

BIOGAS CLEAN-UP TECHNOLOGIES

Presented to:

INNOVATIONS IN AGRICULTURE

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PRESENTATION OUTLINE

- ◆ Background & Problem Description
- ◆ Detrimental Biogas Impurities
- ◆ H₂S Detrimental Effects
- ◆ Typical Farm Digester Biogas Composition
- ◆ Biogas Clean-Up Technologies
- ◆ H₂S Removal Using Liquid Adsorption Processes
- ◆ H₂S Removal Using Dry Adsorption Processes
- ◆ H₂S Removal Using Biological Processes
- ◆ Water Vapor and Particulate Removal Technologies



BACKGROUND & PROBLEM DESCRIPTION

- ◆ Anaerobic digestion generates biogas and provides a viable option for nutrient management and odor reduction at farms
- ◆ Collected biogas can be used to generate energy for farm use and sale to the power grid
- ◆ An estimated 280 Giga Watt-Hours can be generated from manure digestion at dairy farms in NYS alone



BACKGROUND & PROBLEM DESCRIPTION (continued)

- ◆ Primary operational difficulty in biogas utilization is presence of H_2S
- ◆ H_2S corrodes engine parts in the combustion chamber, exhaust system, and in various bearings
- ◆ Water vapor along with H_2S can produce ionic hydrogen (cracks and blisters steel)
- ◆ Combustion of H_2S generates SO_2 , which reacts with water to form H_2SO_4 (highly corrosive acid)



DETRIMENTAL BIOGAS IMPURITIES

- ◆ Hydrogen Sulfide and Mercaptans
- ◆ Carbon Dioxide
- ◆ Hydrocarbons
- ◆ Siloxanes
- ◆ Water Vapor and Particulates
- ◆ Nitrogen and Oxygen



H₂S CHEMICAL REACTIONS IN BIOGAS UTILIZATION EQUIPMENT

- ◆ $\text{H}_2\text{S}_{(\text{aq.})} \leftrightarrow \text{HS}^-_{(\text{aq.})} + \text{H}^+_{(\text{aq.})}$ (weak acid)
- ◆ $\text{HS}^-_{(\text{aq.})} \leftrightarrow \text{S}^{2-}_{(\text{aq.})} + \text{H}^+_{(\text{aq.})}$ (weak acid)
- ◆ $2\text{H}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{SO}_2 + 2\text{H}_2\text{O}$ (combustion)
- ◆ $\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3$ (combustion)
(2% to 5% of incoming H₂S is oxidized to form SO₃)
- ◆ $\text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \leftrightarrow \text{H}_2\text{SO}_4$ (strong acid)
- ◆ $\text{SO}_3 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{SO}_4$ (strong acid)



H₂S DETRIMENTAL EFFECTS

- ◆ Adverse effects on steel products (corrosion, cracking and blistering)
- ◆ Problem is enhanced by frequent starts, short running times, low operational temperatures (start-up and shut-down), and use of water as a coolant
- ◆ Increased SO₂ emissions from combustion processes can cause adverse human health effects
- ◆ Removal of hydrogen sulfide from the biogas is critical for operation and longevity of biogas utilization equipment



PREFERRED OPERATIONAL LIMITS FOR H₂S CONTENT IN BIOGAS EQUIPMENT

- ◆ Boilers: ≤ 500 ppm
- ◆ Turbine generators: $> 10,000$ ppm
(However upstream biogas compressors typically tolerate only 75-100 ppm)
- ◆ Internal combustion engines: $< 200 - 400$ ppm
(Manufacturers typically require total S $< 1,000-1,500$ ppm)
- ◆ Fuel cells: Trace amounts
(Manufacturers require high-grade biogas)



TYPICAL FARM DIGESTER BIOGAS COMPOSITION

<u>Parameter</u>	<u>Concentration</u>
Methane	55% - 60%
Carbon dioxide	40% - 45%
Hydrogen sulfide	2,000-3,000 ppm*
Ammonia	3-4 ppm*
Other	Trace Amounts

* ppm is part per million on a volumetric basis



BIOGAS CLEAN-UP TECHNOLOGIES

- ◆ Hydrogen sulfide selective removal
- ◆ Carbon dioxide and hydrogen sulfide combined removal
- ◆ Hydrocarbon compounds removal
- ◆ Mercaptan compounds removal
- ◆ Water vapor and particulate removal
- ◆ Nitrogen and oxygen content reduction



