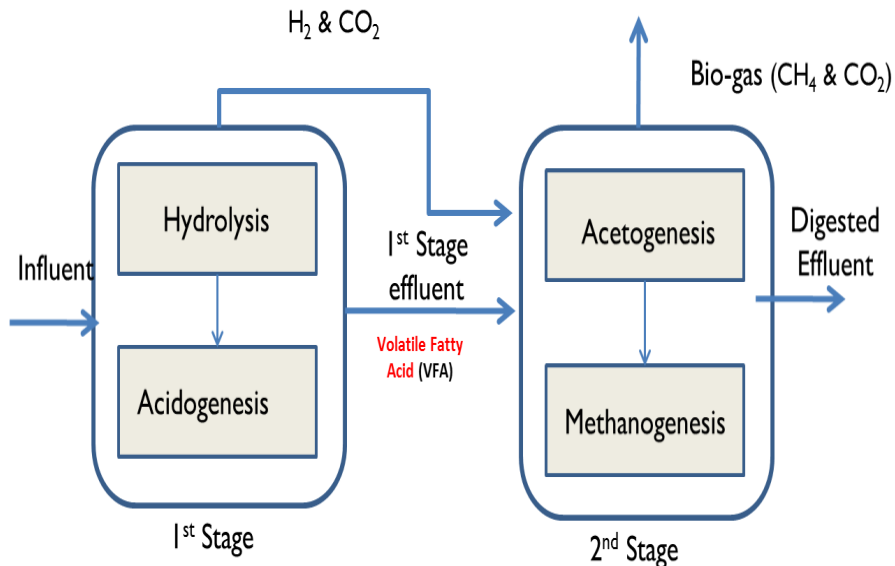
Solution: Anaerobic Digester

- Biogas: CH₄ & CO₂
- Effluent: High ammonia for fertilizer use



Clarkson's Anaerobic Digester

- Mesophilic two-phase pilot scale digester
- 30-60 day RT
- 300 lb/day loading (600 lb/day capacity)
- Biogas production is 30% higher than similar systems
- But can we do any better?

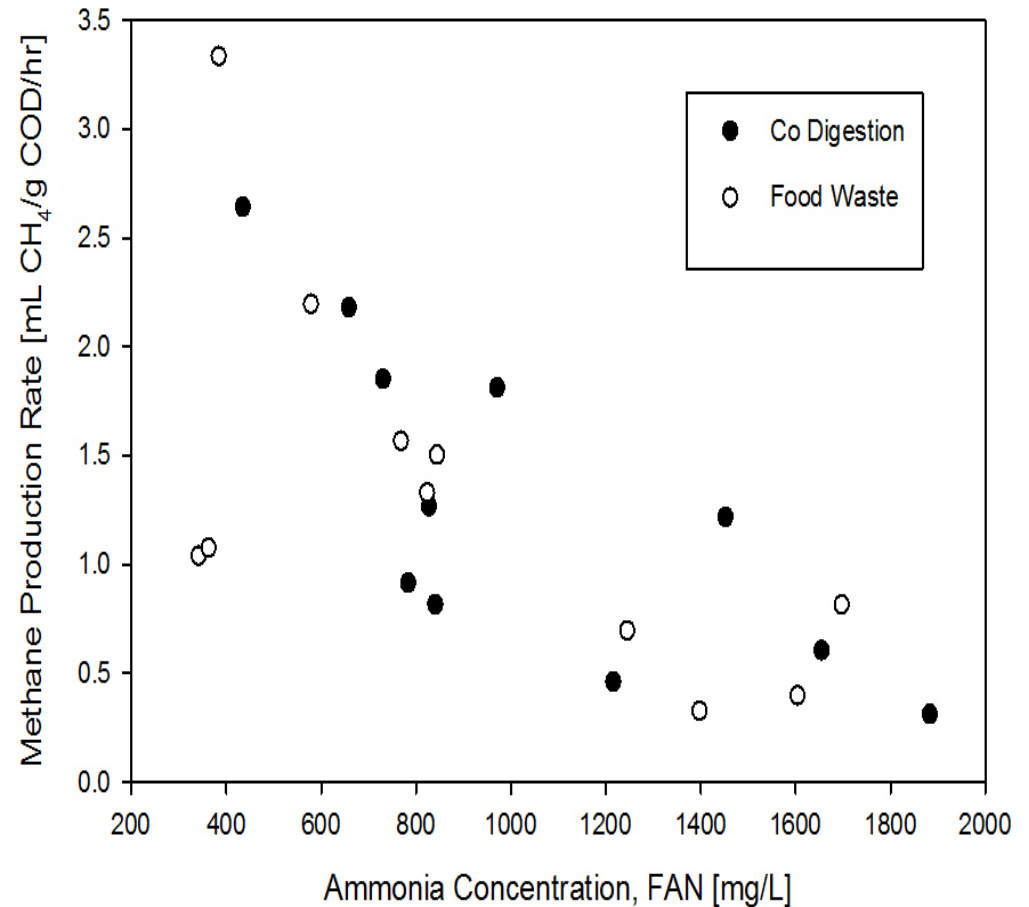


*K. Venkiteshwaran "Two-Stage Anaerobic Co-Digestion using crude glycerol or cheese whey with dairy manure to improve methane production"



