A NEW ADSORBENT FOR AMBIENT TEMPERATURE DESULFURIZATION OF NATURAL GAS

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ABSTRACT

The sulfur content of natural gas or any hydrocarbon fuel needs to be reduced to very low levels to ensure long-term stable electrochemical performance for both high and low temperature fuel cells. This paper presents the development and test results of a new physical adsorbent for natural gas desulfurization. The sorbent effectively removes all naturally occurring sulfur compounds and sulfur-bearing odorants at ambient temperature with very high capacity. In a series of tests, the sulfur adsorption capacity of the new material is compared to other commercially available and specially prepared sorbents. The new sorbent can also be fully regenerated. The effectiveness of the sorbent was tested in the presence of water vapor, which is present in natural gas at ppmv levels. The effect of operating temperature on capacity was evaluated. The efficacy of the sorbent for carbonyl sulfide removal was also investigated.

INTRODUCTION

Fuel cells have the potential to revolutionize the way the power is produced and distributed, and distributed power generation is becoming a viable alternative to buying power from a central grid. However, there are still some hurdles to be overcome if fuel cells are to fully reach their commercial potential. One of the issues to be addressed is the need to provide an ample supply of high quality fuel to operate the fuel cells. Pipeline natural gas is the fuel of choice in distributed power generation systems because of its abundance and well-developed supply infrastructure. However, the natural gas contains sulfur impurities that can degrade the performance of the fuel cells. Although the majority of the sulfur in the natural gas is removed at the wellhead, some hydrogen sulfide (H2S) and carbonyl sulfide (COS) exist as contaminants at low concentrations. In addition to the naturally occurring sulfur, pipeline gas also contains other organic sulfur species used as odorants. Because natural gas has no distinct odor, for safety reasons pipeline companies commonly odorize natural gas as it enters the transmission lines or local distribution facilities. These odorants allows detection of even minute leaks in the gas lines. Common odorants include mercaptans (such as ethyl, isopropyl, tertbutyl mercaptan), thiols (such as tetrahydrothiophene) and sulfides (such as dimethyl or diethyl sulfide). The concentration of sulfur in odorized natural gas can be as high as 15-20 ppm on volume basis.

Fuel cells, however, require clean feed streams with very low levels of sulfur and other impurities. Sulfur poisons the anode catalysts for both high and low temperature fuel
cells. The problem is most severe in polymer electrolyte fuel cells (PEMFC), both because they operate at low temperature, and their platinum group catalysts are highly susceptible to sulfur poisoning. Sulfur also degrades the performance of the high temperature solid oxide fuel cells (SOFCs). A recent study by Siemens Westinghouse Power Corporation [1] shows that the performance of their fuel cell drops about 15% in the presence of 1 ppmv sulfur in the fuel. Although this poisoning effect is reversible, long-term stable electrochemical performance of the SOFCs requires sulfur concentrations to be reduced to sub ppmv levels.

In large central stations, sulfur removal is carried out upstream of the fuel cell with a two-step process consisting of hydrodesulfurization of organic sulfur species to H2S and subsequent H2S removal with a sorbent. However, this method is not practical for small-scale residential units. Most fuel cell manufacturers prefer a low temperature adsorbent that can directly remove organic sulfur from natural gas in a single step. A successful sorbent must meet a number of requirements. First of all, it must exhibit a high sulfur adsorption capacity to reduce the size of the sorbent bed and decrease the replacement frequency of the sorbent. It has to be low cost, so that it is affordable by households. It must reduce the total sulfur concentration of the fuel to ppb levels to ensure maximum protection for the fuel cell catalyst. It must operate in a passive manner and should not catalyze any undesirable side reactions or alter the composition of the gas by adsorbing hydrocarbons. It must tolerate other natural gas contaminants such as the heavy hydrocarbons, CO2 and humidity. Finally, it should be easy to dispose of. The sorbent itself should be easy to handle and should not pose any toxicity, flammability or pyrophoricity problems.

In a project funded by the Department of Energy project, TDA Research, Inc. is developing a passive adsorbent for the ambient temperature desulfurization of natural gas. This paper summarizes the test results showing the effects water vapor and higher than ambient temperature operation on sorbent performance and the effectiveness of the sorbent for removing COS.