HYDROGEN SULFIDE CLEAN-UP TECHNOLOGIES

- ◆ Liquid adsorption processes
- ◆ Dry adsorption processes
- ◆ Biological processes



H₂S CLEAN-UP USING LIQUID ADSORPTION PROCESSES

- ◆ Low temperature, high-pressure conditions to maximize H₂S solubility
- ◆ Absorbent regeneration by heating
- ◆ Collect S via Claus Process:





LIQUID ADSORPTION MEDIA FOR SELECTIVE H₂S REMOVAL

- ◆ Sodium or potassium carbonate with ferric hydroxide or arsenic
- ◆ Sodium carbonate
- ◆ Sodium bicarbonate
- ◆ Anthraquinone disulfonic acid and sodium vanadate
- ◆ Sodium carbonate with naphthaquinone



LIQUID ADSORPTION MEDIA FOR COMBINED H₂S & CO₂ REMOVAL

- ◆ Water
- ◆ Methanol
- ◆ Dimethyl Ether of Polyethylene Glycol
- ◆ Tetrahydrothiophene dioxide and di-isopropanol amine
- ◆ Anhydrous propylene carbonate
- ◆ N-methyl pyrrolidone
- ◆ Alkanolamines
- ◆ Alkaline salt absorbents



SELECTIVE H₂S REMOVAL USING DRY ADSORPTION PROCESSES

- ◆ Iron sponge
- ◆ Molecular sieves or zeolites
- ◆ Activated carbon
- ◆ Regenerable and non-regenerable amines/triazines solutions
- ◆ Caustic sodium nitrate systems



DRY ADSORPTION PROCESSES FOR COMBINED H₂S & CO₂ REMOVAL

- ◆ Activated carbon
- ◆ Molecular sieves
- ◆ Hollow fiber membrane separation



SELECTIVE H₂S REMOVAL USING BIOLOGICAL PROCESSES

- ◆ Oxidation reaction relying on sulfur-oxidizing bacteria (e.g. *Thiobacillus denitrificans*)
- ◆ $2n(\text{H}_2\text{S}) + n(\text{CO}_2) + \text{light} \rightarrow$
 $2n\text{S} + n(\text{CH}_2\text{O}) + n(\text{H}_2\text{O})$
- ◆ Does not require regeneration and H₂S is destroyed not just separated, but process is highly dependent on inhibitory effects of other biogas components



WATER VAPOR AND PARTICULATE REMOVAL TECHNOLOGIES

- ◆ Molecular sieves
- ◆ Refrigeration
- ◆ Drip traps
- ◆ Water outlet devices
- ◆ Scrubbers



WATER VAPOR AND PARTICULATE REMOVAL USING DRIP TRAPS

- ◆ Tee Traps
- ◆ U-Pipe Traps
- ◆ Siphon Traps
- ◆ Sediment Traps



ALTERNATIVE TECHNOLOGIES

- ◆ NYS ERDA Sponsored project with EMG International, Inc.
- ◆ Anaerobic digestion process control rather than Biogas clean-up or emission controls
- ◆ Project Title: “Assessment of Biochemical Process Controls for Reduction of H₂S levels in biogas from Farm Digesters”



PROJECT SUMMARY

- ◆ Anaerobic Digestion:
 - (i) hydrolysis, liquefaction and fermentation
 - (ii) hydrogen and acetic acid formation
 - (iii) methane formation.
- ◆ Complex biochemical process involving:
 - (i) *fermentation bacteria*
 - (ii) *H⁺ producing bacteria*
 - (iii) *H⁺ consuming bacteria*
 - (iv) *CO₂ reducing methanogens*
 - (v) *acetoclastic methanogens*



TECHNOLOGY CONCEPT

- ◆ Use controlled addition of macro-nutrients, micro-nutrients to optimize anaerobic digestion process
- ◆ Use controlled addition of H_2S reducing chemicals (lower H_2S bio-availability to sulfur-reducing bacteria)
- ◆ Potential H_2S reducing compounds include: Iron phosphate, ferric chloride, ferrous chloride
- ◆ Design an automated chemical feed system for H_2S reduction