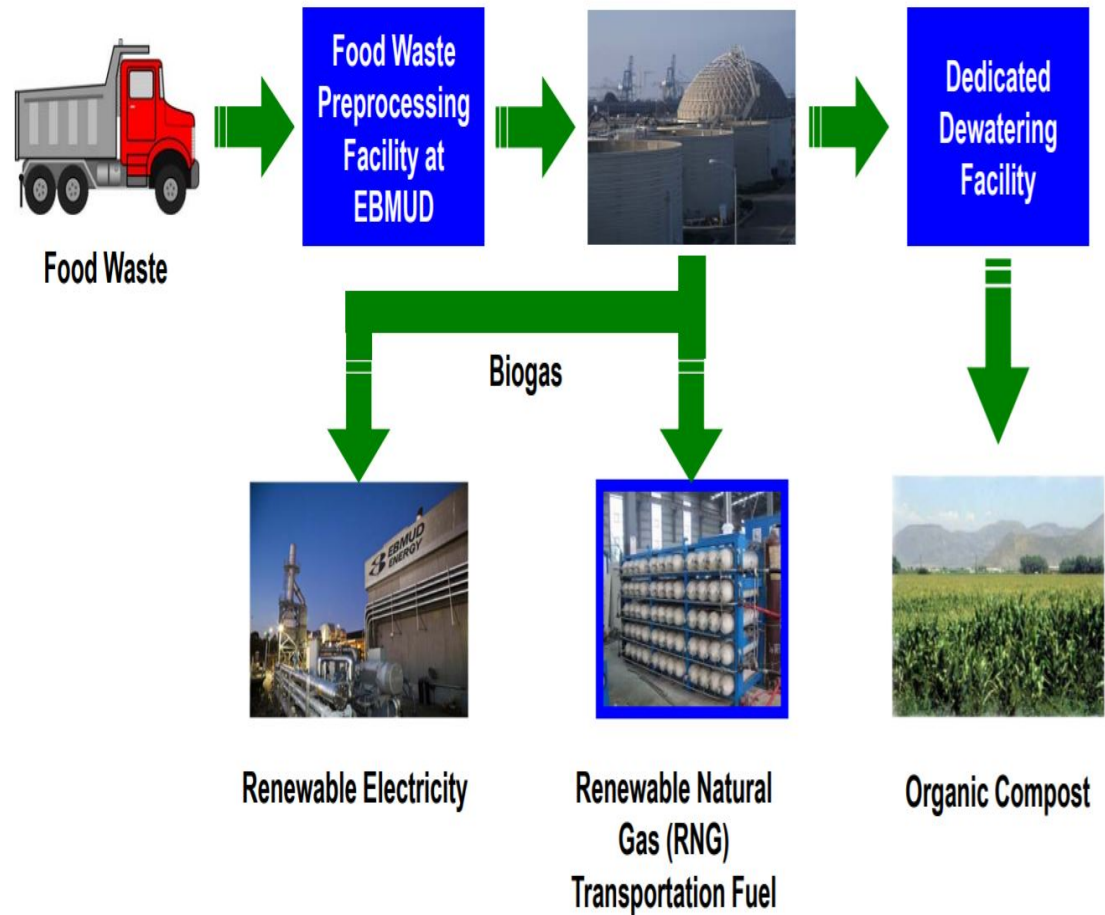
Ammonia Toxicity

- Major cause of full-scale digester upset
 - Methanogens most susceptible
- Clarkson's food digester operates around 6 to 7 g/L TAN
- IWA-ADM1 model uses
$$I = 1 / (1 + s_{NH} / K_{NH})^4$$
 - s_{NH} - ammonia concentration
 - K_{NH} - inhibition parameter of ammonia
- Suggests that any ammonia concentration would result in some inhibition
- Removal of ammonia should increase in methane production



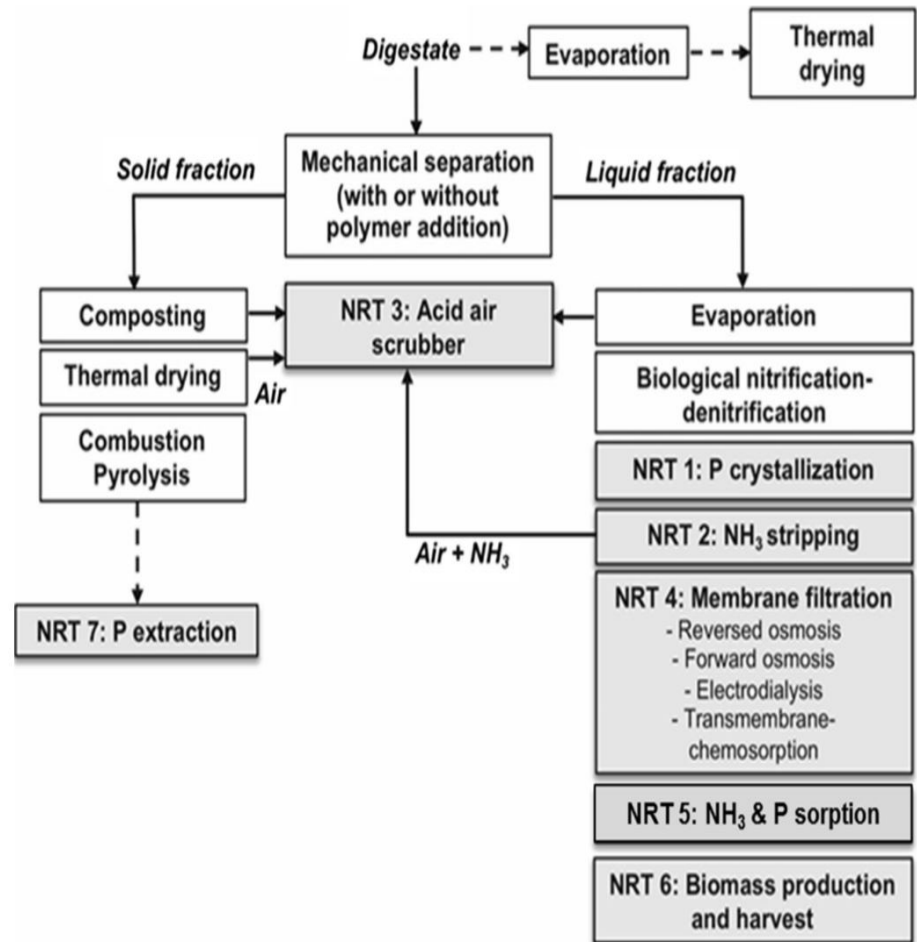
Relevance to Municipal WWTPs

- Ammonia toxicity not significant in conventional wastewater digesters
- Co-digestion gaining more prominence
- Food waste as a co-substrate:
 - Easily degradable
 - High COD → High energy yields
- Ex: East Bay Mud, CA
 - 0.6 MGD ($\leq 1\%$ of their avg flow)
- Co-digestion of FW could lead to ammonia inhibition



