# Desulfurization of Liquid Fuels by Adsorption

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# Introduction

- **In 2006 the EPA reduced the allowable sulfur levels in liquid fuels**
- **Gasoline sulfur limit was reduced from 300 ppmw to 30 ppmw**
- **Diesel fuel sulfur limit was reduced from 500 ppmw to 15 ppmw**
- **Sulfur must be further reduced to sub ppm sulfur levels for fuel cell applications**
- **TDA is developing the SulfaTrap™ line of physical adsorption-based, expendable and regenerable sorbents for liquid phase desulfurization**
- **In this presentation we demonstrate the technical feasibility of the concept**
  - Sulfur capacity, removal efficiency, regenerability and stability

# Transportation Applications

- **Commercial vehicles could benefit from use of a fuel cell auxiliary power unit (APU) to increase efficiency and comply with noise and emission regulations**
  - The potential fuel savings provided by improved fuel efficiency could exceed $2 billion per year
  - The power need for the truck-based APUs are 2-3 kWe
- **Another application in diesel vehicles is to protect the catalyst/sorbent used in NOx traps**
- **The use of Ultra Low Sulfur Diesel (ULSD < 15 ppmw S) eases the desulfurization requirement**
  - Sulfur content of the ULSD fuel still needs to be reduced to ppb levels

**Heavy Duty Truck**
Diesel

**Recreational Vehicles**
Diesel, LPG


**Truck and Trailer Refrigeration**
Diesel



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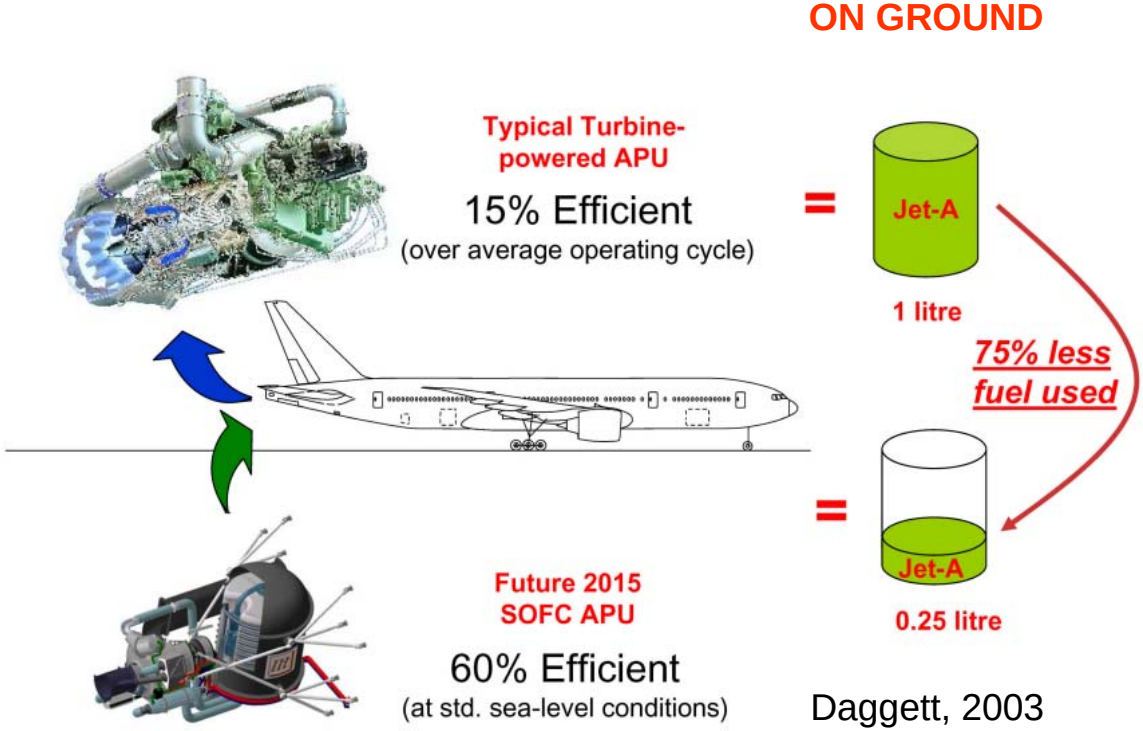
# Transportation Applications




Daggett, 2003

- **Fuel cell powered APUs for large commercial aircraft reduce the fuel use by ~ 75% compared to turbine powered APUs**
- **Improved fuel efficiency in fuel cell – APUs greatly reduces the ground and overall emissions**
- **Noise from the fuel cell and catalytic combustor are predicted to be negligible, benefiting the future airport APU operation restrictions**



