Bio-Fueled Solid Oxide Fuel Cells

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Overview

Timeline

- Start date: 10/1/2010
- End date: 9/30/2013
- Percent complete: ***75%***

Budget

- Total project funding
  - DOE share: $1,155,400 (reduced from $1,944,516)
  - Contractor share: $ 0
- Funding received in FY11
  - $354,542
- Funding received in FY12
  - $539,557
- Funding for FY13
  - $261,301

Barriers

- Barriers addressed
  - Anaerobic digester biogas generated from wastes has harmful trace poisons (such as organic sulfur species and siloxanes) that must be removed to less than 10 ppbv
  - Impurities present in biogas poison the catalysts and stacks of SOFCs and other fuel cells reducing their efficiency and lifetime
- Targets
  - Provide ultraclean biogas to fuel cells
  - Increase reliability and efficiency of electricity generation using biogas generated from wastes

Partners

- Project lead
  - TDA - Biogas Cleanup Sorbent & System; Field tests
- Interactions/ collaborations
  - FuelCell Energy - SOFC Module, Field Tests
  - SMUD* - Demonstration Site
  - Infilco Degremont - Demonstration Site
  - MeadWestvaco - Sorbent Cost Analysis

* SMUD – Sacremento Municipal Utility District

Project Objectives – Relevance

- **Overall Objective**
  - Provide ultraclean biogas to demonstrate the operation of a high efficiency SOFC stack in a waste-to-energy application
- **Specific Objectives**
  - Develop and demonstrate a high capacity sorbent to remove sulfur species from biogas, thereby providing an essentially sulfur-free biogas that meets the cleanliness requirements of SOFC fuel cells
  - Demonstrate operation of a 2 kW_e biogas fueled SOFC stack integrated with a biogas cleanup system, in a waste-to-energy application
  - Demonstrate the economic viability of our sorbents to cleanup biogas
  - Project was on hold between Feb 15, 2012 – July 5, 2012 due to funding restriction from DOE and the overall project funding was reduced by $789,116
    - This resulted in a delay in the Year 3 work and the size of demonstration is reduced from 10 to 2 kW_e and the number of demonstrations is reduced from two to one and the duration is reduced to 3 months

Work Plan – Relevance

Task	Objectives
1. Sorbent Production and Scale-up	Optimize the sorbent formulations to remove all of the harmful contaminants in biogas and scale-up the production of the sorbent
2. Gas Cleanup Demonstration System	Design and build a gas cleanup demonstration system for a 2 kW_e SOFC demonstration system that operates on biogas from wastes
3. SOFC Test Module	Build a 2 kW_e SOFC test system for the slip stream demonstrations with biogas
4. Shakedown Tests	Test the integrated 2 kW_e SOFC system (both the cleanup system and the SOFC) in-house prior to biogas site deployment
5. Slipstream Demonstrations	TDA and FCE to jointly perform one field demonstration (revised from two due to funding reduction) of the integrated system, each 6 months using a different slipstream of biogas generated from wastes
6. Engineering Analysis	Carry out a detailed engineering and cost analysis to assess the economic viability of the new sorbent technology for biogas fed fuel cell power plants
7. Business Development	Develop a marketing and commercialization strategy to advance the technology and to turn the concept into a practical product
8. Reporting	Submit quarterly and annual progress reports and a comprehensive final report at the end of the project

Biogas Composition – Approach

- **Typical ADG gas composition after bulk sulfur removal**

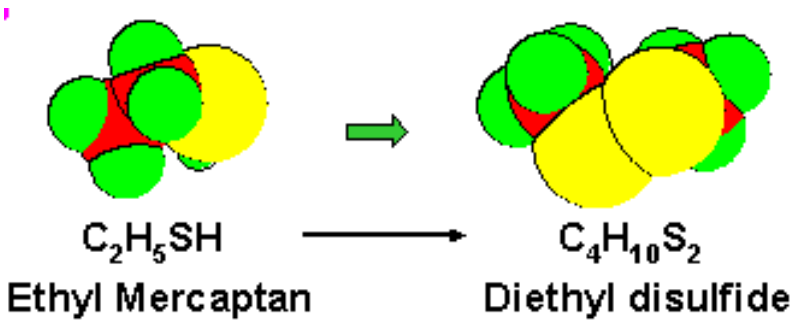
Gas Pressure	5-20 iwc, positive
Gas Temperature	110°F (max)
Gas Composition, by volume	60% CH_4, 30% CO_2 8% N_2 and 2% O_2
Moisture Content	Saturated
Siloxanes	
Total	4.5 ppmv
D4	0.4 ppmv
D5	4.1 ppmv
Halogens	1 ppmv
Sulfur	
Hydrogen sulfide	200 ppmv
Carbonyl sulfide	5 ppmv
Carbon disulfide	1 ppmv
Dimethyl sulfide	5 ppmv
Dimethyl disulfide	5 ppmv
Other disulfides	2 ppmv
Methyl mercaptan	5 ppmv
Ethyl mercaptan	1 ppmv
BTX	less than 1 ppmv

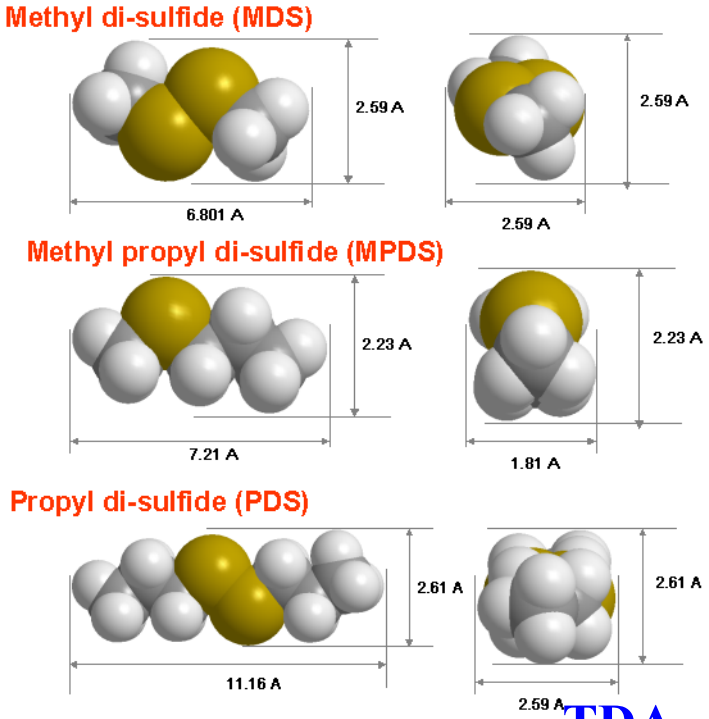
- **ADG contains high concentrations of sulfur and other contaminants (e.g., siloxanes and halides) that are detrimental for the fuel cell**
  - The main source of the volatile sulfur compounds in bio-solids is the degradation of proteins such as the amino acid methionine and cysteine, forming H_2S and MeSH
- **Sulfur is a well-known poison for fuel cell electrocatalysts**
- **Hence, sulfur and siloxanes need to be removed to ppb levels so that biogas can be used in fuel cells**