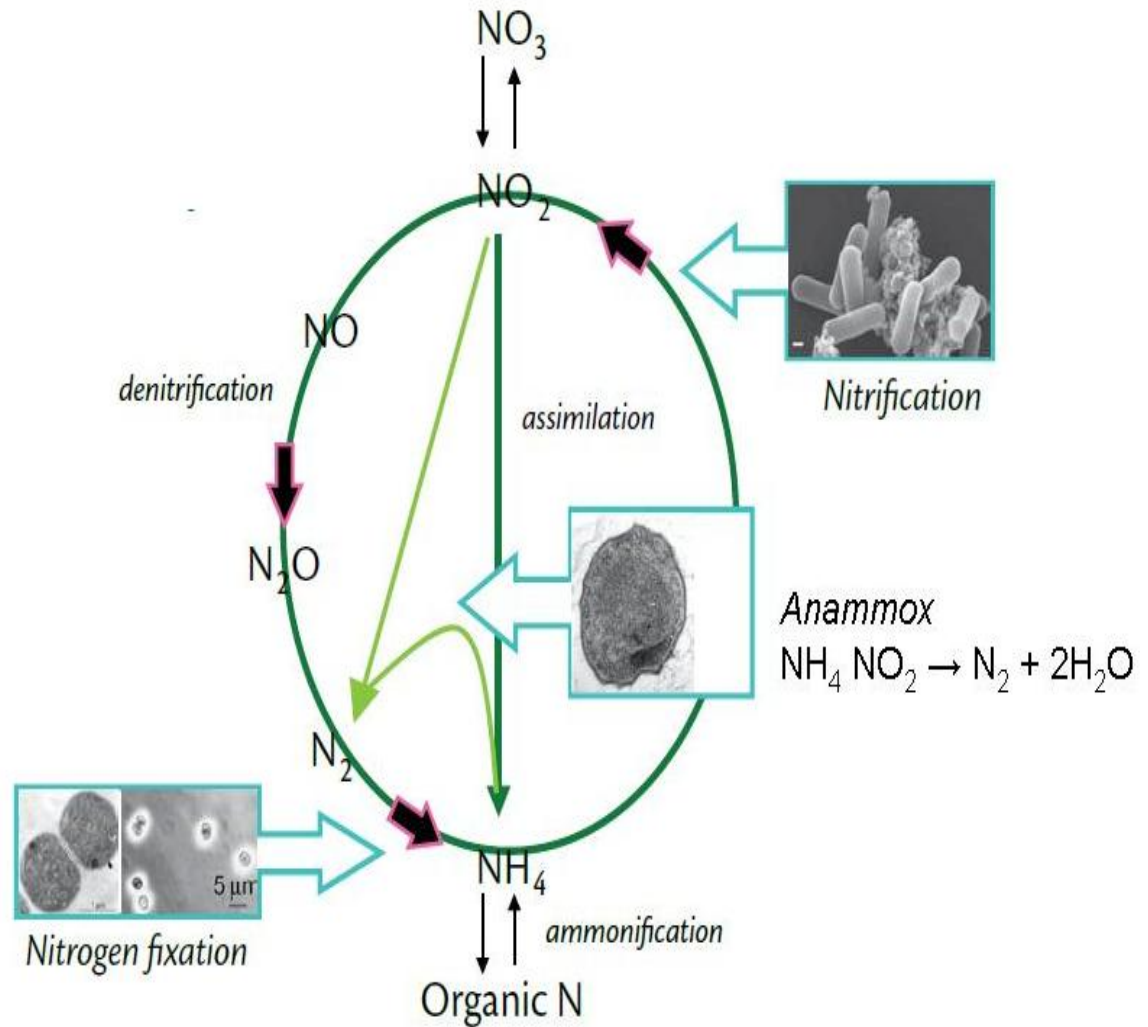
Purpose & Objectives

- Ammonia is inhibitory⁵⁻⁸
- Requires ammonia removal system to increase carbon recovery
- Ammonia loss may result in loss of effluent fertilizer potential
- Design an ammonia removal and **recovery** mechanism
 - Selective membranes



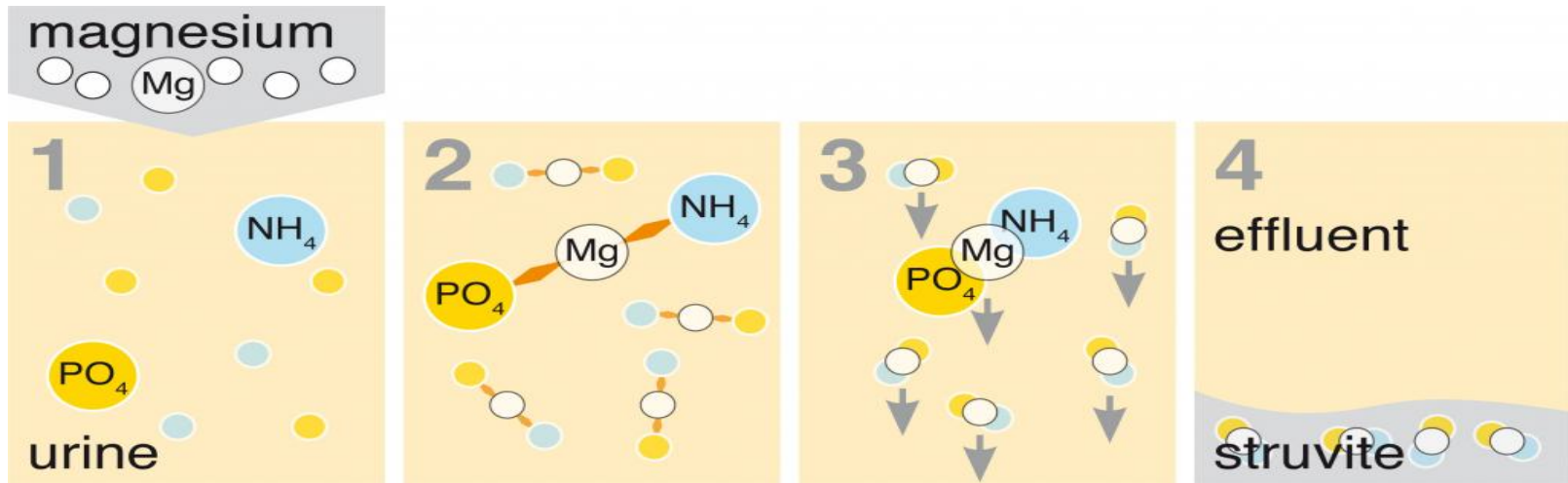
Anammox

- Autotrophic bacteria
- Oxidizes ammonium with nitrite to N₂ gas
- Implemented at several WWTPs
- Long start up times
- Lacks potential for recovery