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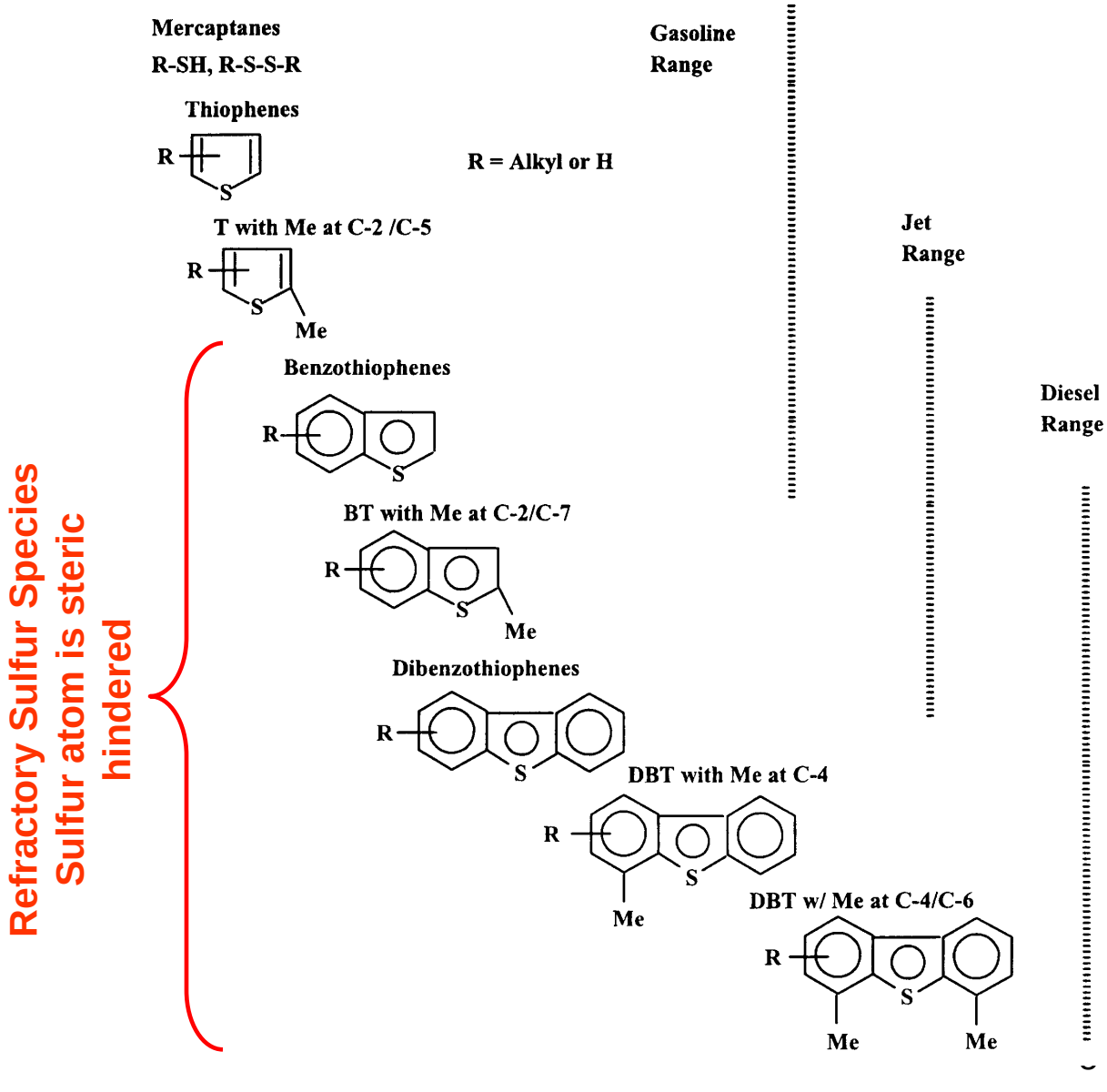
# Sulfur in Liquid Fuels

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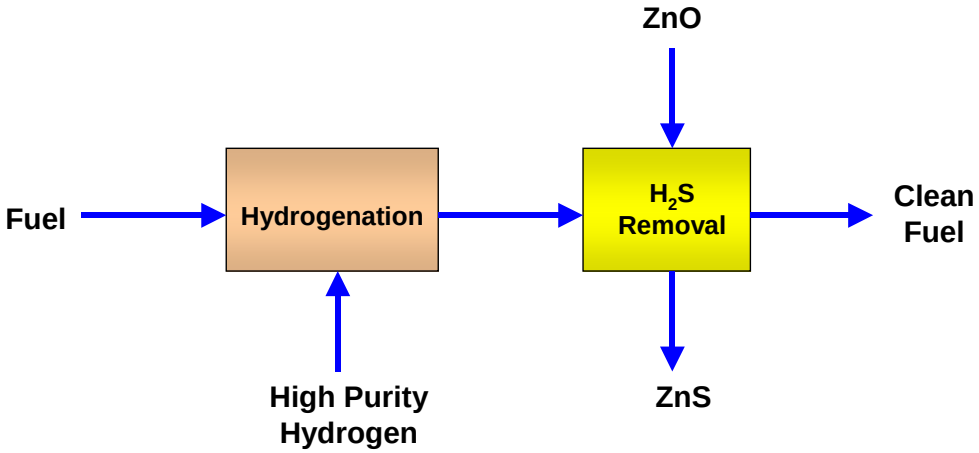
# Effect of Sulfur on Fuel Cells

- **Sulfur is a known poison for both high (e.g., SOFCs) and low temperature fuel cell (e.g., PEMFC) electrocatalysts**
- **Even sub-ppm levels of $H_2S$ degrades performance of the SOFCs**
  - **0.3 ppmv sulfur reduces performance by approximately 15%**
  - **$H_2S$ poisons the Ni-based anode catalyst**
  - **Sulfur poisoning is reversible if the inlet sulfur concentration is low**
- **The impact of $H_2S$ on low temperature fuel cells is even more detrimental, the poisoning effect is <u>not</u> reversible**
- **The catalysts used in the steam reforming, WGS and PROX steps are also very sensitive to sulfur**

# Conventional Desulfurization

- **Conventionally, the deep sulfur removal is achieved by HDS**
- **The common metal oxide sorbents cannot directly remove organosulfur species, requiring the conversion of all sulfur to $H_2S$**
  - Sulfur atom is steric hindered preventing sulfur/sorbent interaction




- **Two-step, complex process**
- **Requires high purity, high pressure $H_2$, not feasible for fuel cells**
- **Ultra deep desulfurization with state-of-the-art catalysts requires a 7-fold increase in reactor size**
- **Hydrogen consumption also increases very sharply at very low product sulfur levels**