- **Current technologies lack the capability to remove complex biogas sulfur species such as organic di- and tri-sulfides down to less than 10 ppb level needed for fuel cells**

Contaminants in Biogas – Approach

- **Several desulfurization technologies are available to remove H_2S, but these are not very effective for organic sulfur compounds**
  - Mercaptans constitutes up to 500 ppmv sulfur in wastewater plants
- **Iron sponge and iron-oxide based adsorbents are used to remove H_2S**
- **Not only these are ineffective for mercaptan removal, but iron oxides in the presence of high concentrations of water catalyzes the formation of complex sulfur compounds**





- **These sulfur species may then be methylated to form higher sulfides (e.g., Me_2S) or can be oxidized to form higher sulfides (Me_2Se_2), all of which are harmful and the current desulfurization cannot remove**

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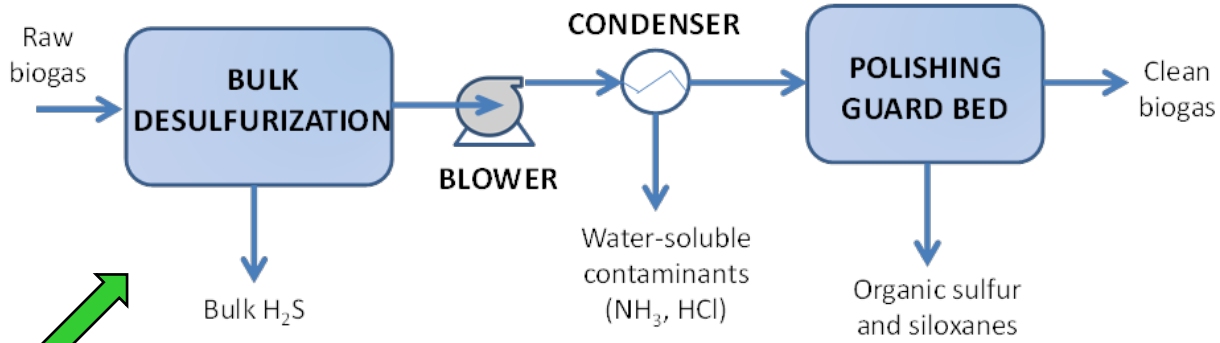
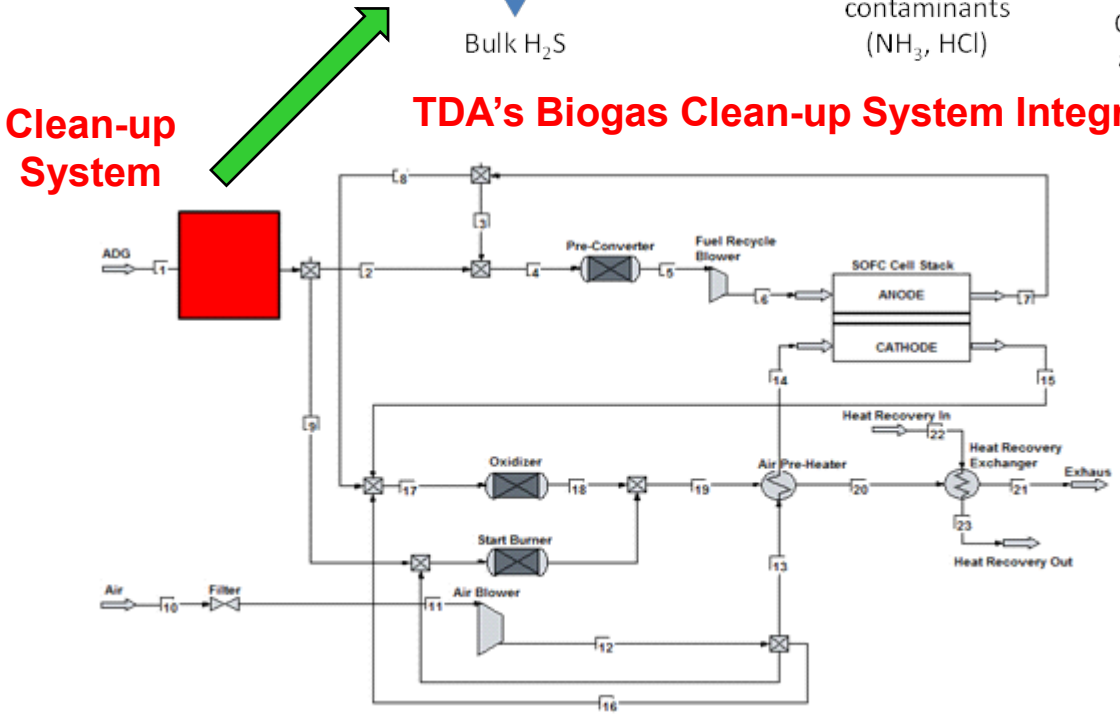
Biogas Cleanup - Approach

TDA's Biogas Clean-up System



TDA's Biogas Clean-up System Integrated with a SOFC



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Biogas Cleanup – Approach

- **TDA's biogas cleanup system uses our own bulk desulfurizer and an additional polishing bed**
  - We decided to use our own bulk desulfurization system because we have found that some of the commercially available bulk sulfur removal systems are contributing to the formation of very complex sulfur species that are difficult to remove, such as the di- and tri-sulfides
- **Bulk desulfurization field tests will evaluate two different types of sorbents**
  - Expendable and Regenerable Sorbent will be evaluated in the field test
- **Polishing bed is designed to remove siloxanes and the organic sulfur species**
- **FCE is developing a 2 kW_e SOFC test module to demonstrate the operation of the higher efficiency SOFC using biogas from wastes**

<u>Field Test Plans</u>

- **The Field Tests are being carried out with our biogas desulfurization sorbents**
  - Cal-DeNier Dairy, Grand Valley, CA – 2 CFM – Demonstration of complete gas clean-up skid with 2 kW_e SOFC

Accomplishments & Progress

Task 1: Sorbent Production and Scale-up – Completed 09/30/2011

- **Optimized our sorbent formulation to remove all the organic and inorganic sulfur species including mercaptans, thiophenes, COS and H_2S from the ADG**
- **Increased the production batch size from 20 mL to 35 L**
- **Optimized the binder composition and drying conditions for our biogas desulfurization sorbent and the sorbent achieves significantly higher capacity than commercial desulfurization sorbents**

Task 2: Gas Cleanup Demonstration System – Completed 02/29/2012

- **Completed the fabrication of our skid-mounted field-deployable prototype biogas clean-up system**

Task 3: SOFC Test Module

- **FuelCell Energy (FCE) has completed the design of the SOFC Test Skid and begun the integration of the 2 kW_e SOFC stack on a test skid**

