IV.B.7 Sorbents for Desulfurization of Natural Gas and LPG

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Objectives

- Develop a low-cost, high capacity expendable sorbent that can reduce the concentration of organic sulfur species in natural gas and liquified petroleum gas (LPG) to less than ppb levels.
- Develop a regenerable version of the sorbent for large-scale stationary power generation applications.
- Scale-up sorbent production.
- Demonstrate combined operation of the desulfurizer with a solid oxide fuel cell (SOFC).
- Carry out an independent engineering analysis to fully assess the potential of the new desulfurization sorbent.

Approach

- Carry out bench-scale screening tests to identify materials that adsorb organic sulfur species with high capacity.
- Perform parametric experiments with selected sorbents to optimize operating conditions.
- Demonstrate the regeneration potential and long-term durability of the best sorbent through many consecutive adsorption/regeneration cycles.
- Produce larger batches of the new material using high throughput equipment (e.g., spray dryers, screw extruders) representative of commercial production.
- Establish partnerships with SOFC technology developers in the Solid State Energy Conversion Alliance (SECA) to demonstrate the potential of the new desulfurization sorbent in combination with SOFCs.
- Based on the performance results assess the technical and economical impact of the new materials in SOFC-based distributed and stationary power generation systems.

Accomplishments

- TDA developed the SulfaTrap™ sorbent platform for cost-effective desulfurization of different light hydrocarbon streams
  - SulfaTrap™-R3 sorbent, the baseline sorbent material recommended for common natural gas streams could achieve a sulfur capacity greater than 3.12 wt% (lb of sulfur removed per lb of sorbent) provided that the water vapor content of the gas is within the pipeline specifications (7 lb/MMSCF or 154 ppmv).
  - SulfaTrap™-R2 sorbent can treat gas streams with high moisture content (1,000 to 5,000 ppmv H_2O).
  - SulfaTrap™-R5 sorbent is specifically designed for desulfurizing natural gas streams with high concentrations of carbonyl sulfide (COS). The sorbent reduces the COS content to less than 10 ppbv and tolerates the presence of water vapor and CO_2 impurities in the gas.
  - SulfaTrap™-P sorbent is designed for desulfurization of heavier hydrocarbons (LPG or natural gas oil).
- The performance of TDA's SulfaTrap™ sorbents was demonstrated in several field tests at the 1 to 300 kWe range through collaborations with Siemens Power Corporation, Delphi Corporation and FuelCell Energy with successful results.

Future Directions

TDA will identify a commercial partner to scale-up the production of its sorbent well above the current levels (40 kg per batch) to meet the growing demand for its sorbents and to provide a lower cost product.

Introduction

Pipeline natural gas is the fuel of choice for fuel cell-based distributed power generation systems because of its abundant supply and well-developed infrastructure. However, effective utilization of natural gas in fuel cells requires that sulfur impurities (naturally occurring sulfur compounds and sulfur bearing odorants) be removed to prevent them degrading the performance of the fuel cell stacks and poisoning of the catalysts used in the fuel processor. Sulfur removal is important in all types of fuel cells. Even the more sulfur tolerant SOFCs need the sulfur content of the natural gas to be reduced to less than 0.1 ppmv. TDA is developing a low-cost, high-capacity sorbent that can remove odorants from natural gas and LPG and enable effective utilization of these fuel gases in fuel cells.

Approach

While there are large-scale commercial technologies (e.g., hydrodesulfurization) that can remove organosulfur compounds to levels that fuel cells can tolerate, they are far too complex and expensive for small-scale systems (less than 1 MW). Most of the fuel cell technology developers prefer to remove sulfur from the feed gases using expendable (once-through) sorbents that operate at ambient temperature (a simple addition to the fuel cell fuel processor).

In our work, we first prepared a large number of formulations and carried out bench-scale screening tests to identify materials that adsorb sulfur-bearing odorants with high capacity. We then performed parametric experiments with selected sorbents to optimize the conditions for their operation. We demonstrated the full potential of the new desulfurization sorbents in combination with SOFCs. We scaled-up the sorbent production to be able to provide quantities of samples to support relatively large-scale field trials (up to 300 kW). In the future, we will produce even larger batches of the new material using high throughput equipment (e.g., spray dryers, screw extruders) representative of commercial production. Based on the field performance results, we will assess the technical and economical impact of the new materials in distributed and stationary power generation systems.

Results

We supplied our sorbent to the technology developers in the SECA group to support various demonstrations in combination with the SOFC systems ranging from 1 to 300 kW in size. TDA delivered three 100 kW desulfurizers to Siemens Power Corporation in 2006. Figure 1 shows one of the 100 kW TDA desulfurizer delivered to GTT, Milan, Italy. This particular device, topped with an activated carbon sorbent for COS removal, successfully reduced all the sulfur species to levels tolerable by the SOFC system.