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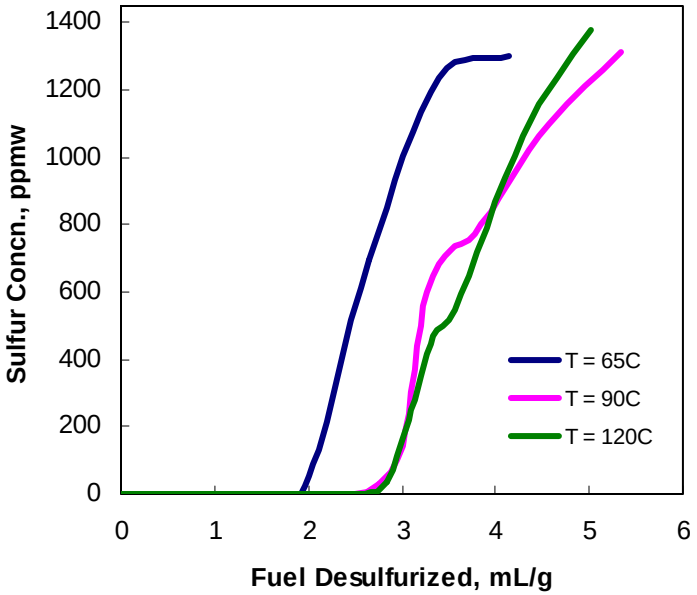
# Sorbent Specifications

- **TDA Research, Inc. is developing a regenerable, physical adsorbent for ambient (or low) temperature desulfurization of transportation and logistics fuels**
- **Requirements on the sorbent**
  - High sulfur adsorption capacity
    - Small size
  - Regenerability
    - Small size
    - Long life, reduces replacement frequency
  - Low cost
  - Reducing total sulfur concentration to sub-ppm levels
  - Inertness
    - High selectivity to sulfur
    - Must not catalyze undesirable side reactions (the fuel composition should not be altered)
  - Ease of handling and disposal
    - No toxicity, flammability, pyrophorocity

# SulfaTrap™-D1: JP-8 Desulfurization

**JP-8 fuel with 1,450 ppmw sulfur content, LHSV= 1.6 $h^{-1}$**




**Sulfur Breakthrough capacities as a function of temperature**

| Ads. Temp. (°C) | Breakthrough Capacity (% wt.) | Saturation Capacity (% wt.) |
|---|---|---|
| 65 | 0.22 | 0.28 |
| 90 | 0.28 | 0.42 |
| 120 | 0.30 | 0.41 |

- At higher temperatures the sorbent's interactions with unsaturated hydrocarbons are significantly weaker than those with sulfur.
- At 90°C, the sulfur uptake of the sorbent improved significantly. However, a further increase in temperature to 120°C did not further improve the saturation capacity because the interactions with sulfur also becomes weaker.
- Higher temperature adsorption reduces the ΔT for regenerable systems



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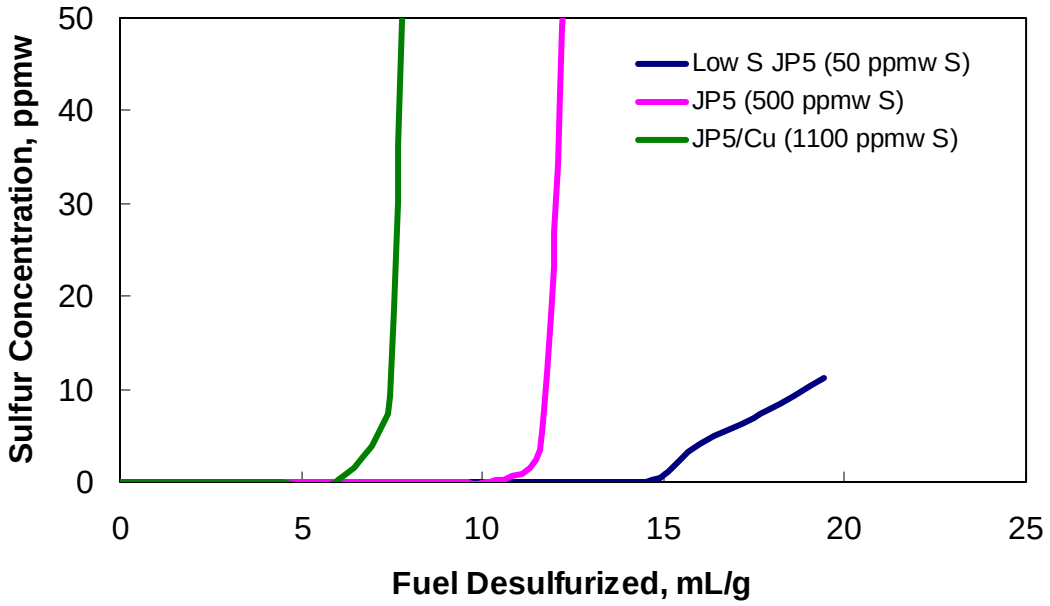
# SulfaTrap$^{TM}$-D1: JP-5 Desulfurization

**JP-5 fuel – $T_{ads}$ = 120°C, LHSV= 1.6 $h^{-1}$**




**Sulfur Breakthrough capacities as a sulfur level**

| Sulfur concn. (ppmw S) | Breakthrough capacity (% wt.) |
|---|---|
| 1100 | 0.66 |
| 500 | 0.46 |
| 50 | 0.06 |

- **TDA's SulfaTrap$^{TM}$-D1 achieved very high sulfur adsorption capacities**
- **Sorbent could remove sulfur from JP-5 fuels of varying concentrations and reduce it to sub ppm levels**
- **Since the sorbent can desulfurize ~ 15 mL/g of low sulfur JP-5. It can be used as an expendable polishing sorbent.**