Task 4: Shakedown Tests – Completed 12/31/2012

- **We completed the shakedown testing of the biogas cleanup system**

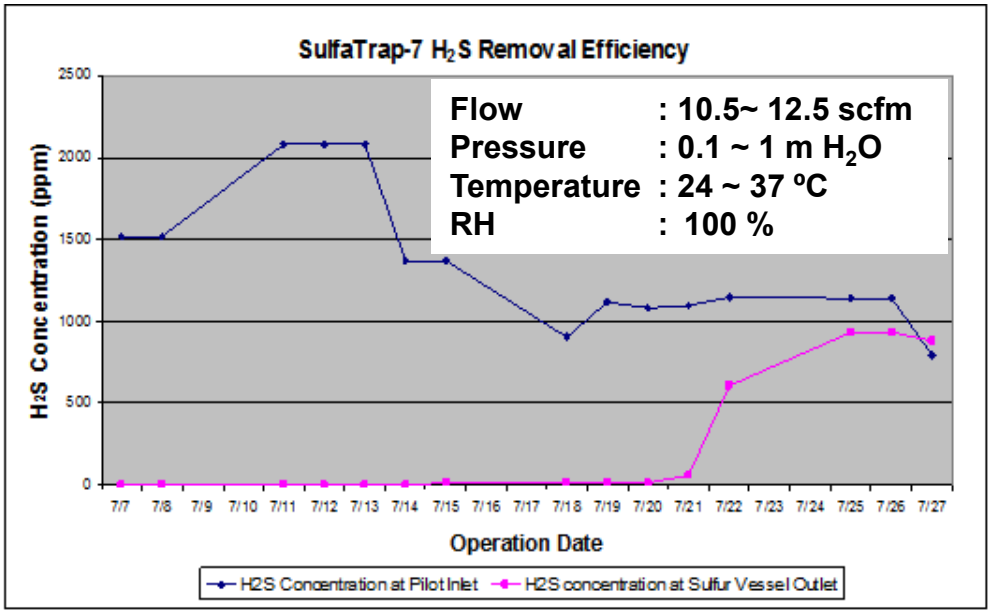
Task 5: Slipstream Demonstrations

- **FCE has initiated the subcontract with SMUD and SMUD has provided the historical ADG gas analysis data for the Cal-DeNier Dairy Farm**

Expendable Bulk Sorbent Field Test – Accomplishments & Progress

12 CFM gas clean-up skid built by TDA for Degremont

Field Test Results for our Expendable Bulk Desulfurization Sorbent SulfaTrap™-R7



- Infilco Degremont carried out field tests with our expendable sorbent at Nasdemond Wastewater Treatment Plant, Suffolk, VA at no-cost to the DOE project
- TDA sorbent achieved 17.5% wt. sulfur capacity (lb of sulfur per lb sorbent)
  - Two times higher than other commercially available sorbents, while reducing the sulfur concentration to undetectable levels i.e., sub ppmv levels

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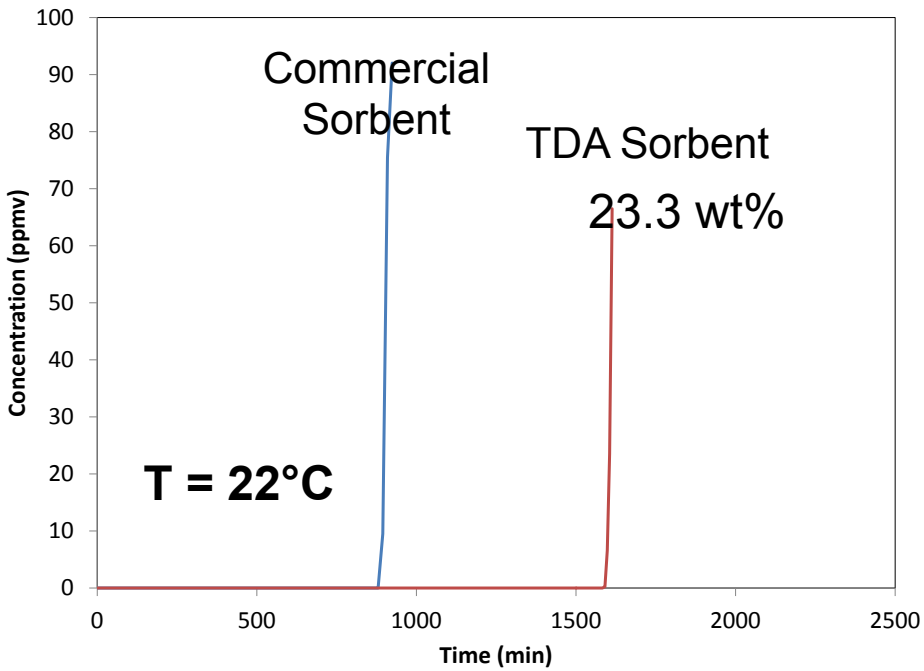
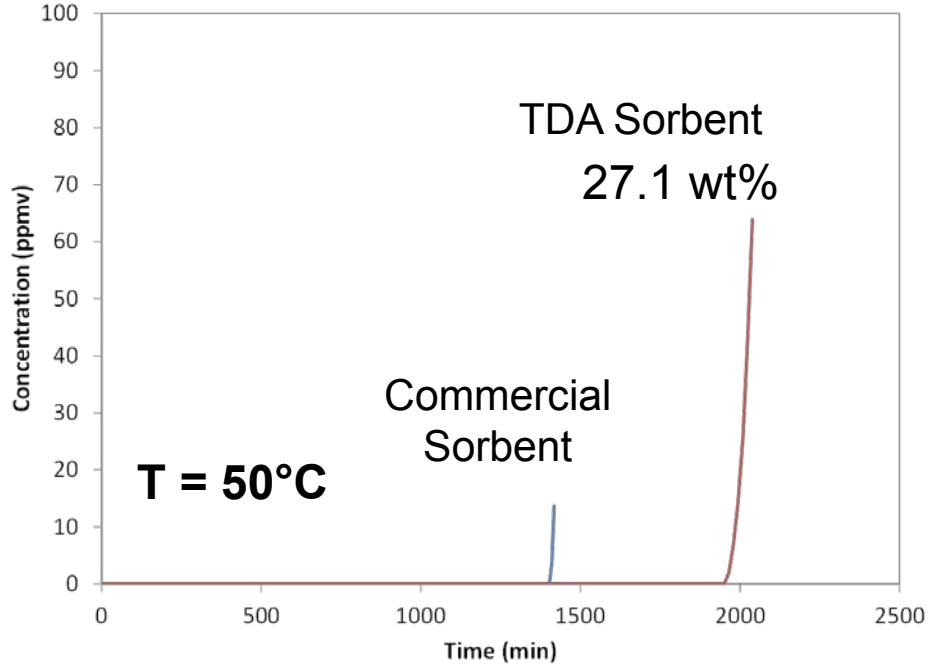
FY 2011

Comparison Against Commercial Sorbents – Accomplishments

2000 ppmv H_2S, 22-50ºC, 60% CH_4, 40% CO_2, Saturated Moisture @ RT





- TDA's Bulk Desulfurization Sorbent achieved significantly higher capacity for H_2S than the commercial sorbent.

