DESULFURIZATION OF LOGISTIC FUELS FOR FUEL CELL APUs

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ABSTRACT

The sulfur level in logistic fuels is very high; up to 3,000 ppmw S for jet fuels (JP-8, JP-5) and 10,000 ppmw S for naval distillate (NATO F-76) compared to the commercial gasoline (30 ppmw S) and diesel (15 ppmw S). The effective utilization of logistic fuels in fuel cell applications requires removal of refractory sulfur species (organosulfur compounds) to below 0.1 ppm. Sulfur removal is critical for fuel cells and adsorption is a promising technology for reducing the sulfur content to such low levels. TDA has developed a sorbent-based fuel desulfurization system that can easily be integrated with any fuel cell fuel processor. TDA's desulfurizer removes all of the refractory organic sulfur compounds in a regenerable manner from the military fuels (both JP-5 and JP-8) while it is still in the liquid phase, and reduces the total fuel sulfur content to sub-ppm levels (e.g., less than 0.1 ppmw). TDA has built a 4-bed prototype jet fuel desulfurization system that could be integrated with a 1.5 kW fuel cell powered APU. Demonstration of the desulfurizer is being carried out with two types of jet fuels i.e., JP-5 (from ONR Fuel Cell Research Program, NAVAIR) and JP-8 (from Wright-Patterson Air Force Base in Ohio) fuels. We will be presenting test data from demonstration of the prototype desulfurization system in the conference.

1. INTRODUCTION

The effective utilization of logistic fuels in fuel cell applications requires removal of refractory sulfur species (organosulfur compounds) to below 0.1 ppm. Low temperature fuel cells (e.g. PEM) require clean (essentially pure) hydrogen feed to prevent the poisoning of the anode catalyst. Even the more robust high temperature fuel cells (e.g., solid oxide fuel cells) are poisoned with low levels of sulfur contaminants. Sulfur removal is critical for fuel cells and adsorption is a promising technology for accomplishing such low levels of sulfur. TDA has developed a sorbent-based fuel desulfurization system that can easily integrate with any fuel cell fuel processor. TDA's desulfurizer removes all of the refractory organic sulfur compounds from military fuels (both JP-5 and JP-8) while they are still in the liquid phase and reduces the total fuel sulfur content to sub-ppm levels (e.g., less than 0.1 ppmw). In order to increase the utilization of the sorbent and minimize the logistics burden and manpower associated with frequent replacements, the desulfurization system operates in a regenerable manner.

2. JET FUEL DESULFURIZATION

We observed that at higher adsorption temperatures the interaction between the sorbent and the sulfur species are stronger than the interaction between the sorbent and the unsaturated hydrocarbons. This resulted in removal of some of the hydrocarbons from the surface at higher temperature and increased the number of sorbent sites available for sulfur removal. Figure 1 shows the impact of temperature on the sulfur removal performance of the sorbent. At 90°C, the sulfur uptake of the sorbent improved significantly. However, a further increase in temperature to 120°C did not improve the sulfur capacity any further. It is anticipated that at higher temperatures the affinity of the sulfur species to the sorbent is also reduced.

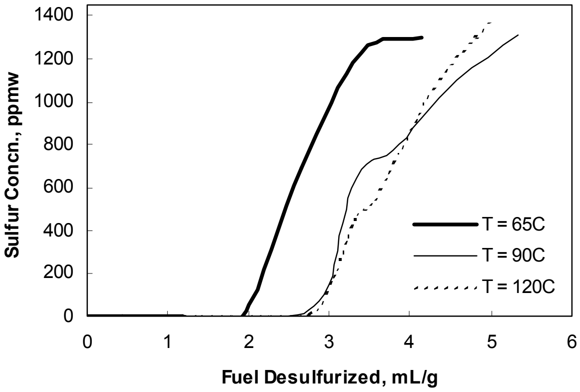

Figure 1. The impact of adsorption temperature on SulfaTrap^{TM}-D1 performance. 51 ppmw sulfur containing JP-8 fuel spiked with 700 ppmw of benzothiophene and 700 ppmw of 2-methyl benzothiophene. LHSV = 1.6 h^{-1}.

We tested our SulfaTrap^{TM}-D1 sorbent with different JP-5 fuels containing varying levels of sulfur species in them (1100, 500 and 50 ppmw S). Figure 2

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shows the impact of fuel sulfur level on the sulfur removal performance of the sorbent. The sorbent achieved very high sulfur adsorption capacities and could remove sulfur from JP-5 fuels of varying concentrations and reduce it to sub ppm levels. The sorbent could desulfurize ~ 15 mL/g of low sulfur JP-5. Hence, SulfaTrap^{TM}-D1 could be used as an expendable polishing sorbent downstream of a bulk desulfurizer. A comparison of the sorbent performance in the two types of jet fuels JP-8 and JP-5 is shown in Figure 3. The sorbent showed better performance in JP-5 than JP-8. JP-5 typically has slightly lower aromatic content than JP-8, though the US military specification is the same < 25% for both. JP-8 could also have slightly more polyaromatic hydrocarbons (PAHs) than JP-5. The presence of additives, moisture, PAHs and organo-nitrogen compounds in jet fuels can all affect the desulfurization of liquid fuels by adsorption.