We evaluated the effect of water on the performance of various sorbents. Although the U.S. pipeline natural gas specification requires the water vapor content of the gas reduced below 154 ppmv (~7 lbs of water per million cubic foot of natural gas), in our demonstrations we observed much higher water concentrations (up to 5,000 pmmv) in most of the natural gas used in the demonstration tests. We developed a new sorbent to enhance the water tolerance of our standard sorbent. Figure 2 shows the performance of our SulfaTrap™-R2

FIGURE 1. Pictures of the Two 100 kW TDA Desulfurizers

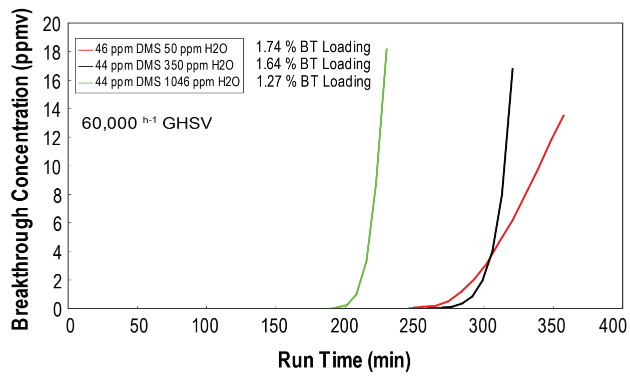

FIGURE 2. The effect of water vapor on the performance of TDA's SulfaTrap™-R2 sorbent at various water vapor concentrations. T= 22°C, P= 5 psig, natural gas with 46 ppmv DMS at 60,000 h^{-1}.

sorbent in natural gas streams with high water vapor content. We used a simulated natural gas with 46 ppmv dimethyl sulfide (DMS); we selected DMS as the sulfur contaminant since it is one of the most difficult to remove organic sulfur species. Our water tolerant sorbent could achieve over 1.27% sulfur capacity on weight basis (lb of sulfur removed per lb of sorbent) even when 1,046 ppmv of water vapor is present in the gas.

Under the SulfaTrap™ sorbent platform, we also developed a sorbent that is effective for the removal of COS. In fact, the sorbent is capable of removing all sulfur species. To maximize its COS capacity it is recommended to be used in combination with our baseline sorbent material, where the SulfaTrap™-R3 and R5 sorbents are placed into the same desulfurizer device in sequential manner, where the former removes all sulfur species with the exception of COS, and the latter removes any COS not captured in the preceding bed. Figure 3 shows the performance of the SulfaTrap™-R5 in comparison with the commercially available adsorbents. In this experiment, we used a simulated natural gas that contains 100 ppbv of COS and 50 ppbv of water vapor. The SulfaTrap™-R5 showed the highest sulfur capacity, while reducing the sulfur level to less than single digit ppb levels (the sulfur detection capability of the analyzer used in this experiment was measured as 4 ppbv). The

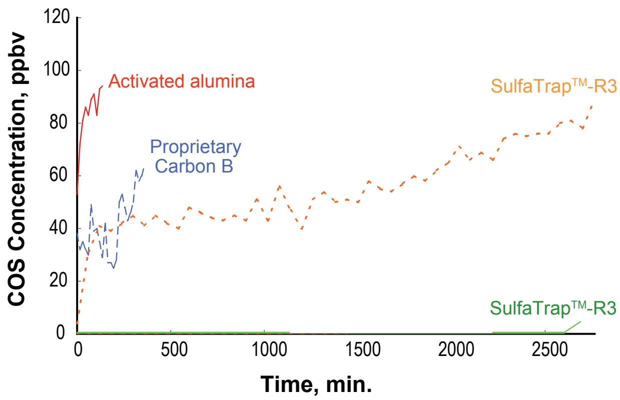

FIGURE 3. COS breakthrough over various commercially available sorbents and SulfaTrap™-R5 sorbent. T= 22°C, P= 5 psig, natural gas with 100 ppbv COS and 50 ppmv H_2O at 6,000 h^{-1}.

FIGURE 4. Picture of Two TDA Desulfurizers using a Mixture of SulfaTrap™-R3 and R5 Sorbents

R5 sorbent could achieve 0.78% wt. sulfur capacity for COS. We also showed that the SulfaTrap™-R5 sorbent could also be regenerated by heating the sorbent bed up to 150°C, using a purge gas of clean humidified natural gas without any signs of degradation in a three-cycle test.

We supplied a number of desulfurizers to Delphi Corporation using a mixture of the two sorbents (Figure 4). These desulfurizers were used as guard beds to support Delphi's SOFC tests using pipeline gas. TDA desulfurizers successfully reduced the sulfur content of the gas, which contained fair quantities of COS to the desired levels.

To meet the growing demand for its sorbents, TDA invested in a small-scale in-house production facility with a capability of supplying finished products at a rate of 200 lb/month.

Conclusions

Low-cost, high capacity, regenerable sorbents were developed for removing sulfur compounds from natural gas at ambient temperature to sub-ppm levels. The sorbent performance was demonstrated not only in bench-scale tests but also in various field trails in combination with the SOFC power generation systems.

FY 2007 Publications/Presentations

1. "Sorbents for Desulfurization of Natural Gas and LPG", G. Alptekin, Presented at the Annual SECA Workshop and Peer Review Meeting, Philadelphia, PA, 2006.

2. "Sorbents for Desulfurization of Hydrocarbons", G. Alptekin, Presented at the Fuel Cell Seminar, Honolulu, HI, 2006.