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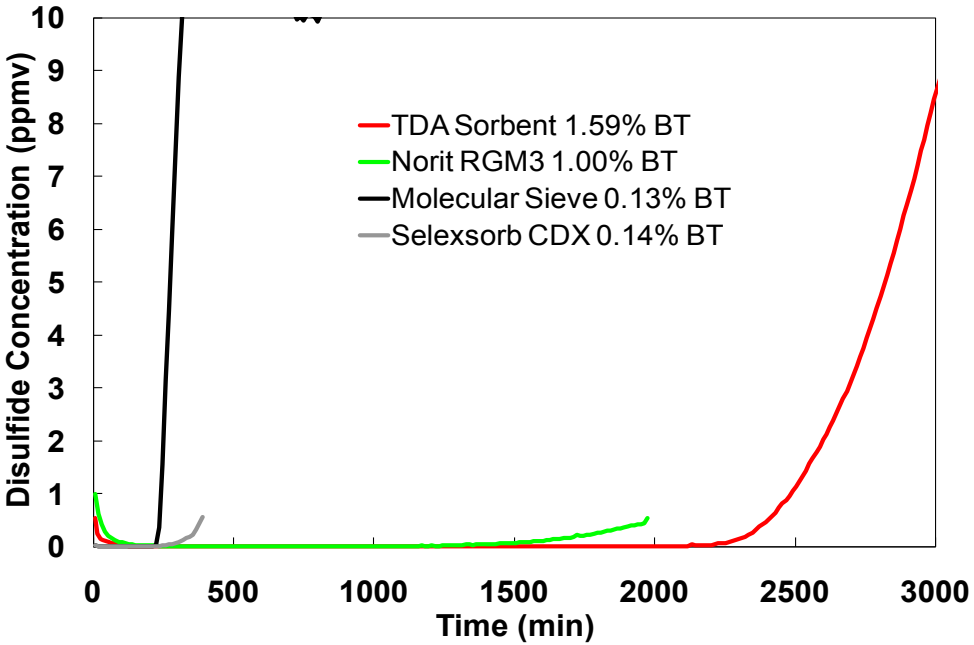
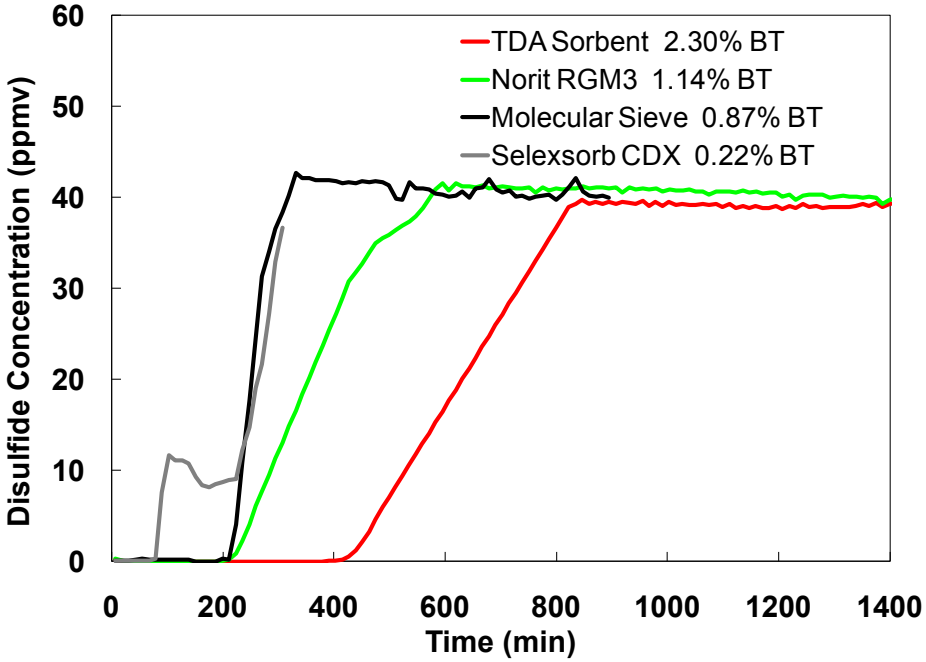
Comparison Against Commercial Sorbents – Accomplishments

T= 45ºC, 15 ppmv EM, 10 ppmv PDS, 10 ppmv MPDS, 40 ppmv MDS, GHSV=3,750 h^{-1}





- TDA's Sorbent achieved significantly higher capacities for di-sulfides present in biogas over commercial sorbents such as activated carbon (Norit RGM3), zeolites (molecular sieve) and specialty alumina (Selexsorb®)

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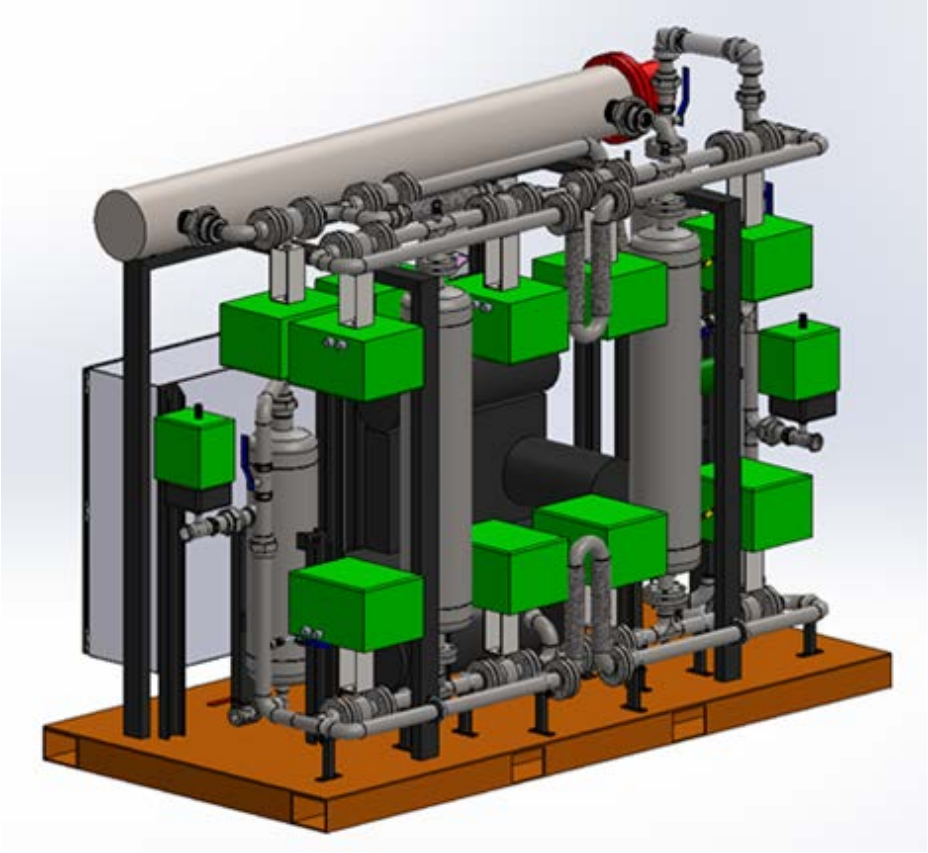
Biogas Cleanup Skid – Accomplishments & Progress