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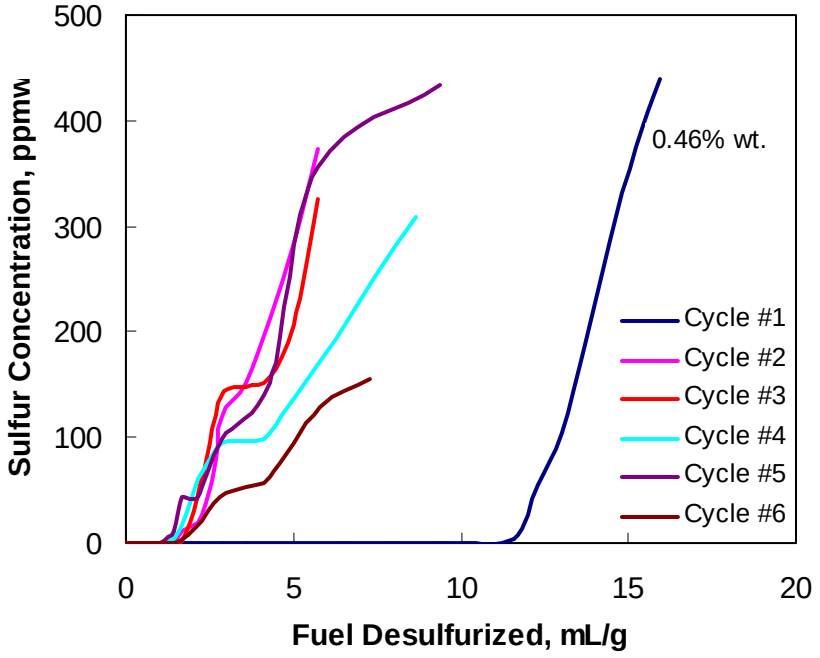
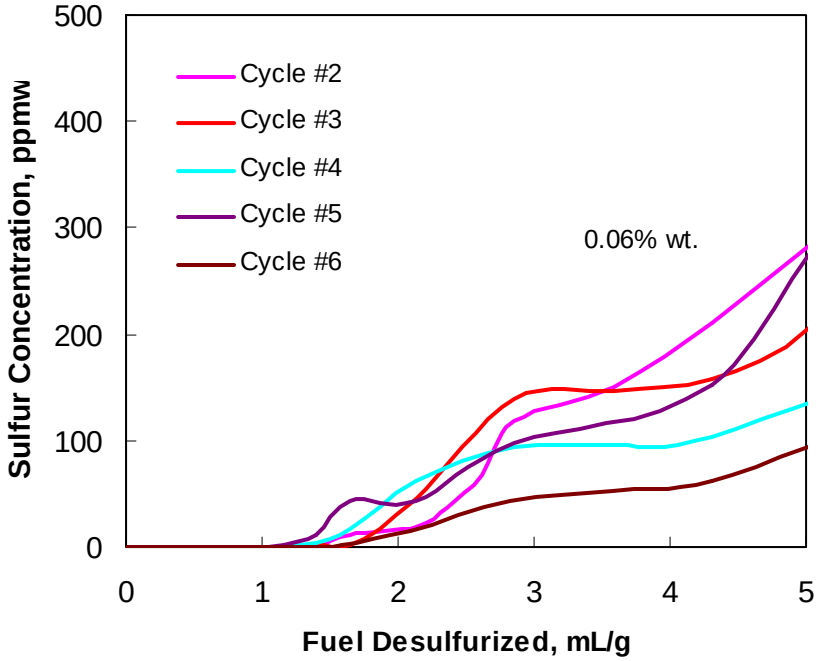
# SulfaTrap™-D1 Regeneration with Fuel Gas

**T=120°C, JP-5 fuel with 500 ppmw sulfur content, LHSV= 1.6 $h^{-1}$**




- **We carried out 6 cycles using reducing gas 2%$H_2$/He at 350°C for sorbent regeneration**
- **After an initial decline, the sorbent maintained a stable 0.06% wt. breakthrough (0.20% wt. saturation) capacity while reducing the sulfur content to less than 1 ppmw**



