BIOGAS CLEAN-UP TECHNOLOGIES

Presented to:

INNOVATIONS IN AGRICULTURE

SPONSRED BY NYS ERDA

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PRESENTATION OUTLINE

- Background & Problem Description
- Detrimental Biogas Impurities
- H_2S Detrimental Effects
- Typical Farm Digester Biogas Composition
- Biogas Clean-Up Technologies
- H_2S Removal Using Liquid Adsorption Processes
- H_2S Removal Using Dry Adsorption Processes
- H_2S 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

H_2S CHEMICAL REACTIONS IN BIOGAS UTILIZATION EQUIPMENT

- $H_2S_{(aq.)} \leftrightarrow HS^-_{(aq.)} + H^+_{(aq.)}$ (weak acid)
- $HS^-_{(aq.)} \leftrightarrow S^{-2}_{(aq.)} + H^+_{(aq.)}$ (weak acid)
- $2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$ (combustion)
- $SO_2 + ½\ O_2 \rightarrow SO_3$ (combustion)

  (2% to 5% of incoming H_2S is oxidized to form SO_3)
- $SO_2 + H_2O + ½\ O_2 \leftrightarrow H_2SO_4$ (strong acid)
- $SO_3 + H_2O \leftrightarrow H_2SO_4$ (strong acid)

H_2S 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 SO_2 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 H_2S 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

Parameter	Concentration
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

H_2S CLEAN-UP USING LIQUID ADSORPTION PROCESSES

- Low temperature, high-pressure conditions to maximize H_2S solubility
- Absorbent regeneration by heating
- Collect S via Claus Process:

$$H_2S + 3O_2 \rightarrow H_2O + SO_2$$

$$2H_2S + SO_2 \leftrightarrow 2H_2O + 3S$$

$$3H_2S + 3O_2 \leftrightarrow 3H_2O + 3S$$

LIQUID ADSORPTION MEDIA FOR SELECTIVE H_2S 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 H_2S & CO_2 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 H_2S 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 H_2S & CO_2 REMOVAL

- Activated carbon
- Molecular sieves
- Hollow fiber membrane separation

SELECTIVE H_2S REMOVAL USING BIOLOGICAL PROCESSES

- Oxidation reaction relying on sulfur-oxidizing bacteria (e.g. *Thiobacillus denitrificans*)
- $2n(H_2S) + n(CO_2) + \text{light} \rightarrow 2nS + n(CH_2O) + n(H_2O)$
- Does not require regeneration and H_2S 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 H_2S 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) CO_2 reducing methanogens*
  - *(v) aceticlastic 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