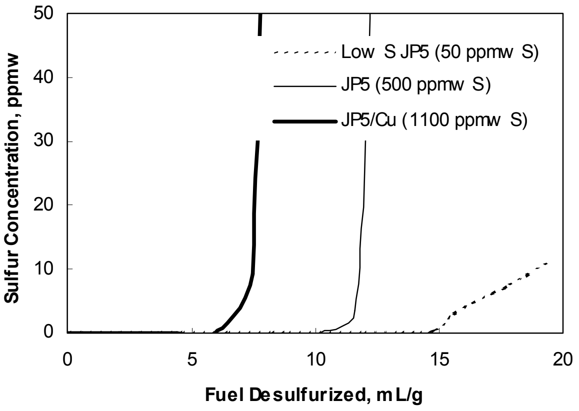

Figure 2. The impact of fuel sulfur level on SulfaTrap^{TM}-D1 performance. JP-5 fuel. T = 120°C. LHSV = 1.6 h^{-1}.

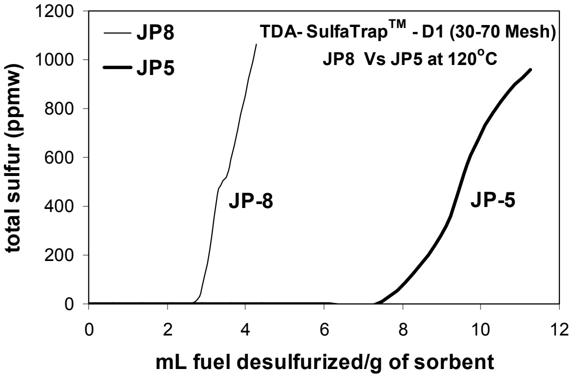

Figure 3. Comparison of sorbent performance in JP-8 and JP-5.

3. DIESEL DESULFURIZATION

We also carried out desulfurization of ultra low sulfur diesel (ULSD) containing 10.5 ppmw S with TDA-SulfaTrap^{TM}-D1. The results are provided in Figure 4. The sorbent could desulfurize 100 L of ULSD per kg of sorbent with 90+% removal efficiency. The sorbent performance improved significantly with increases in adsorption temperature and pressure. As shown in Figure 5, the sorbent was able to achieve 90+% removal efficiency while desulfurizing 300 L of ULSD per kg of sorbent (which corresponds to 165 mL/mL sorbent) and 80+% removal efficiency for 725 L of ULSD per kg sorbent (which corresponds to 400 mL/mL of sorbent). Hence, the sorbent could be used as an expendable sorbent for diesel fuel (ULSD) powered fuel cell APUs with the sorbent replacement being carried out during routine servicing of the heavy-duty vehicle.

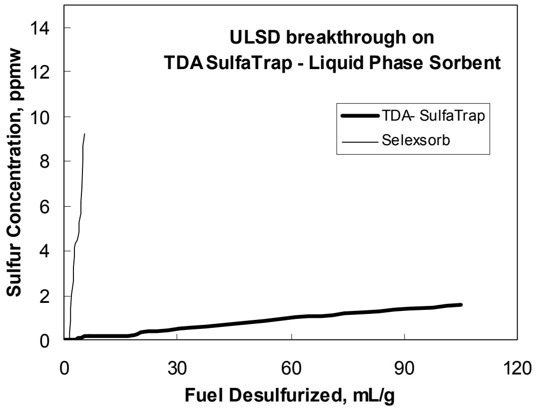

Figure 4. Diesel fuel breakthrough on TDA-SulfaTrap^{TM}-D1 sorbent. T = 120°C. LHSV = 1.6 h^{-1}.

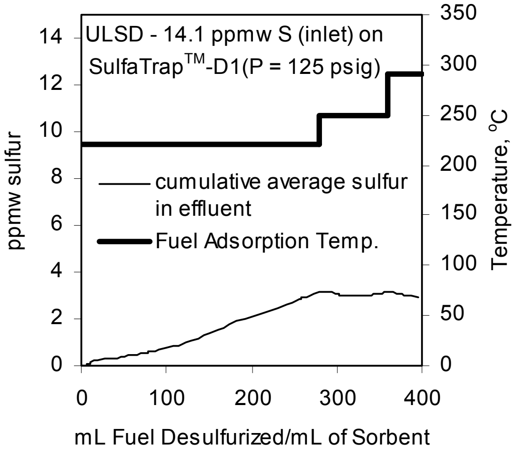

Figure 5. Diesel fuel breakthrough on TDA-SulfaTrap^{TM}-D1 sorbent at higher temperatures. P = 125 psig. LHSV = 0.8 – 1.9 h^{-1}.