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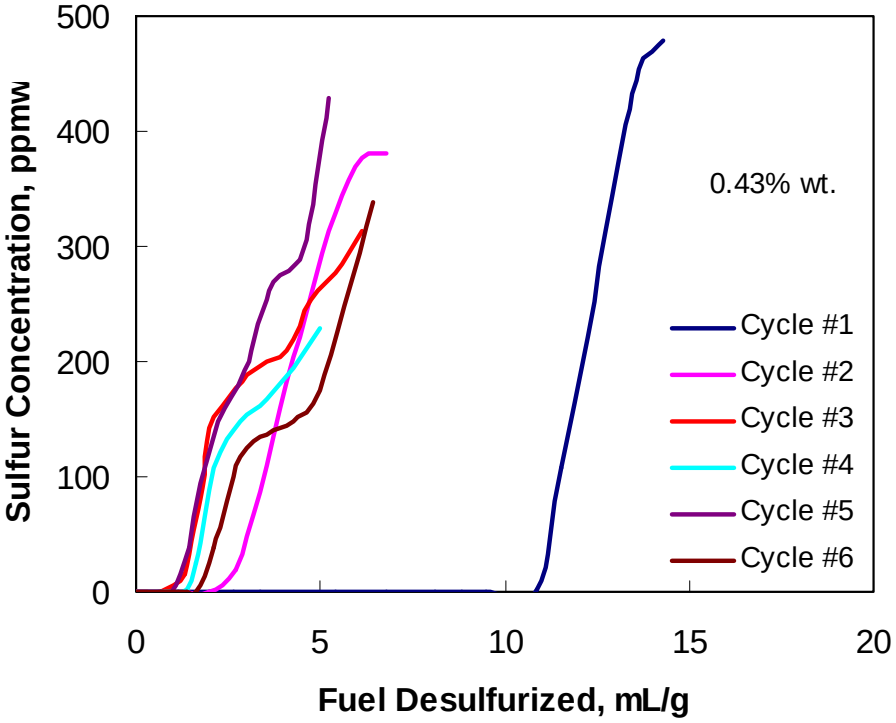
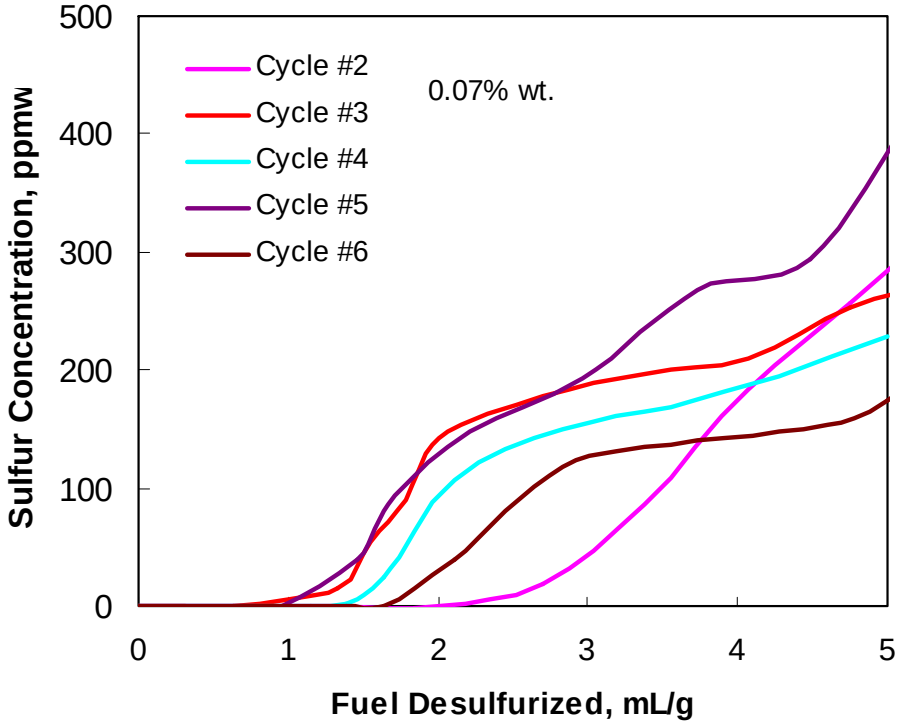
# SulfaTrap™-D1 Regeneration with Air

**T=120°C, JP-5 fuel with 500 ppmw sulfur content, LHSV= 1.6 $h^{-1}$**




- **We carried out 6 cycles using air at 350°C for sorbent regeneration**
- **After an initial decline, the sorbent maintained a stable 0.07% wt. breakthrough (0.20% wt. saturation) capacity while reducing sulfur content to less than 1 ppmw**



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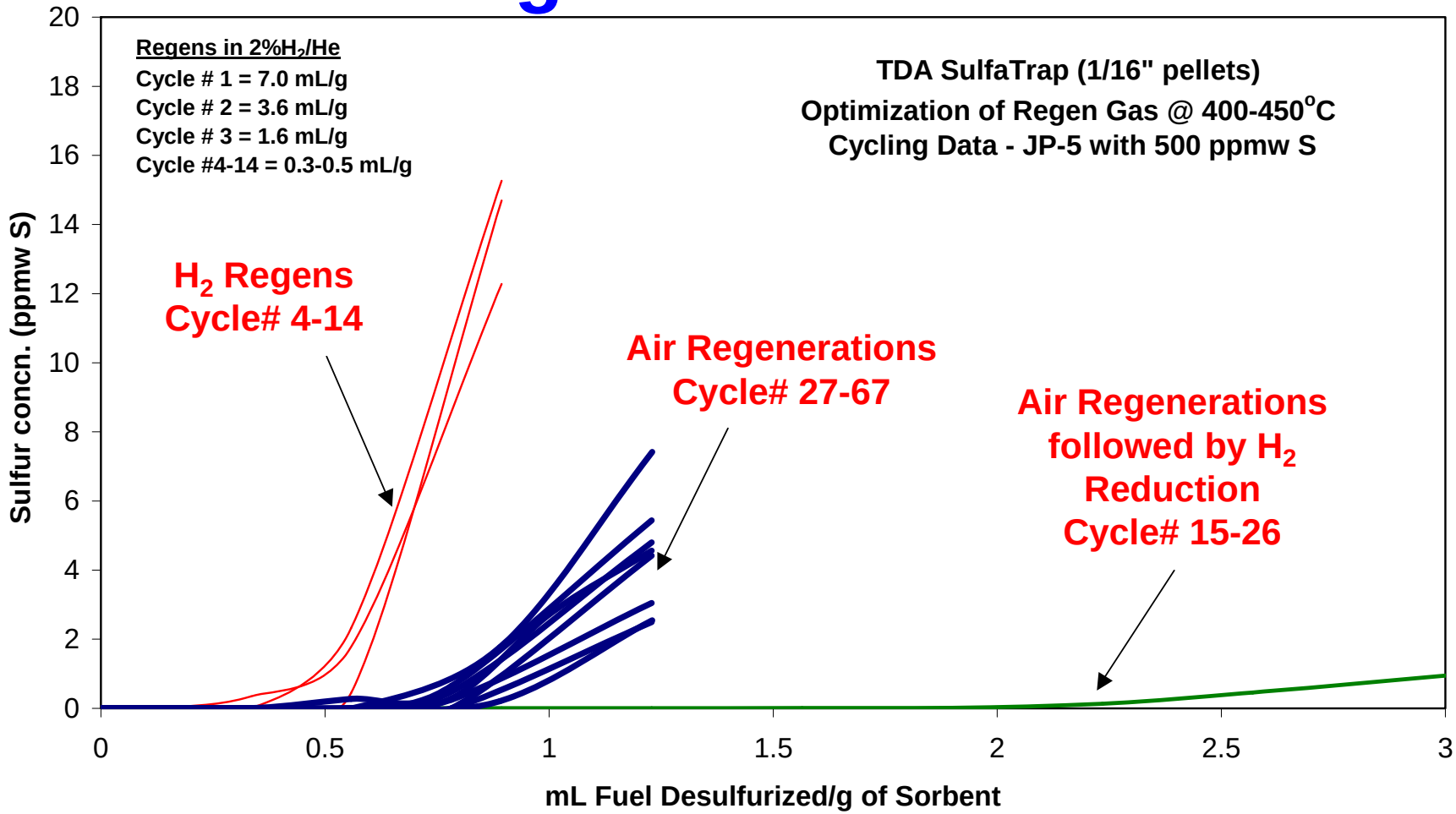
# SulfaTrap™-D1: Impact of Regeneration Gas