**EXPERIMENTAL**

**Testing System**

The sorbent performance was measured in an automated bench-scale test unit. In this setup, the reactor cell consists of a quartz tube that contains a frit in the middle to support the pellets. We were able to test 0.5 to 2.0 g of sample (1/8" pellets were crushed into 1-5 mm size to be tested). The reactor was inserted in a tube furnace to provide heating as needed. All gas flows were controlled with electronic mass flow controllers. To introduce organic sulfur species we used calibrated gas cylinders that contain mixtures of odorant species with natural gas. The content of the cylinder was metered into a manifold and mixed with a natural gas mixture to achieve the desired gas composition. A valve system was used to direct gases to a reactor by-pass line to make accurate measurements of the feed gas. All system components were made of either quartz, Teflon or Silcosteel (steel lines with a special glass coating) to minimize the adsorption of sulfur on the system components. All testing was done at near ambient pressure (5
psig). The apparatus is fully automated and can run without an operator for long periods of time, including overnight.

**Sulfur Analysis**

For the analysis of sulfur compounds we used a gas chromatograph equipped with a flame photoionization detector that is selective to sulfur species. The capillary column used to separate the odorants is a RTX-1, 30 meter, 0.53 mm ID, with 7.0 µm film thickness manufactured by Restek Corporation. Our detection limit was approximately 0.1 ppmv. Figure 1 shows peak separation for selected odorant compounds and their retention times in minutes. At the end of some tests, we sent samples of the tested sorbent to an outside laboratory for elemental analysis. The correlation between the amount of sulfur-bearing gases passed over the sorbent and the amount of sulfur accumulated in the bed allowed us to identify the effectiveness of the sorbent and provided an independent check on our analytical methodology.

**Natural Gas Analysis**

In these tests, we used simulated natural gas. A typical gas composition is given in this Table I. This gas mostly consists of lower alkanes from methane to hexane, with the chief constituent being methane and some branched hydrocarbons such as the iso-butane or neo-pentane at representative concentrations. The gas also contained some nitrogen and CO2. We used a GC equipped with a thermal conductivity detector to measure the concentration of the hydrocarbon species throughout the test.

| Component     | Volume % | Volume % |
|---------------|----------|----------|
| Methane       | 92.39    | 92.86    |
| Ethane        | 3.42     | 3.31     |
| Propane       | 0.56     | 0.60     |
| Butane        | 0.11     | 0.10     |
| Isobutane     | 0.12     | 0.12     |
| Pentane       | 0.11     | 0.10     |
| Isopentane    | 0.10     | 0.10     |
| Neopentane    | 0.10     | 0.10     |
| Hexane        | 280 ppmv | 251 ppmv |
| Carbon Dioxide| 0.81     | 0.70     |
| Nitrogen      | 2.08     | 2.01     |
RESULTS AND DISCUSSION

Performance Comparison with Other Sorbents

In the evaluation of new sorbents, TDA Research collaborated with Siemens Westinghouse Power Corporation (SWPC). In 2000, SWPC initiated a test program to identify a strategic supplier for a natural gas desulfurization process and carried out extensive engineering scale tests to evaluate potential natural gas desulfurization sorbents. In their study, they evaluated a number of commercial and specially prepared physical adsorbents and high temperature chemical sorbents for removing sulfur odorants. The results of their screening study were presented elsewhere [1]. Several low temperature adsorbents were received from SWPC, and we tested their sorbents to compare their performance to that of the new materials developed at TDA. Some of these sorbents were cerium and copper exchanged zeolite-Y, respectively. Sample 4 was prepared to be similar to those reported by University of Michigan [2] as effective for desulfurizing gasoline and Penn State [3] for desulfurizing jet fuel. Sample 5 was similar to the sorbents reported by Pacific Northwest National Laboratory [4] and Pennsylvania State University [3]. For quick comparison, accelerated tests were carried out at high gas hourly space velocities, 60,000 h\(^{-1}\) (corresponding to very short gas solid contact times). The performance of each sorbent was evaluated at an identical baseline condition; the sulfur-laden natural gas stream contained 12.3 ppmv dimethyl sulfide (DMS), 8.9 ppmv tert-butyl mercaptan (TBM), 8.9 ppmv tetrahydrothiophene (THT). These higher than pipeline gas sulfur concentrations and short contact times allowed observation of the breakthrough profiles of these odorants in relatively short times.