3-D layout of TDA's Skid



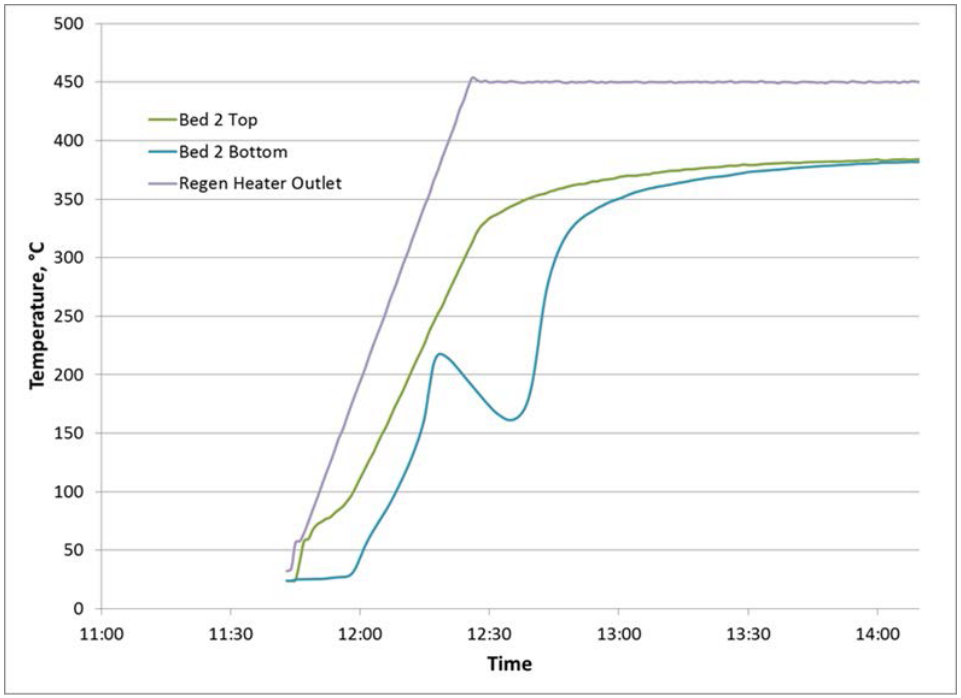
TDA's Biogas Cleanup Skid

- **Completed the fabrication of our skid-mounted field-deployable prototype biogas clean-up system**

Shakedown Testing – Accomplishments & Progress

TDA's Biogas Cleanup Skid

Bed 2 Regeneration Profile with SulfaTrap™-R2 loaded



- **Completed shakedown testing of the biogas cleanup system**

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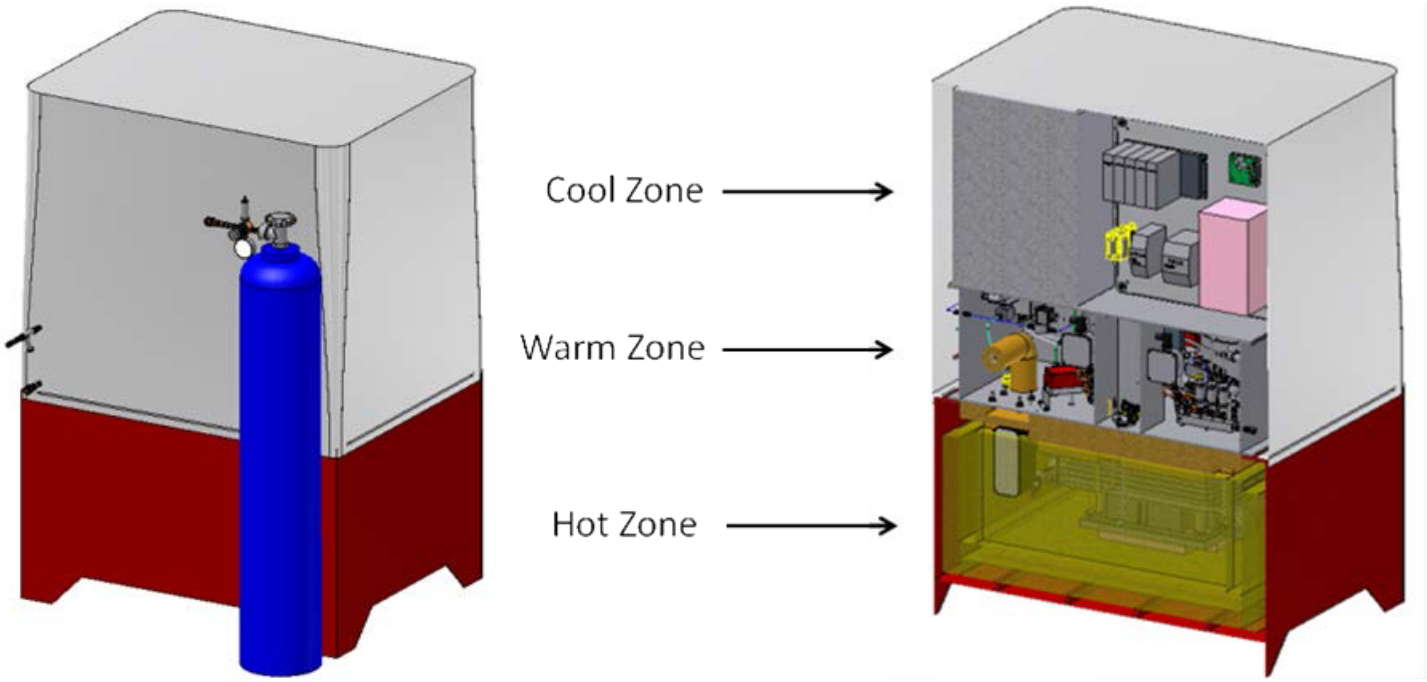
SOFC Test Module – Accomplishments & Progress

3-D layout of FCE's SOFC Test Skid



- **FuelCell Energy (FCE) has completed the integration of the 2 kW_e SOFC stack module on a test skid**