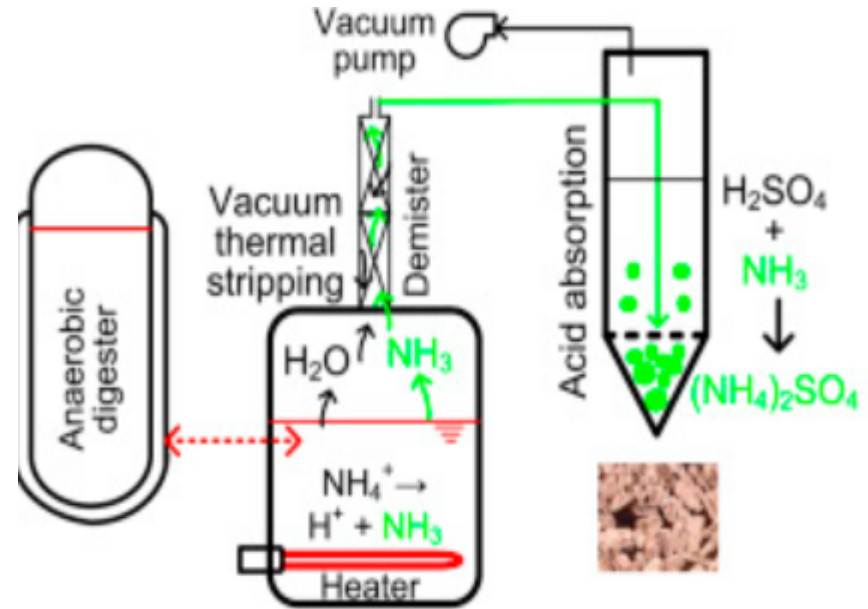
Struvite

- Magnesium ammonium phosphate (kidney stones)
- General Reaction:
$$\text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O} \rightarrow \text{MgNH}_4\text{PO}_4 \cdot 6(\text{H}_2\text{O})$$
- Solubility increases with pH; (target 8.5)
- Used as slow release ammonia fertilizer
- Clarkson Digestate: 8 to 1 N:P

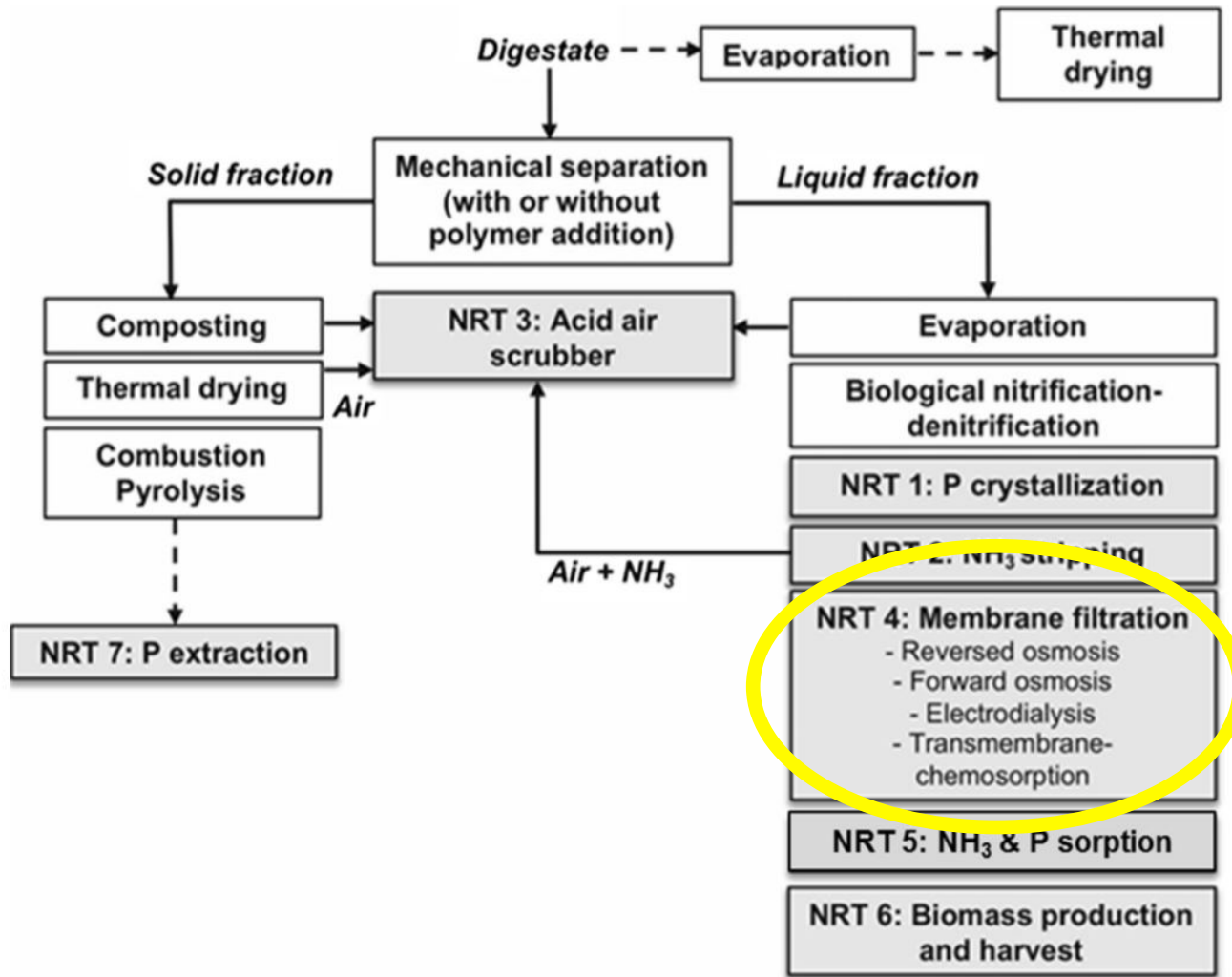


Air Stripping

- Physical transfer of NH_3 in the aqueous phase to gas phase
 - $\text{NH}_4^+ (aq) \leftrightarrow \text{NH}_3 (aq) + \text{H}^+$
 - $P_{\text{NH}_3} = H \cdot [\text{NH}_3]$
 - pH dependent; requires elevated pH
 - $pK_a = 9.25 @ T = 298 \text{ K}$
- Usually coupled with an acid scrubber
- Ammonia salts generated can be used as fertilizer
- High energy inputs
- Clarkson's digestate: strongly buffered \rightarrow high chemical inputs