Figure 4 shows the DMS breakthrough profiles for various sorbent samples. A special emphasis is given to the DMS because in all prior work DMS was found to be the most difficult sulfur compound to be removed from the natural gas [1,4]. Among the samples tested at 60,000 h\(^{-1}\) in a natural gas mixture containing 12.3 ppmv DMS, 8.9 ppmv TBM and 8.9 ppmv THT at 5 psig.
provided by SWPC, the DMS breakthrough occurred first with the Norit carbon sample at 30 min followed by the un-promoted zeolite-X at 72 min (indicating that the zeolite-X has approximately 2.5 times higher DMS capacity than the Norit carbon). The specially prepared samples provided by SWPC showed better performance than the commercial sorbents, but one of TDA’s preparations (referred to as SulfaTrap™) showed the best performance of all the sorbents. The DMS breakthrough occurred at 720 min corresponding to a sulfur adsorption capacity of 3.12% wt. Table 2 shows the breakthrough adsorption capacities for all samples shown in Figure 4. The pre-breakthrough sulfur adsorption capacity is defined as the lb of total sulfur adsorbed per lb of sorbent when the breakthrough of the first sulfur compound was observed.

| Sample                              | Pre-Breakthrough Capacity (% wt.) |
|-------------------------------------|-----------------------------------|
| TDA’s SulfaTrap™ Sorbent            | 3.12%                             |
| Siemens Cu-Zeolite Y                | 1.96%                             |
| Siemens Ce-Zeolite Y                | 0.85%                             |
| Grace X Zeolite                     | 0.36%                             |
| Norit RGM3 Activated Carbon         | 0.18%                             |

The breakthrough profiles of all sulfur species for TDA’s SulfaTrap™ sorbent are presented in Figure 5. In agreement with the prior literature, DMS breakthrough occurred first at 720 minutes, followed by the breakthrough of TBM at 1080 minutes. The breakthrough of THT was never observed during 1400 minutes of testing. These results suggest that the affinity of the sorbent is weakest for the DMS and strongest for the THT. The saturation sulfur capacity of the sorbent was calculated as 3.88% wt. (the saturation capacity is defined as the total sulfur loading of the sorbent measured when the DMS concentration at exit of the bed was equal to its inlet value).

Figure 3. Breakthrough profiles of sulfur components from TDA’s SulfaTrap™ sorbent. Natural gas with 12.3 ppmv DMS, 8.9 ppmv TBM and 8.9 ppmv THT at 60,000 h⁻¹.
Effect of Water on Sorbent Performance

In the screening tests, the samples were tested using certified gas mixtures of simulated dry pipeline gas. However, typical U.S. pipeline natural gas may contain up to 155 ppmv of water vapor (~7 lbs of water per million cubic foot of natural gas). It is anticipated that the competition by water vapor for adsorption sites will reduce the sulfur capacity of activated carbon, zeolite-based sorbents in real world applications due to their high affinity to water. Therefore, some of the samples were evaluated using a gas stream containing 50 ppmv water vapor with all other gas concentrations remaining identical (i.e., 12.3 ppmv DMS, 8.9 ppmv TBM and 8.9 ppmv THT at a GHSV of 60,000 h\(^{-1}\)). Figure 4 shows the effect of water vapor on the performance of Norit RGM3 Activated Carbon, unmodified zeolite-X (Grace) and TDA's SulfaTrap\textsuperscript{TM} sorbent. The presence of water reduced the sulfur adsorption capacity of all sorbents. The capacity of the zeolite-X is reduced the most by approximately 83%, showing zeolite-X's high affinity for the water vapor. The water most likely adsorbs on the surface of the sites, competing with the sulfur. As shown in Table III, the capacity of the SulfaTrap\textsuperscript{TM} sample is also reduced in the presence of 50 ppmv water vapor. However, the competition with water vapor was less of a problem for the SulfaTrap\textsuperscript{TM} sorbent.

![Figure 4. The effect of water vapor on the performance of TDA’s SulfaTrap\textsuperscript{TM} sorbent and other common sulfur sorbents. T= 22°C, P= 5 psig, Natural gas with 12.3 ppmv DMS, 8.9 ppmv TBM and 8.9 ppmv THT at 60,000 h\(^{-1}\).](image)

**Table III. Effect of water vapor on sulfur adsorption capacity of the sorbents.**

| Sample                  | Dry Capacity (% wt) | Wet Capacity (% wt) | Percent Capacity Loss |
|-------------------------|---------------------|---------------------|-----------------------|
| TDA’s SulfaTrap\textsuperscript{TM} Sorbent | 3.1% | 2.41% | 24% |
| Norit RGM3 Activated Carbon | 0.18% | 0.17% | 3% |
| Grace X Zeolite         | 0.36% | 0.06% | 84% |
Effect of Temperature on Sorbent Performance

Depending on the geographic location and the season, the desulfurization system used in residential units has to work at a wide range of temperatures. In the bench-scale tests, we evaluated the performance of the SulfaTrap™ sorbent at 5, 22 and 40°C. To carry out the 5°C test, the reactor was placed in a chiller to maintain a low and stable temperature. For the 40°C test, the reactor was heated using heat tapes. Figure 5 shows the DMS breakthrough profiles at each temperature.