4. MULTIPLE CYCLE TESTS

A regenerable system could benefit from high temperature adsorption since it reduces the time required for heating and cooling transitions. Further, TDA SulfaTrap^{TM}-D1 sorbent showed better desulfurization performance at higher temperatures. Hence, we carried out the multiple cycle tests at an adsorption temperature of 120°C. Figure 6 shows the impact of various regeneration gases on desulfurization of jet fuel (JP-5). We observed that the sorbent could be regenerated either in air and/or a reducing gas at 400-450°C. We also carried out a multiple cycle test (90 cycles) of SulfaTrap^{TM}-D1 sorbent with air regeneration. The use of air regeneration allowed us to cool the system rapidly and minimized the cooling time. Figure 7 shows the summary of the results from the 90-cycle test. The sorbent showed a stable breakthrough capacity of 0.9-1.1 mL/g over 90 cycles in a 500 ppmw S JP-5 fuel. We optimized the regeneration time and temperature during these experiments and found that a regeneration time of 2-4 hrs at 400°C was sufficient to remove the adsorbed sulfur compounds.

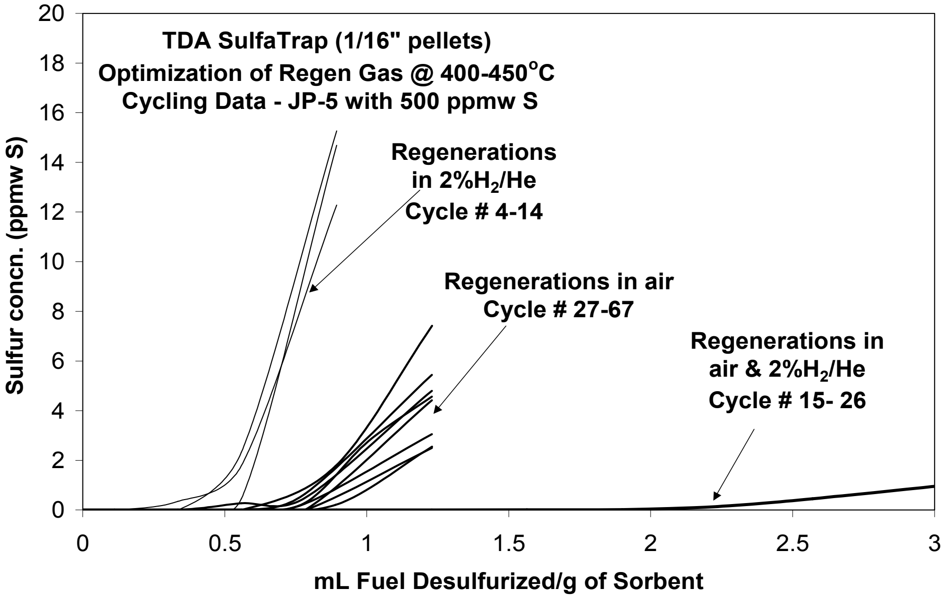

Figure 6. The impact of regeneration gas on desulfurization of jet fuel by SulfaTrap^{TM}-D1. T = 120°C. LHSV = 0.8 h^{-1}.