- **TDA's SulfaTrap™-D1 sorbent can be regenerated either by using hot air, reducing gas or an inert gas**



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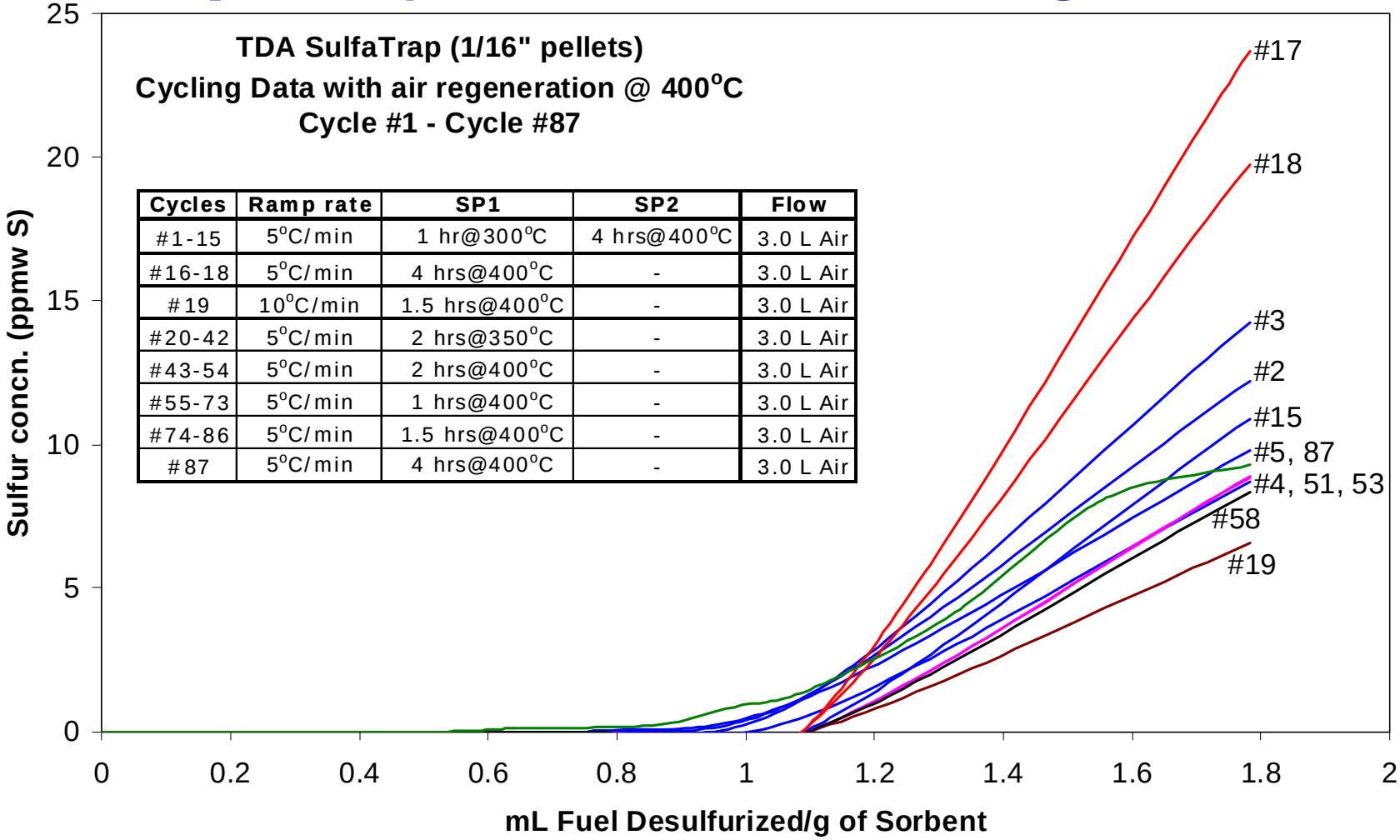
# Multiple Cycles with Air Regeneration




| Cycles | Ramp rate | SP1 | SP2 | Flow |
|---|---|---|---|---|
| #1-15 | 5°C/min | 1 hr@300°C | 4 hrs@400°C | 3.0 L Air |
| #16-18 | 5°C/min | 4 hrs@400°C | - | 3.0 L Air |
| #19 | 10°C/min | 1.5 hrs@400°C | - | 3.0 L Air |
| #20-42 | 5°C/min | 2 hrs@350°C | - | 3.0 L Air |
| #43-54 | 5°C/min | 2 hrs@400°C | - | 3.0 L Air |
| #55-73 | 5°C/min | 1 hrs@400°C | - | 3.0 L Air |
| #74-86 | 5°C/min | 1.5 hrs@400°C | - | 3.0 L Air |
| #87 | 5°C/min | 4 hrs@400°C | - | 3.0 L Air |

