

Novel Oxidative Fuel Desulfurization System

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The major drawback to the use of fuel cells as electric generators and auxiliary power units (APUs) by deployed forces is their inability to directly use battlefield fuels. Fuel Cells require a clean, essentially sulfur-free feed stream to prevent poisoning of the anode catalyst. TDA Research, Inc. (TDA) is developing a novel oxidative fuel desulfurization system, a key component of a compact fuel processor, to produce a sulfur-free feed for fuel cell power generators that run on high sulfur JP-8 fuel. TDA's desulfurization system uses a catalyst to first oxidize the thiophenic sulfur species in the fuel to their respective sulfones using molecular oxygen in air and then to remove the oxidized sulfur compounds with a novel regenerable, mesoporous sorbent to deliver essentially sulfur-free fuel to the fuel processor. The preliminary results from our catalyst and sorbent development efforts are presented here.

Introduction

The major drawback to the use of fuel cells as electric generators and auxiliary power units (APUs) by deployed forces is their inability to directly use battlefield fuels. Solid Oxide Fuel Cells (SOFCs) require a clean, essentially sulfur-free feed stream to prevent poisoning of the anode catalyst. Adsorptive removal of refractory sulfur species is highly attractive due to its simple operation and ease of integration with the balance of plant. A successful sorbent must exhibit very high selectivity to sulfur compounds in the presence of a large excess of aromatic and poly-aromatic species. The aromatics have a structure very similar to those of the organic sulfur compounds, making it difficult to develop an effective adsorbent with high selectivity. One way to improve sorbent selectivity is to oxidize the thiophenic sulfur compounds by electrophilic addition of oxygen atoms and convert them into their respective sulfoxides (1-oxides) and sulfones (1,1-dioxides). The chemical and physical properties of sulfoxides and sulfones are significantly different from those of the hydrocarbons in the fuel, and they are much easier to remove by selective adsorption. Early work in oxidative desulfurization (ODS) of thiophenic compounds was carried out using strong oxidizers, such as 30% vol. hydrogen peroxide (H_2O_2) and other aqueous and organic acids [1]. This approach requires Army to ship large amounts of chemicals to the battlefields in addition to the fuel, and imposes a large logistics burden (the shipment of H_2O_2 is particularly problematic due to its instability). Alternatively, molecular oxygen could be used to convert the thiophenic compounds to sulfones and/or sulfoxides.

Traditionally, hydrodesulfurization (HDS) is used to remove organosulfur compounds in refineries. HDS process is too complex and the cost of using HDS to remove sulfur compounds to sub ppm levels is far too large for fuel cell systems. Due to the major cost

advantages, most developers of the small-scale fuel cell systems have opted to remove sulfur from the feed gases using adsorbents. Several materials have been tested for desulfurization of both liquid and gaseous fuels, including a range of commercially available sorbents (i.e., zeolites, activated carbon, activated alumina). However, an important drawback of adsorbents is the fact that their sulfur uptake capacity is generally low (i.e., <1g of tetrahydrothiophene per liter of sorbent), requiring large quantities of sorbent. Hence there is a need for high capacity sorbents. High capacities will also ensure a long operating life, which would increase the interval between the periodic removals of the sorbent beds (ideally, the life of the sulfur guard bed should be equal or greater than the life of the fuel cell stack).

TDA Research, Inc. (TDA) is developing a novel oxidative fuel desulfurization system, a key component of a compact fuel processor, to produce a sulfur-free feed for fuel cell power generators that run on high sulfur JP-8 fuel. TDA's desulfurization system uses a catalyst to first oxidize the thiophenic sulfur species in the fuel to their respective sulfones using molecular oxygen in air and then to remove the oxidized sulfur compounds with a novel high capacity regenerable, mesoporous sorbent to deliver essentially sulfur-free fuel to the fuel processor. The preliminary results from our catalyst and sorbent development efforts are presented here.

TDA's Oxidative Desulfurization System (ODS)

TDA is developing a novel ODS system that uses molecular oxygen from air as the oxidizer. TDA's desulfurizer will be compact, efficient and capable of reducing the fuel sulfur content to sub ppm levels to provide maximum protection to the fuel cell electrocatalyst and all catalysts used in the fuel processor. Because our system will use air and a regenerable sorbent it will not need continual resupply of reactant chemicals. The desulfurizer is located upstream of the fuel processor and operates at or near ambient temperature. In the process, the fuel is first fed to an oxidation reactor where molecular oxygen oxidizes the thiophenic sulfur compounds to their respective sulfoxides or sulfones. The fuel and air are mixed at the inlet of the reactor prior to the catalyst bed. Following the oxidation reactor, the fuel and air (nitrogen and unreacted oxygen) are separated in a flash drum. The de-gassed fuel is then fed to an adsorbent bed, and the highly polar sulfone and sulfoxide molecules are removed using a regenerable adsorbent.