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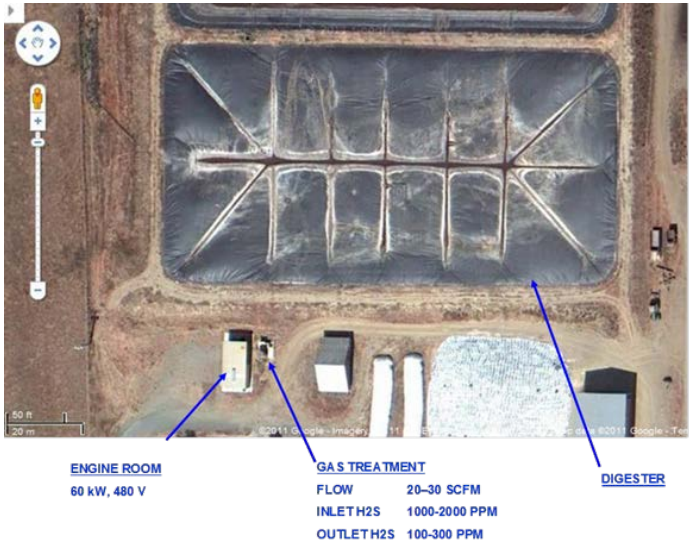
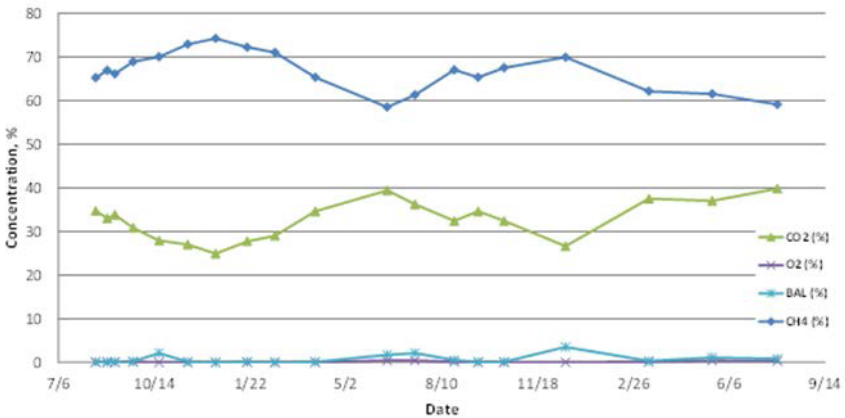
Field Test Site
Cal-DeNier Dairy Farm

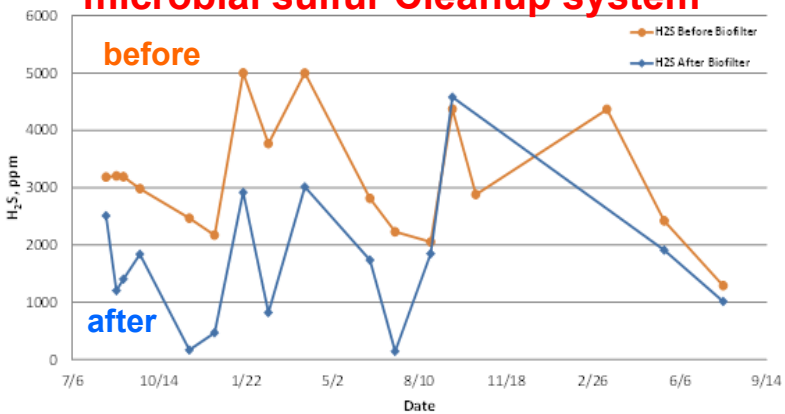
Cal DeNier Dairy Farm Layout



Biogas Composition



H_2S Concentration Before and after existing microbial sulfur Cleanup system



Engine Room

SPACE FOR FUEL CELL

- **FCE and SMUD have an agreement to facilitate a demonstration at Cal-DeNier Dairy Farm located in SMUD**

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SulfaTrap, LLC – Accomplishments

- At the end of SBIR Phase 2 project, TDA developed the SulfaTrap™ line of sorbents initially for desulfurization of natural gas for fuel cell applications
- Since 2008 sorbent has been supplied in increased quantities, 42 tons in 2012 (65 tons expected in 2013) for natural gas-fired fuel cells
- In this project these sorbents are applied for biogas applications and will be demonstrated integrated with a SOFC
- In 2012, TDA has spun-off a separate business, SulfaTrap, LLC to supply these sorbents for the fuel cell market
- The new spin-off raised more than $1 million for initial operation

Collaborations

Packaged Desulfurizers

Lead/Lag Desulfurizer

- TDA worked on providing a universal sorbent or desulfurizer for all applications and also identified alternate suppliers for raw materials
- Submitted several abstracts and papers to national conferences
- Received several enquiries about our sorbents for desulfurization of natural and biogas
- Initiated contact with several fuel cell manufacturers i.e., our potential customers
- Prepared and delivered sorbents and packaged desulfurizers for demonstration with fuel cells or reformers

Future Work

FY 2013

- **Field tests of the integrated system will be carried out in the summer of 2013**
- **Carry out a detailed engineering and cost analysis to assess the economic viability of the new sorbent technology for biogas fed fuel cell power plants**
- **Develop marketing and commercialization strategy to advance the technology and to turn the concept into a practical product**

Project Summary

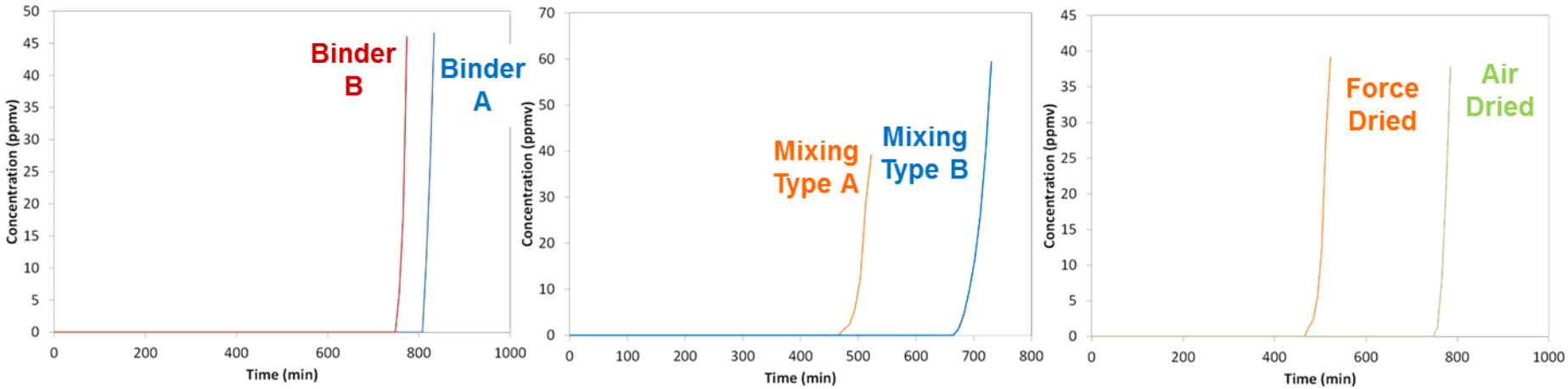
- **Relevance -** Promotes the use of fuel cells in waste-to-energy applications through eliminating one of the greatest barrier; the contaminants present in biogas that area harmful to the fuel cell
- **Approach -** Our Experienced Team Will:
  - TDA leverage its experience with sulfur removal for natural gas to: systematically develop an universal gas cleanup system for biogas that removes all contaminants to ppb levels
  - FCE will leverage their experience in operating MCFCs using biogas to develop a robust and efficient biogas-fired SOFC
  - TDA, FCE and SMUD will carry out field tests using biogas to assess the operation of the integrated system
- **Accomplishments**
  - Spun-off a separate business SulfaTrap, LLC to supply these sorbents to the fuel cell market for natural gas and LPG desulfurization.
  - Completed sorbent scaleup, built the gas cleanup skid, completed design of the SOFC skid, Site identified and contract established, an initial demo at WWTF is successfully carried out
- **Collaboration –** Active Partnerships with FCE, SMUD, Degremont and MWV, contacts established and providing sorbent samples for evaluations to other fuel cell developers.
- **Future Work -** Complete SOFC test skid, the field test and economic analysis