Ukwuani et al. (2016)



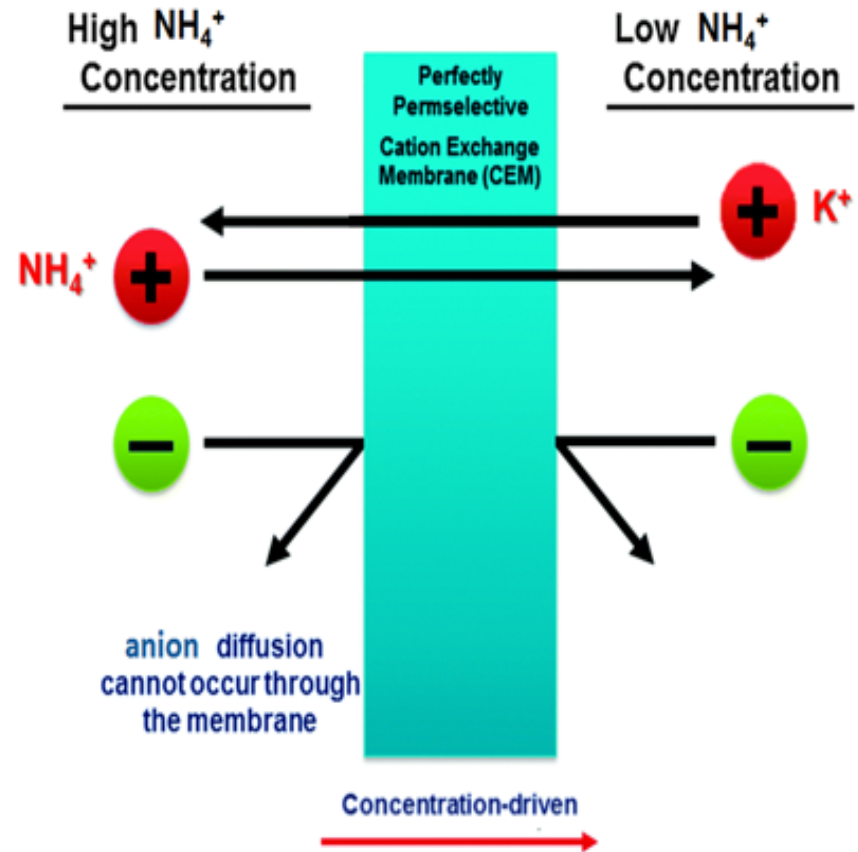
Process Mechanims

Cation Exchange Membranes

- Selectively-permeable
- Molecular passage based on ionic charge
- Concentration gradient driven
- NH_4^+ permeates through membrane
- Exchanging with cation (H^+ or K^+)

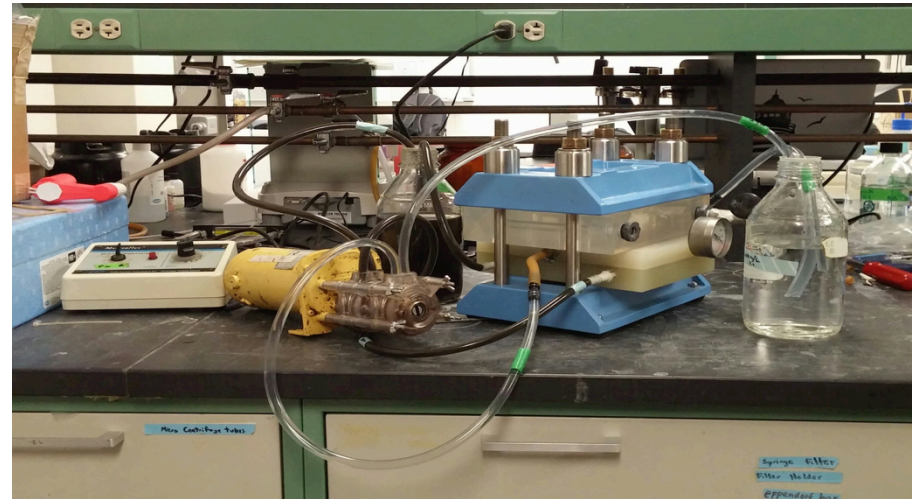
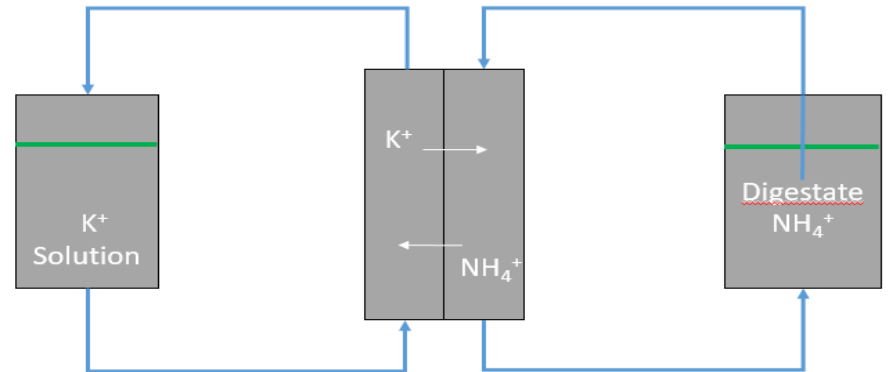
Why?