The adsorption of the sulfone on the sorbent is reversible and the sorbent is regenerated in air by applying a mild temperature swing. The desulfurizer uses two sorbent beds that switch positions using flow selection valves (Figure 1). The sorbent is regenerated at 400°C to remove the adsorbed sulfur species, which are burned with air and converted to sulfur dioxide (SO₂), which is vented. Complete desorption of sulfur species ensures full regeneration of the sorbent so that it can be used hundreds of times. The sorbent regeneration is essential for reducing the amount of expendables to be shipped to the battlefield and the resulting logistic burden. The on-system regeneration of the sorbent also eliminates any limitations on the mission duration imposed by the sorbent capacity.

In Preliminary experiments, we demonstrated the successful operation of the catalyst and the sorbent and carried out an engineering analysis to show the technical feasibility of the concept.

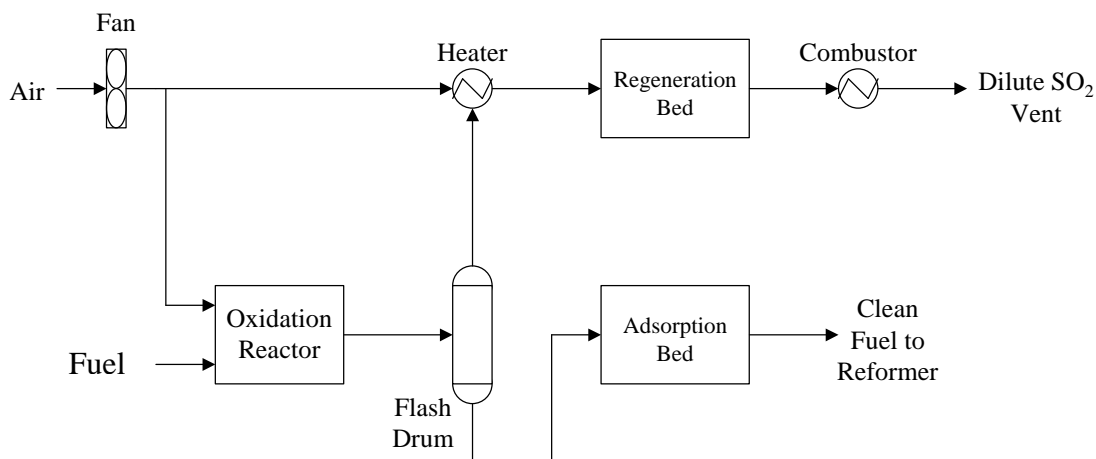


Figure 1. TDA's regenerable oxidative desulfurization system.

Catalyst Development

In the very recent literature, Rossi (2003) and Ma (2007) showed favorable properties of iron bromide and iron nitrate salts ($\text{FeBr}_3/\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) for the oxidation of thiophenic sulfur species to sulfones and sulfoxides [2,3]. Bromine is a well-known oxidizer and could oxidize the sulfur compounds homogeneously in the liquid phase. A major problem for the use of bromine as a homogeneous oxidation catalyst is the contamination of the fuel with bromine. In addition, the highly reactive bromine compounds interact with the fuel forming brominated compounds, which will be carried out from the catalytic reactor, causing degradation of the catalyst.

In preliminary experiments, we identified novel catalysts that are highly active and stable for the oxidation of the thiophenic sulfur compounds into sulfones (achieving over 95% conversion) using neat air as the oxidant near ambient conditions. In these preliminary experiments we showed that the new catalyst has shown very high stability in the fuel. Further, unlike other catalysts reported in the literature, the catalyst retained the active groups responsible for sulfur oxidation, preventing the leaching that leads to fuel contamination and degradation of catalytic activity. Further performance improvements are expected by optimizing the catalyst's active group and the support. Improving catalyst performance will be the focus of our further development work.

Sorbent Development

We developed a low temperature physical adsorbent can directly remove the sulfone species in the fuel with very high capacity (with the highest sulfur capacity reported for any sorbent to date). We showed that the mesoporous alumina support could achieve greater than 3.4 mg/g sulfur capacity when we feed 480 ppmw sulfone containing jet fuel. We demonstrated that the sorbent can also be operated in a regenerable manner by applying a mild temperature swing (400°C) through 50-cycles, with very little degradation in capacity due to cyclic operation (Figure 2).