Technical Back-Up Slides

Sorbent Optimization – Accomplishments & Progress

Impact of Binder Type | **Impact of Mixing Technique** | **Impact of Drying Condition**

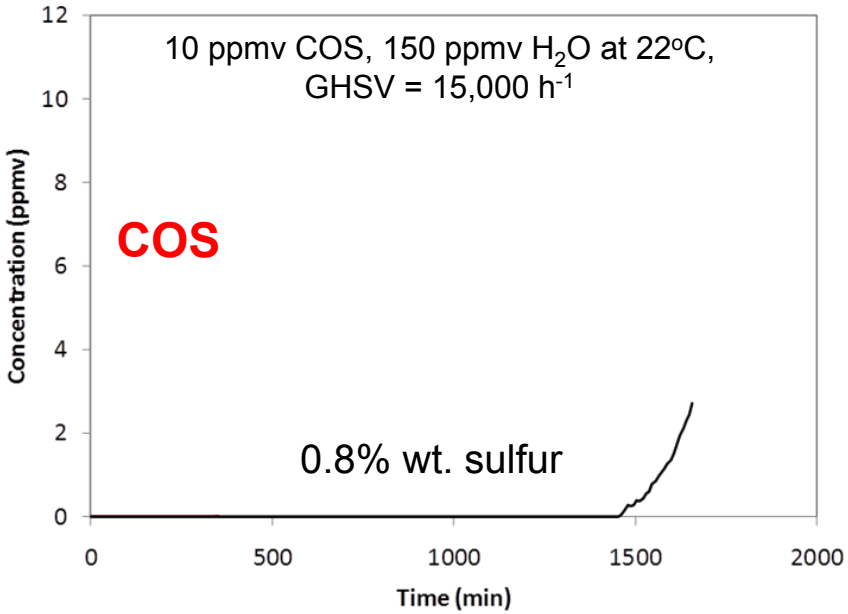
T=21°C, 2,000 ppmv H_2S, 2.2% H_2O, 57.8% CH_4, 40% CO_2, GHSV = 4000 h^{-1}

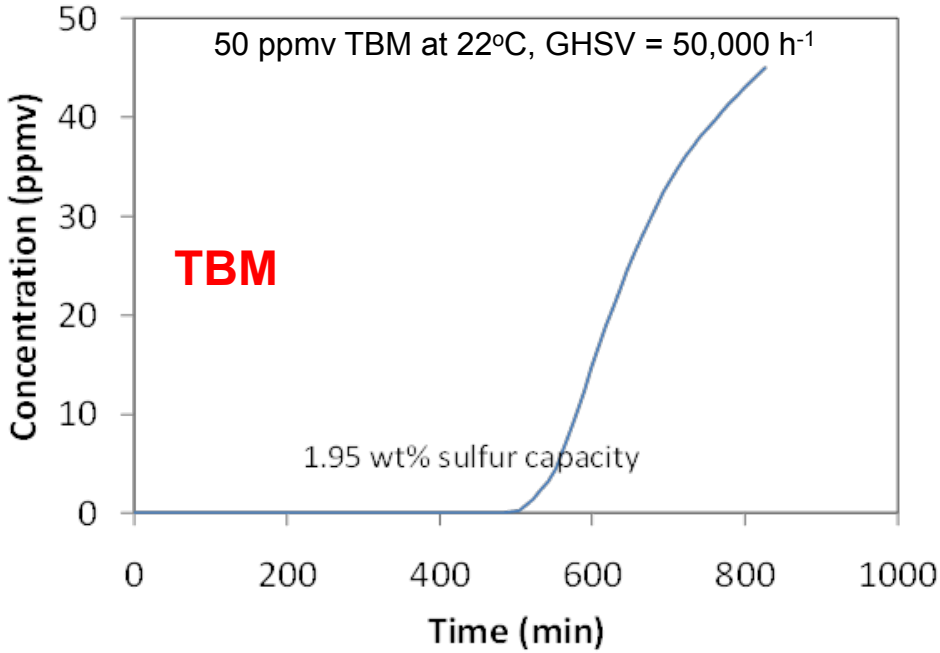


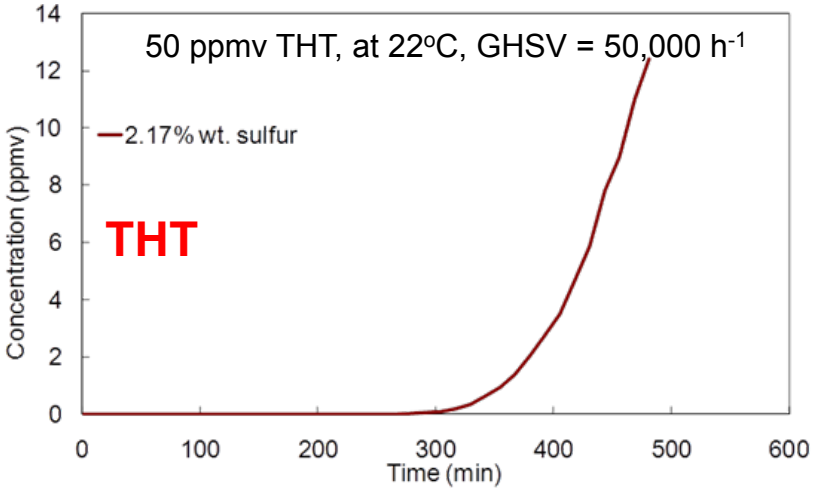
- Optimized our sorbent formulations to remove all the organic and inorganic sulfur species including mercaptans, thiophenes, COS and H_2S from the ADG
- Optimized the binder composition, mixing technique and drying conditions for our biogas desulfurization sorbent
- Optimized the physical properties of the sorbent such as surface area, density, and mechanical strength