- Removal and Recovery



Experimental Methods: Membrane Test

- Nafion 117
- Pump and tubing set up
 - Flow rates: ~ 2 gpm each
- Leak/mixing test ~ 30 minutes
- Duration: 1-2 days
- Analysis: TN Analyzer, pH, 5 mL samples

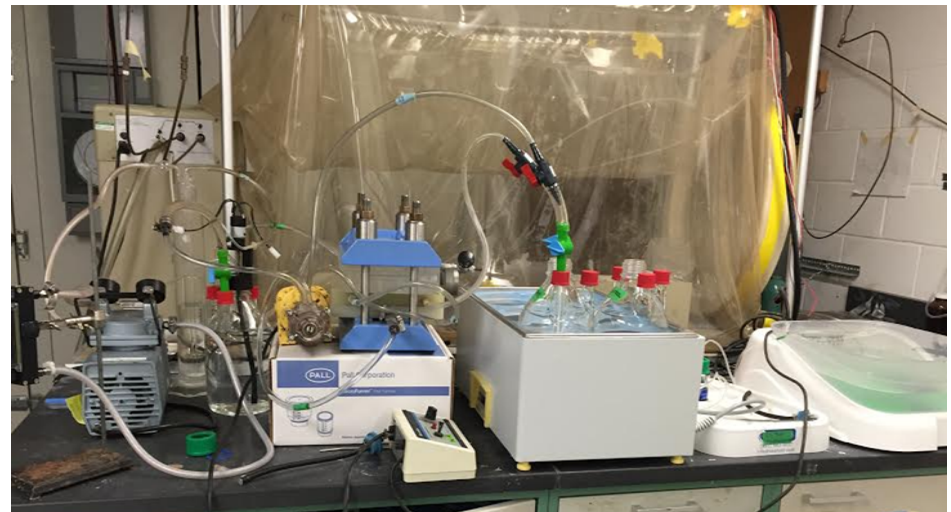
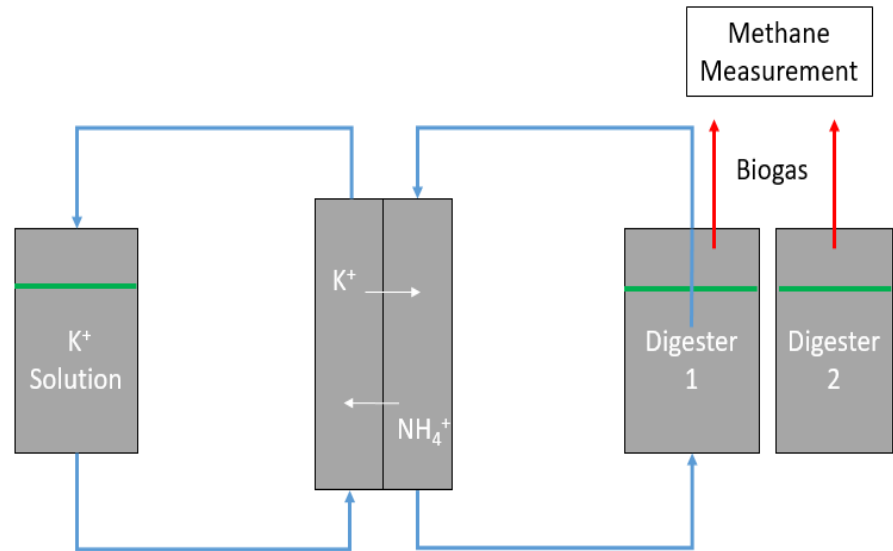


Results: Membrane Test

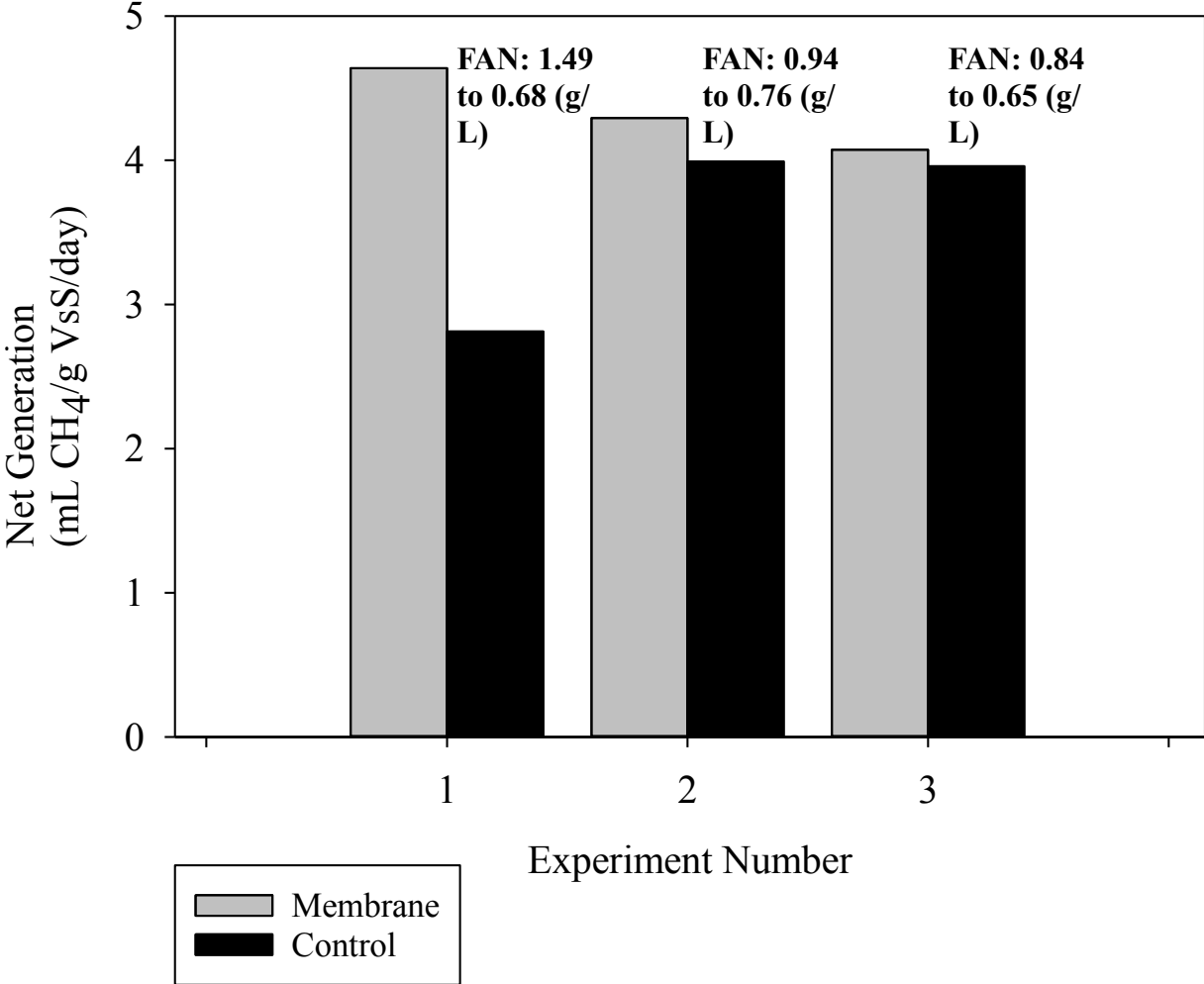
Trial	Membrane	Ammonia-Rich Solution	Draw Solution Composition	Flux mol/d/m ²
1 & 2	Nafion® 117	Ammonium Chloride NH ₄ Cl	Sulfuric Acid pH<2	92.0±8.5
3	Nafion® 117	Stage 2 Digestate Filtered	Sulfuric Acid pH<2	22.8±10.2
4 & 5	Nafion® 117	Stage 2 Digestate Unfiltered	Sulfuric Acid pH<2	14.3±1.04
6	Nafion® 117	Stage 2 Digestate Unfiltered	Potassium Sulfate K ₂ SO ₄	10.7±1.9
7	Neosepta® CMX	Stage 2 Digestate Unfiltered	Potassium Sulfate K ₂ SO ₄	3.71
8	Ultrex™ CMI-7000S	Stage 2 Digestate Unfiltered	Potassium Sulfate K ₂ SO ₄	11.2±8.8