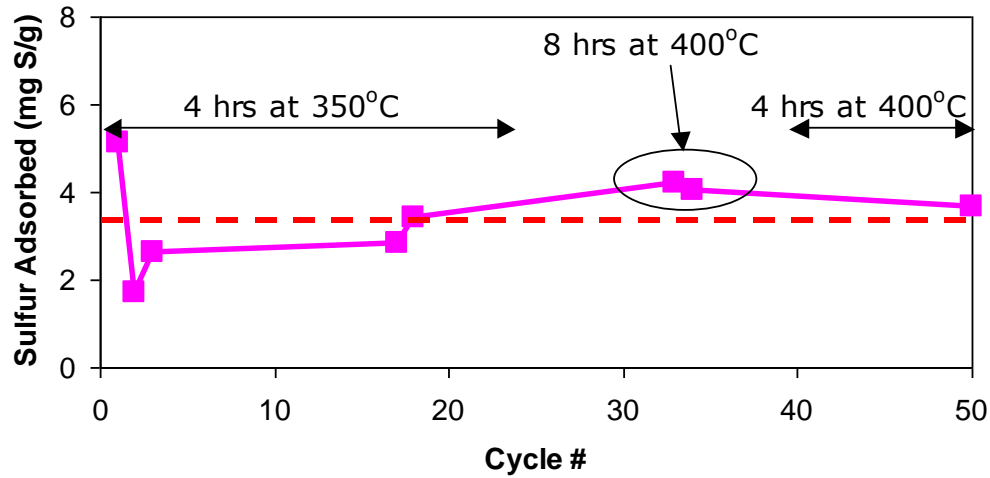


Figure 2. Multiple Cycle results on TDA's ODS Sorbent.

System Design

Based on the catalyst activity and sorbent capacity, we carried out the preliminary design of the oxidative desulfurization system including all the major components. We estimated the overall weight and volume of the system as 18 kg and 22 L, respectively. The unit dimensions are estimated as 12"x8"x14" (corresponding to 91 W/L power density) based on a conservative estimate of 3.4 mg S/g for the sorbent capacity. In the multiple cycle experiments with longer regeneration at 400°C we were able to achieve a sulfur capacity in excess of 4.1 mg S/g sulfur, which will reduce the overall weight and volume of the ODS system by 20% (corresponding to 73 W/L power density). We also estimated the parasitic power loss for the ODS system to be less than 165 W.

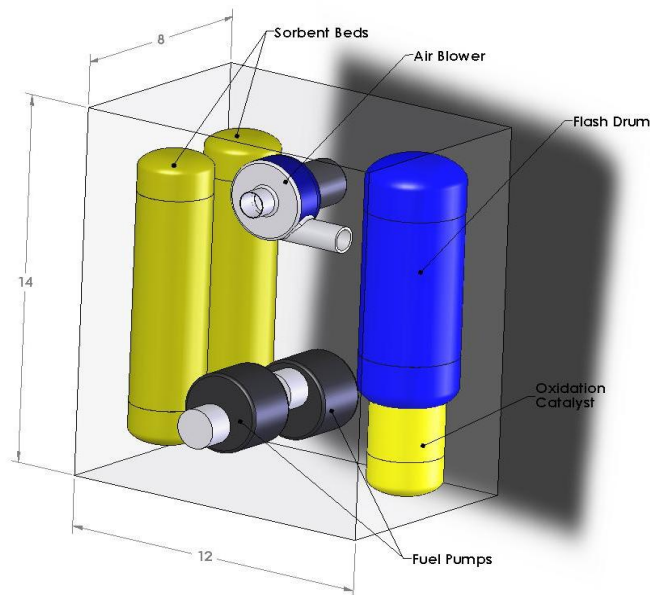


Figure 3. TDA's Oxidative Desulfurization System for a 2-kWe SOFC operating on JP-8.

Conclusions

TDA has demonstrated the feasibility of a novel JP-8 fuel desulfurization system based upon the oxidative desulfurization method that could reduce the sulfur concentration in the fuel to ppb levels to ensure long-term stable operation of a fuel cell-based power generator. TDA's oxidative desulfurization system can be used to purify the hydrocarbon feed stream to portable and also stationary commercial fuel cell systems. The proposed technology will also provide U.S. refiners with a cost-effective way to remove sulfur from various hydrocarbon feedstocks.

ACKNOWLEDGMENTS

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