![Figure 5](image.png)

Figure 5. The effect of temperature on the performance of TDA’s SulfaTrap™ sorbent. Tested at three different temperatures. P= 5 psig, Natural gas with 12.3 ppmv DMS, 8.9 ppmv TBM and 8.9 ppmv THT at 60,000 h⁻¹

Table IV lists the pre-breakthrough sulfur adsorption capacity at each temperature. It is observed that as the temperature increases, the sorbent capacity decreases (at 40°C, the sulfur capacity of the sorbent is reduced by 25% in comparison to that can be achieved at 22°C). It is important to note that the SulfaTrap™ sorbent is fully regenerable, and once the sorbent reaches its capacity all the sulfur-bearing odorants can be driven off from the surface with a mild temperature swing by heating the bed to 300°C. Previously, we demonstrated that the sorbent could maintain its sulfur adsorption capacity through many adsorption/regeneration cycles [5] by simple heating. Thus, the observed decrease in the capacity at higher temperatures was expected.

| Testing Temperature | Run Time (min) | Capacity (% wt.) |
|---------------------|---------------|------------------|
| 5°C                 | 830           | 3.59%            |
| 22°C                | 720           | 3.12%            |
| 40°C                | 237           | 1.02%            |

Table IV. Sulfur adsorption capacity as a function of temperature.
In addition to the sulfur-bearing odorants, pipeline gas also contains naturally occurring sulfur species such as hydrogen sulfide (H₂S) and carbonyl sulfide (COS). Several commercial adsorbents are available that can remove H₂S at low temperature, but they have a much lower capacity for COS. Although not very common in the U.S. natural gas supplies, the pipeline gas in Europe can contain up to 2-5 ppmv of COS. In order to adequately protect the fuel cell, the sorbent must effectively remove COS in addition to other sulfur components. We tested the performance of a modified sorbent in the presence of the COS. These tests were carried out in a bench-scale reactor using a 50 ppmv COS/N₂ mixture at a GHSV of 6,000 h⁻¹. In these tests, COS/nitrogen mixture is selected in order to provide simplicity to gas analysis (in the gas chromatogram, a baseline drift occurred coinciding COS retention time preventing sub-ppm level measurement sensitivity). Tests with the actual natural gas and COS mixture are underway. Figure 6 shows the COS breakthrough profile over TDA's modified SulfaTrap™ sorbent. The breakthrough capacity is calculated as 1.06 % wt. (lb of sulfur removed per lb of sorbent). The saturation sulfur capacity of the SulfaTrap™ sorbent was calculated as 1.25% on weight basis.

Figure 6. COS breakthrough profile over the modified SulfaTrap™ sorbent. T=22°C, P= 5 psig, COS Inlet Concentration= 50 ppmv, GHSV= 6,000 h⁻¹.

CONCLUSIONS
A low-cost, high capacity, regenerable sorbent was developed for removing sulfur-bearing odorants from natural gas at ambient temperature. Table V compares our new material with a state-of-the-art activated carbon sorbent for sulfur removal. Our sorbent does not interact with hydrocarbons or alter the composition of the natural gas. It does not alter the sulfur compounds that it removes by physical adsorption. It does not contain
any toxic ingredients and it is not pyrophoric. Therefore, it does not require any special handling for disposal if its regenerability is not exploited.

TDA's SulfaTrap™ sorbent can achieve a high sulfur capacity in the presence of water although presence of water slightly reduces capacity. It was also shown that the sorbent can successfully remove odorants up to 40°C. However at higher temperatures the capacity decreases. TDA SulfaTrap™ sorbent was tested for COS removal and found to have a capacity of 1.06 wt% COS.

Table V. Comparison of TDA's SulfaTrap™ sorbent with a state-of-the-art activated carbon sorbent to protect a 5kW_e SOFC system for one year.

|                      | SulfaTrap™ Sorbent | Activated Carbon |
|----------------------|---------------------|------------------|
| Operating Temperature| Ambient             | Ambient          |
| Bed Volume           | 4 L                 | ~300-360 L       |
| Hydrocarbon Adsorption| Minimal            | Substantial     |
| End-of-life-indication| Yes                | No               |
| Easy Regenerability  | Yes                 | No               |
| Flammability         | No                  | Yes              |
| Disposability        | Easy, small volume  | Difficult due to |
|                      |                     | flammability, toxicity |

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