Experimental Methods: BMP Test

- Nafion 117
- Leak/mixing test ~ overnight
- 2.1 L volumes
- Draw Solution:
 - 17,000 mg/L K⁺
 - 0.1M Phosphate buffer: pH 8
- Control and Membrane Cell digesters:
 - Pre-consumer FW from CU kitchens
 - Stage 2 Digestate
 - 1:1 ratio based on VS
- Methane measured using AMPTS II
- 6 mL samples collected once a day
 - TN, COD, pH
- Duration: 10-15 days

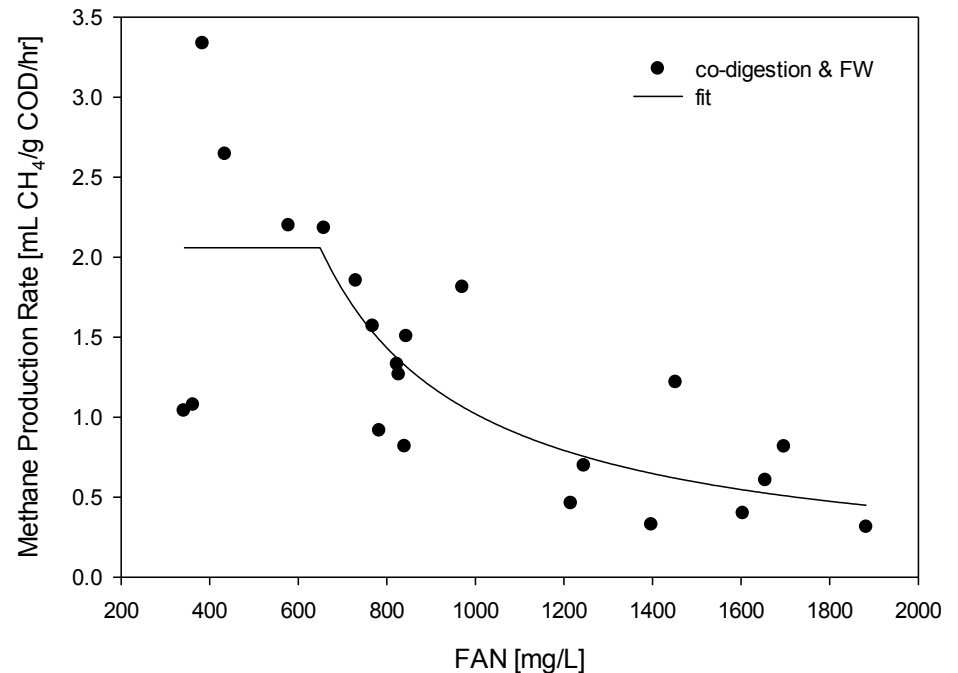
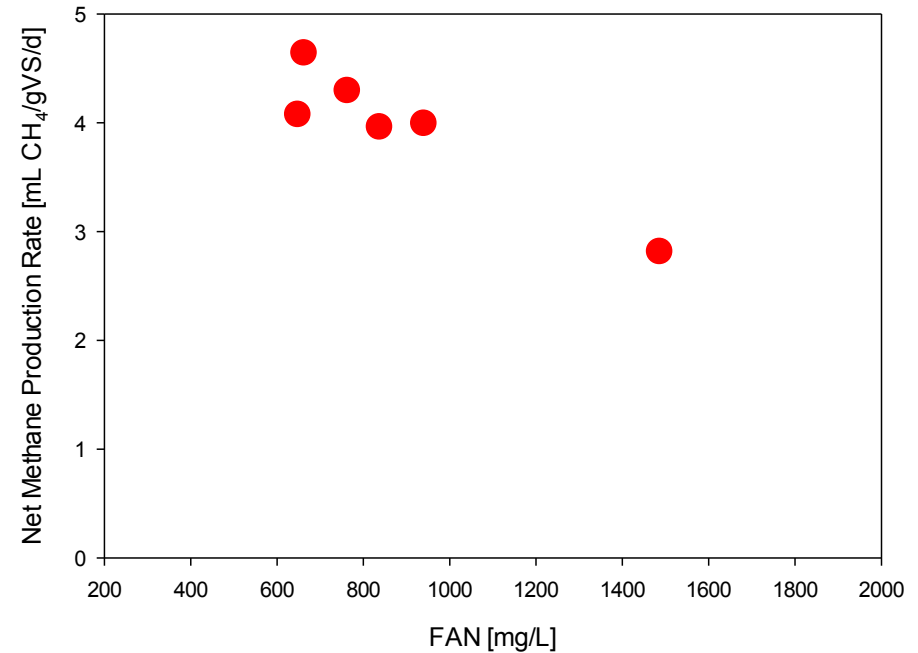


Results: BMP Test



Results

- ADM1 model uses $I = 1 / (1 + S \downarrow I / K \downarrow I)^4$
 - $S \downarrow I$ - ammonia concentration
 - $K \downarrow I$ - inhibition parameter of ammonia
- Threshold model predicts methane rate constant below specific concentration^{6,7,10-15}
 - Threshold concentration: 650 ± 196 (95% C.I.) mg/L FAN
 - Threshold should be microbial culture dependent.