TDA Research

Removal of Other Sulfur Compounds – Accomplishments & Progress





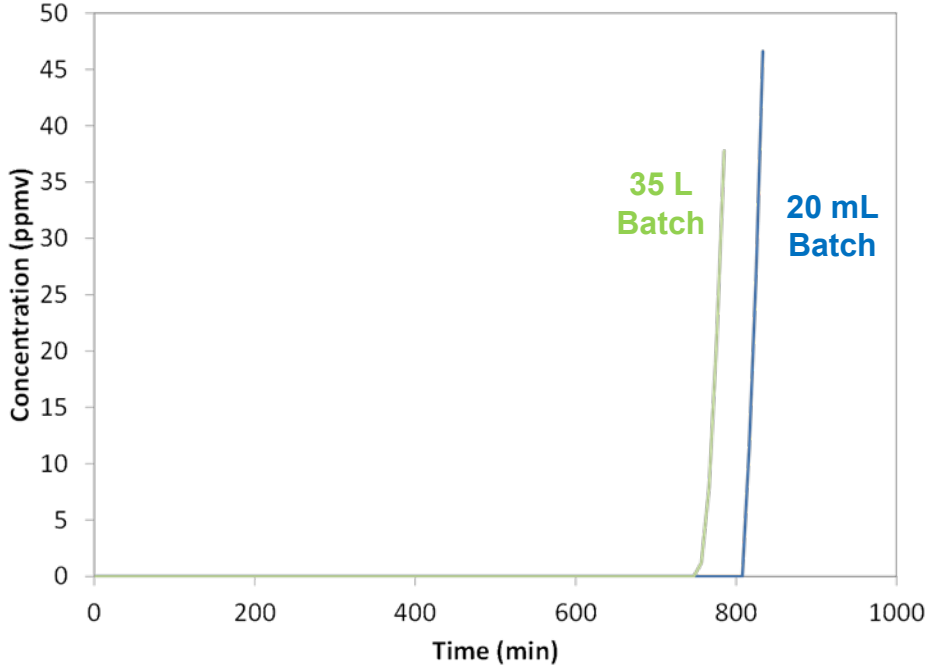


- We optimized our sorbent formulations to remove all the organic and inorganic sulfur species such as H_2S, COS, mercaptans (TBM) and thiophenes (THT) from the ADG

TDA Research

Sorbent Production Scaleup – Accomplishments & Progress

T=21ºC, 2,000 ppmv H_2S, 2.2% H_2O, 57.8% CH_4, 40% CO_2, GHSV = 4000 h^{-1}



- **We increased the production batch size for our biogas desulfurization sorbent from 20 mL to 35 L with virtually no change in the sorbent performance**

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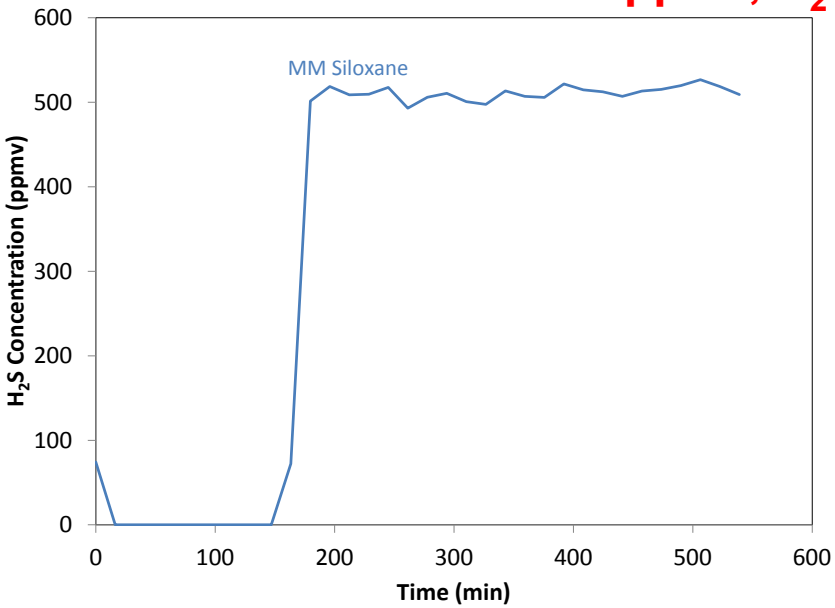
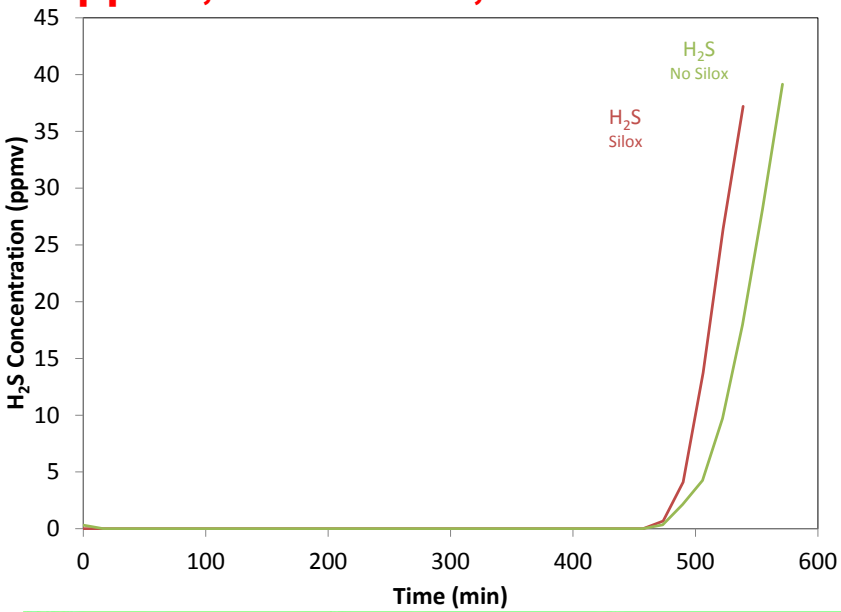
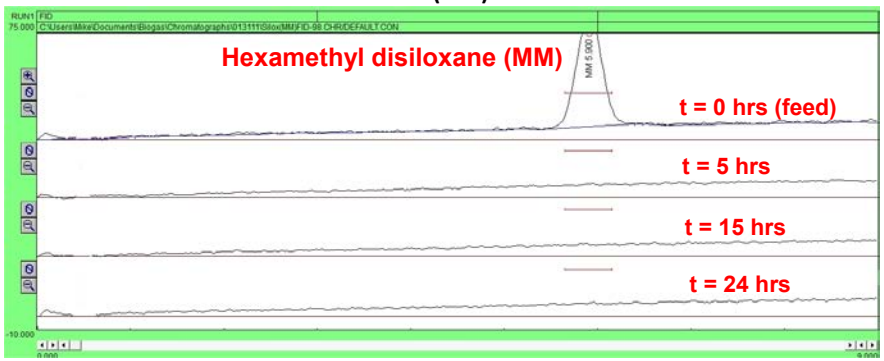
Multi-contaminant Removal – Accomplishments & Progress

SulfaTrap™-R8 Sorbent, T = 20°C, 2.2% H_2O, 7.5% N_2, 36.1% CO_2, 54.2% CH_4, MM siloxane = 500 ppmv, H_2S = 75 ppmv, GHSV = 12,000 h^{-1}





- **SulfaTrap™-R8 sulfur sorbent achieves a high siloxane capacity of greater than 21.5% wt. siloxane capacity and a sulfur loading of 2.15% wt.sulfur**



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