- **TDA's SulfaTrap™-D1 sorbent maintained its capacity for 87 cycles**



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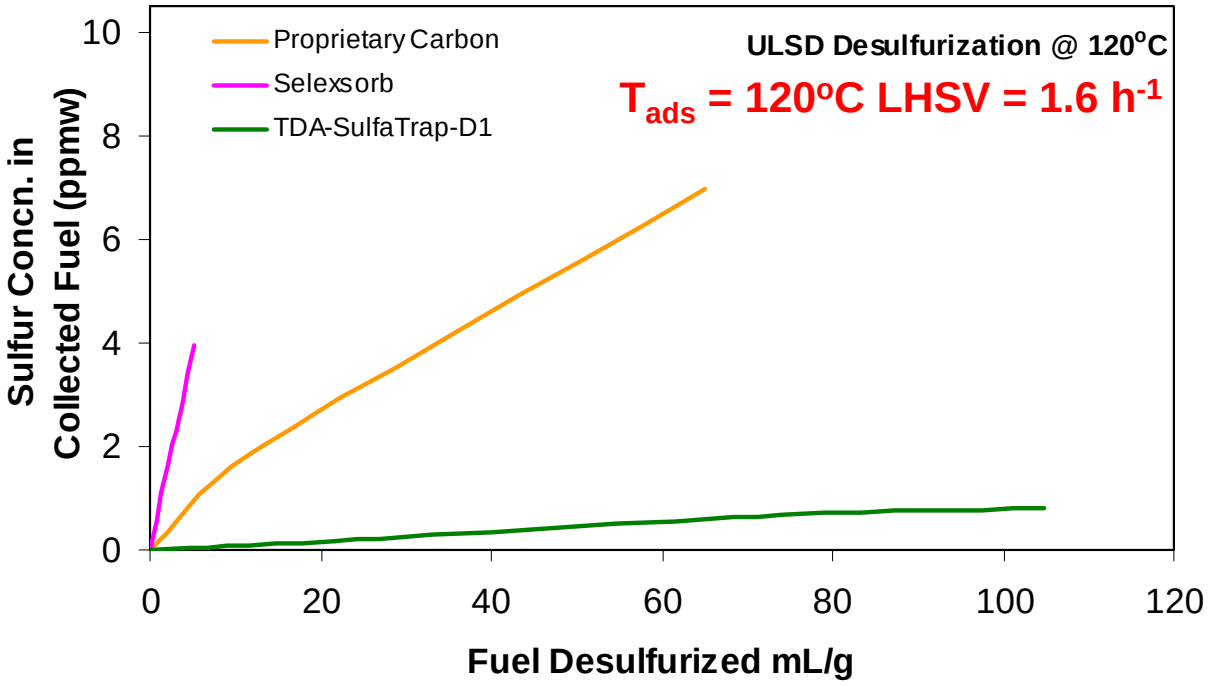
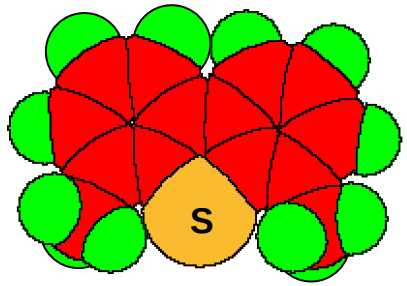
# SulfaTrap™-D1: Diesel Desulfurization




4,6-dimethyl dibenzothiophene




- **TDA's SulfaTrap™-D1 the Liquid Phase Sorbent can desulfurize 100 L of ULSD per kg sorbent with 90+% removal efficiency**
- **It can be used as an expendable sorbent for diesel fuel powered fuel cell APUs**
- **The sorbent replaced during routine servicing of the vehicle**
- **The sorbent can be reused after regeneration in a centralized location**