Results

- Threshold model

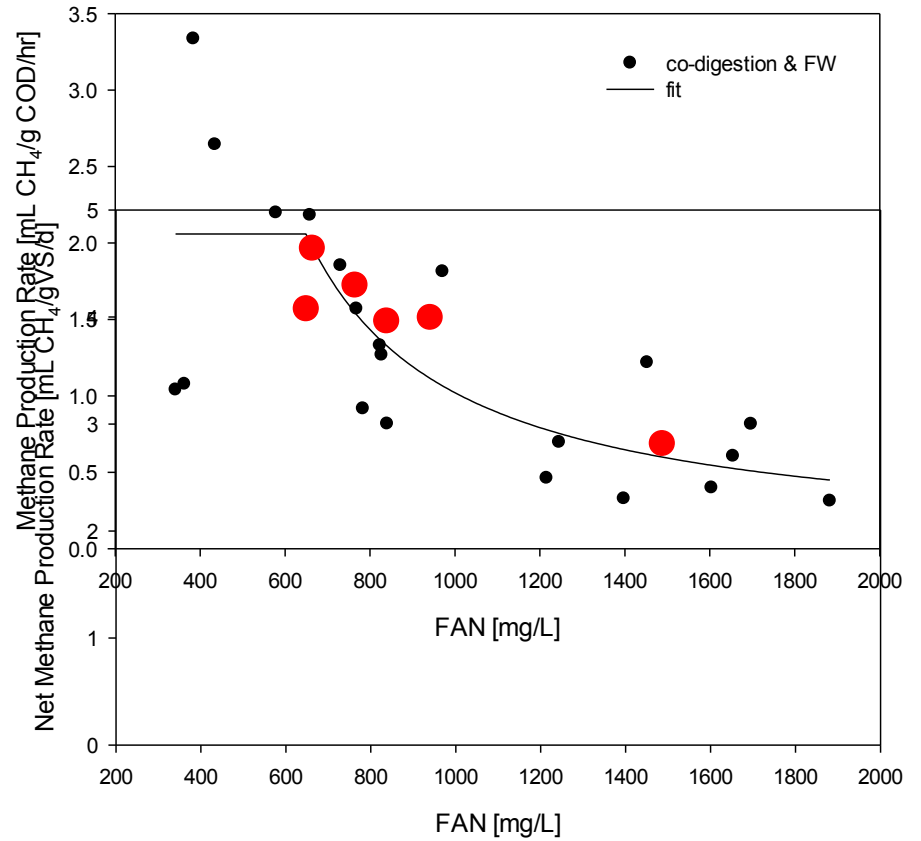
$$I = 1; \quad S_I < T_s$$

$$I = 1 / (1 + S_I - T_s / K_I) ; \quad S_I > T_s$$

S_I - ammonia concentration

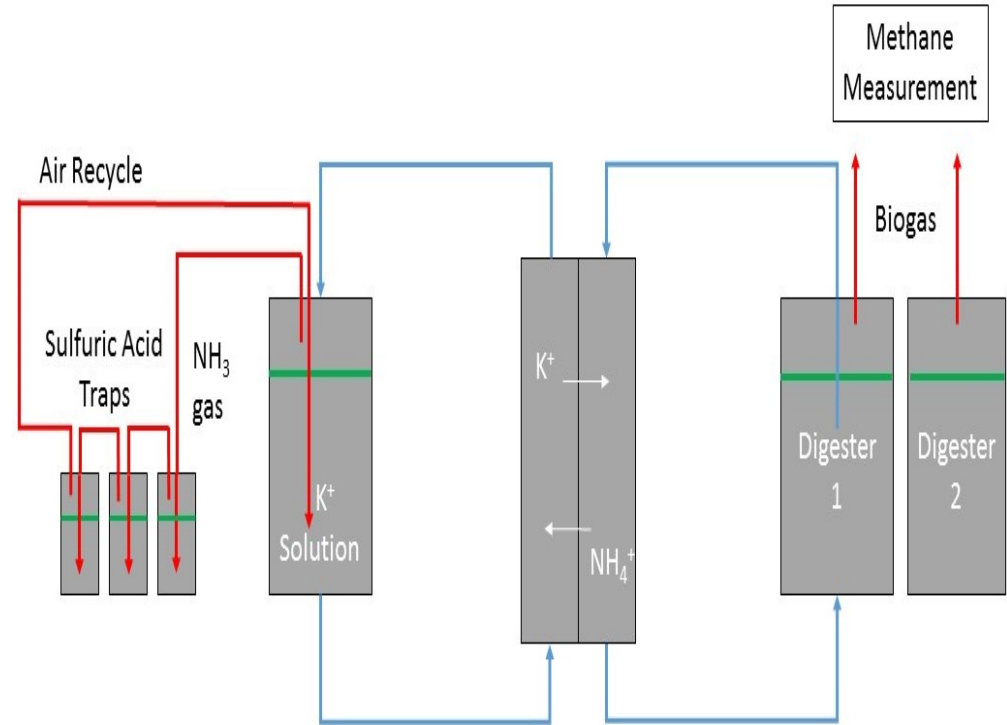
K_I - inhibition parameter of ammonia

T_s - threshold concentration



Summary

- Membrane System has been operated for 2.5 months without significant flux decline
- Membrane system allowed for increased methane production at concentrations well above threshold concentration (650 ± 196 (95% C.I.) mg/L FAN for our seed culture from campus food digester).
- As expected at FAN concentrations close to threshold concentration no increased methane production was observed. Thus a membrane system would have limited value.
- Ammonia recovery in form of ammonium sulfate



Conclusions and Future Work

- Membrane easily achieves removal and recovery of ammonia
- The membrane system allows for blending ammonia with digester effluent to balance nutrient composition of effluent
- Threshold model may better describe ammonia inhibition for food waste digestate
- Further experimentation at higher FAN concentrations to confirm inhibition model
- Characterize digester microbial community
- Scale up for Clarkson's food digester system

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