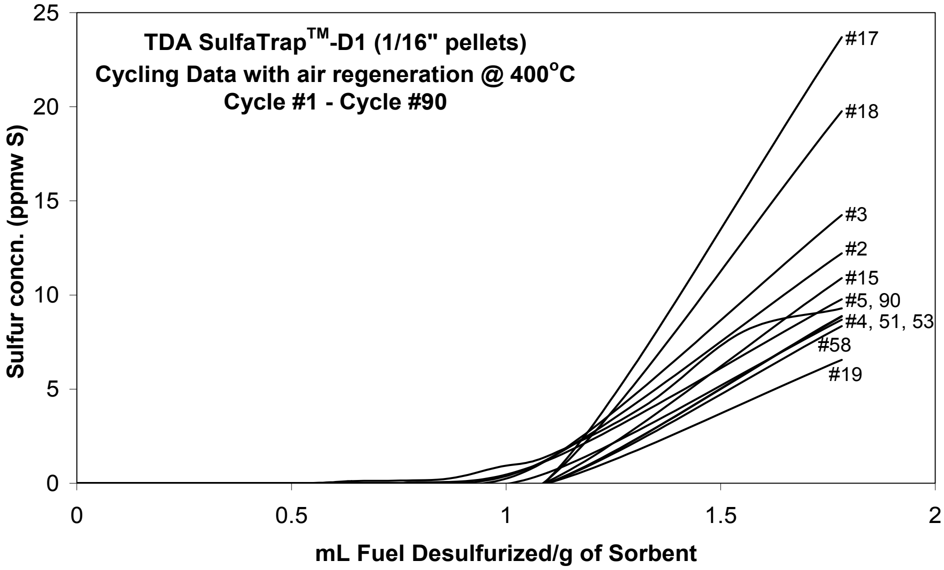

Figure 7. Multiple cycle test results with JP-5 (500 ppmw S) on TDA-SulfaTrap^{TM}-D1 sorbent. T = 120°C. LHSV = 0.8 h^{-1}.

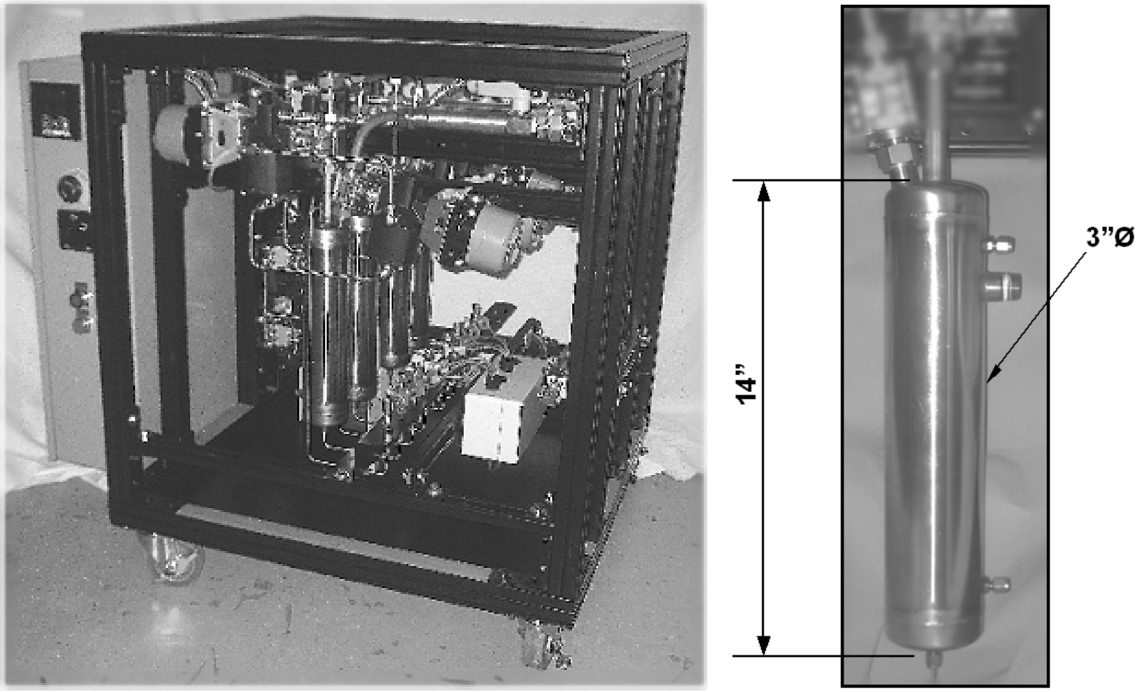

Figure 8. TDA's 4-bed prototype jet fuel desulfurization system.

5. TDA's PROTOTYPE LOGISTIC FUEL DESULFURIZATION SYSTEM

TDA has built a 4-bed prototype jet fuel desulfurization system that could be integrated with a 1.5 kW fuel cell powered APU.

Figure 8 shows the picture of TDA's 4-bed prototype desulfurization system. The system was designed for easy access and modification and is therefore far larger than a commercial unit; note that the unit is virtually all empty space. The desulfurizer system is sized to treat up to 10 mL/min fuel flow rate with sulfur contamination levels up to 3,000 ppmw. The sorbent beds are 1.5L in volume each. The system is equipped with various pumps, valves and heaters and is operated using LabView control software. Demonstration of the desulfurizer is being carried out with two types of jet fuels i.e., JP-5 (from ONR Fuel Cell Research Program, NAVAIR) and JP-8 (from Wright-Patterson Air Force Base in Ohio) fuels. We will be presenting test data from demonstration of the prototype desulfurization system in the conference.

CONCLUSIONS

TDA's liquid fuel desulfurization system reduces the sulfur level in the logistic fuels to sub ppm levels making them suitable for use in military fuel cells. TDA's desulfurization technology will enable the deployment of fuel cell powered APUs in the field for silent and other strategic missions.

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