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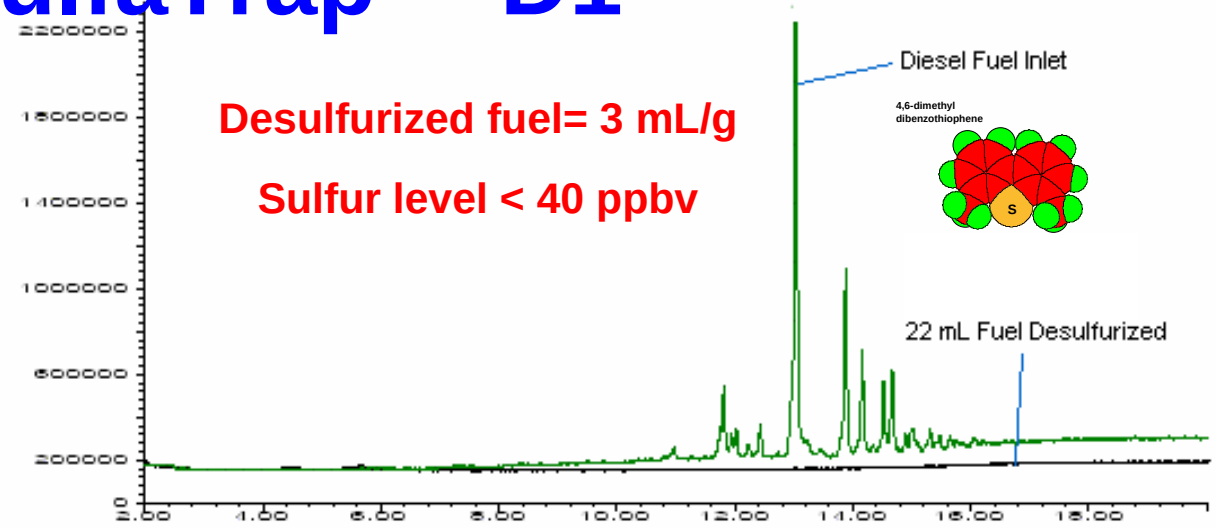
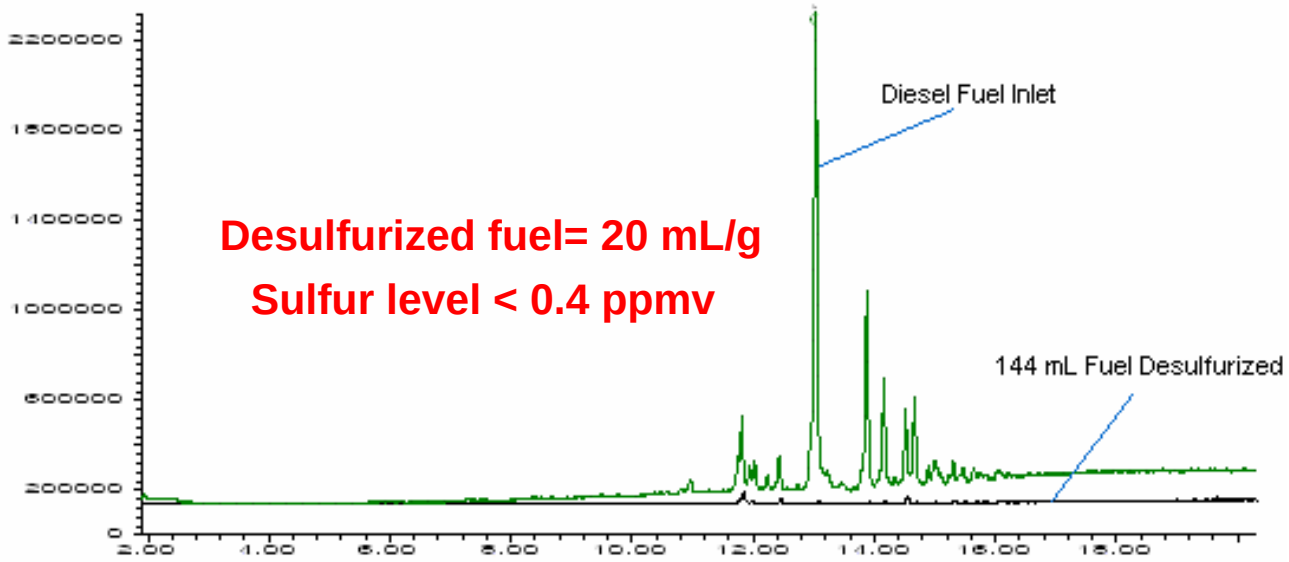
# Diesel – Sulfur Breakthrough on SulfaTrap™-D1

**T=120°C, Sulfur Content= ~10.5 ppmw, LHSV= 1.6 $h^{-1}$**




- **TDA sorbent could effectively desulfurize the ultra low diesel fuel for fuel cell applications**



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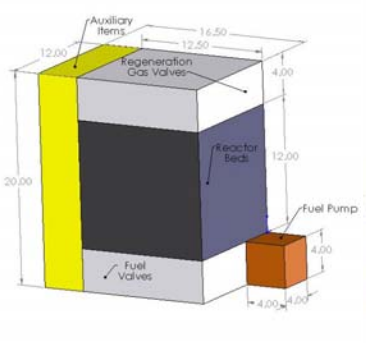
# Desulfurizer Design

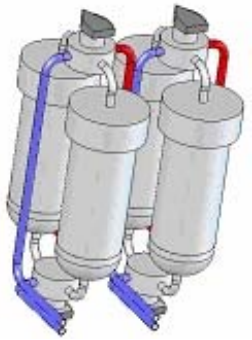
## Diesel – Desulfurizer (Expendable)

| | | |
|---|---|---|
| APU Size | 3 | kWe |
| Fuel Flow Rate | 9.7 | mL/min |
| Fuel Sulfur Content | 15 | ppmw S |
| Hours of Operation | 10 | per day |
| Replacement Frequency | 1.5 | months |
| Sorbent Capacity | 100 | mL/g |
| Sorbent Density | 0.56 | g/cc |
| Sorbent required (wt.) | 2.6 | kg |
| Sorbent required (vol.) | 1.2 | gallons |

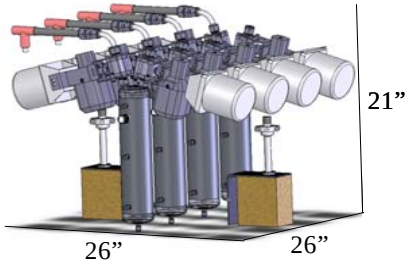
- **Diesel fuel sulfur level is < 15 ppmw S. Hence sorbent could be used in expendable mode to remove sulfur.**
- **Sorbent required is 1.2 gallons of SulfaTrap™-D1 for a service interval of 1.5 months**
- **The sorbent can be reused after regeneration in a centralized location**

## Jet Fuel – Desulfurizer (Regenerable)



**4- bed Desulfurizer Unit (Final Design)**




**4- bed Prototype Desulfurizer Unit (to be delivered in April 2008)**

- **Jet fuel sulfur level could be as high as 3,000 ppmw S. Hence sorbent needs to be used in regenerable mode to remove sulfur.**
- **System dimension for 4-bed desulfurizer unit for 1.5 kWe APU is 20”x16.5”x12”**



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# Conclusions

- **SulfaTrap™-D1 has very good capacity for Jet fuel desulfurization**
- **SulfaTrap™-D1 used as an expendable polishing sorbent for low sulfur jet fuels**
- **SulfaTrap™-D1 is regenerable in air and/or reducing gas at 400-450°C**
- **SulfaTrap™-D1 showed stable cyclic capacity with air regeneration in a 87-cycle test**
- **SulfaTrap™-D1 showed very good performance for ULSD desulfurization**
- **SulfaTrap™-D1 could be used in expendable mode in Diesel vehicles to protect the NOx traps and the fuel cell - APUs**