U.S. Army Research, Development and Engineering Command

2015 Joint Service Power Exposition

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Regenerable Desulfurization of JP-8 for Fuel Cell Power Units

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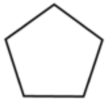
Presentation Outline

- Background
- Program Objectives/Goals
- JP-8 Desulfurizer Design and Operating Parameters
- Performance Results
- Summary
- Questions

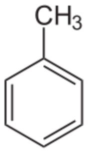
Logistics Fuel Processing Challenges

- JP-8 Fuel
  - JP-8 is a complex hydrocarbon mixture.
  - Boiling range is broad (160 ^{o}C – 300 ^{o}C) making vaporization a challenge.

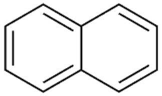
alkanes



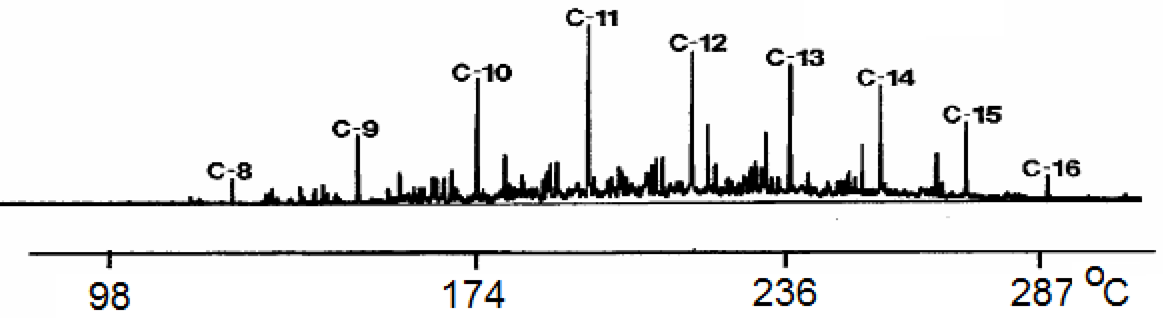
cyclo-alkanes



aromatics

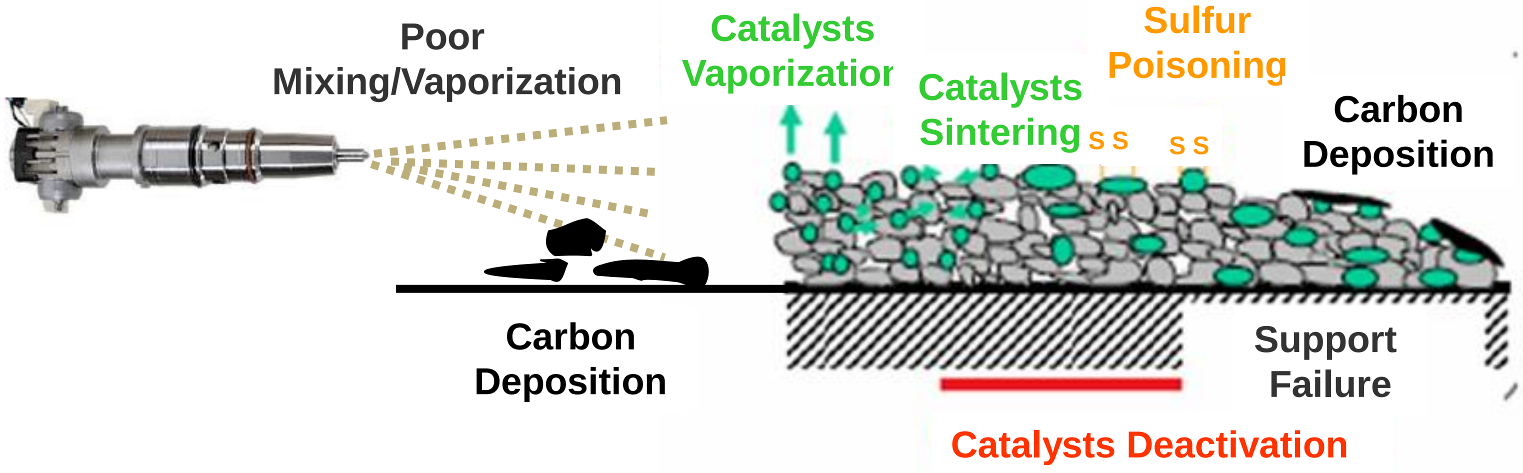


poly-aromatics



- Complex Blend of 100’s of hydrocarbons
- Varies by petroleum feedstock, refinery, season, and daily.
- Contains relatively high levels of sulfur.

JP-8 Fuel Processing Challenges



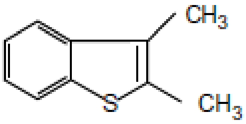
- Logistic Fuel Reforming
  - Catalysts deactivation by carbon deposition and sulfur are primary technology challenges
  - Improper control and/or mixing can lead to both hot and cold spots within the reactor contributing to deactivation.
  - Good operating window can be narrowly defined. [temperature, steam/carbon ratio, oxygen/carbon ratio, fuel flow (space velocity)]

- System Integration
  - Thermal and physical integration
  - Water balance
  - Operating considerations

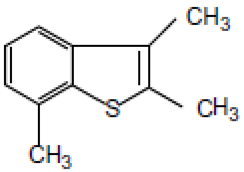
Logistics Fuel Processing Challenges

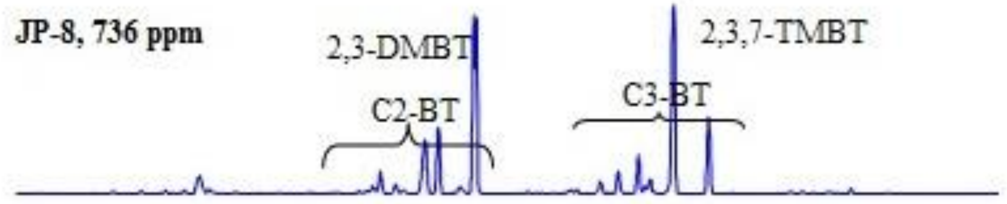
- Logistics Fuel (Diesel and JP-8)
  - Sulfur content

2,3-Dimethylbenzothiophene

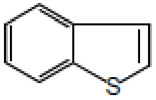


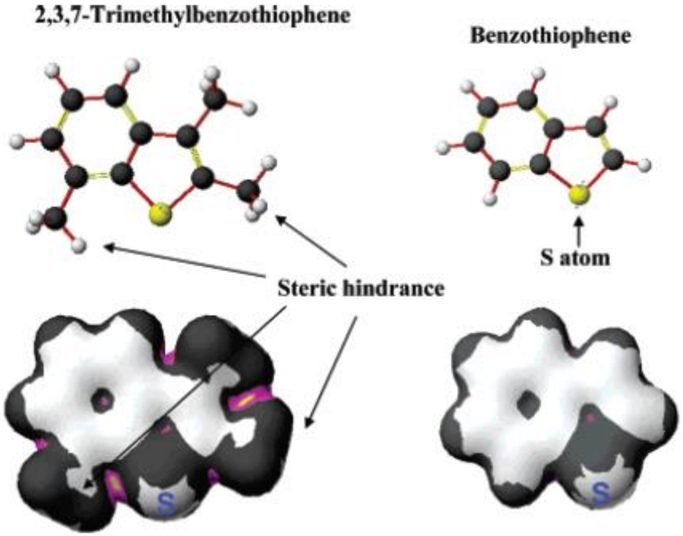
2,3,7-Trimethylbenzothiophene





Benzothiophene





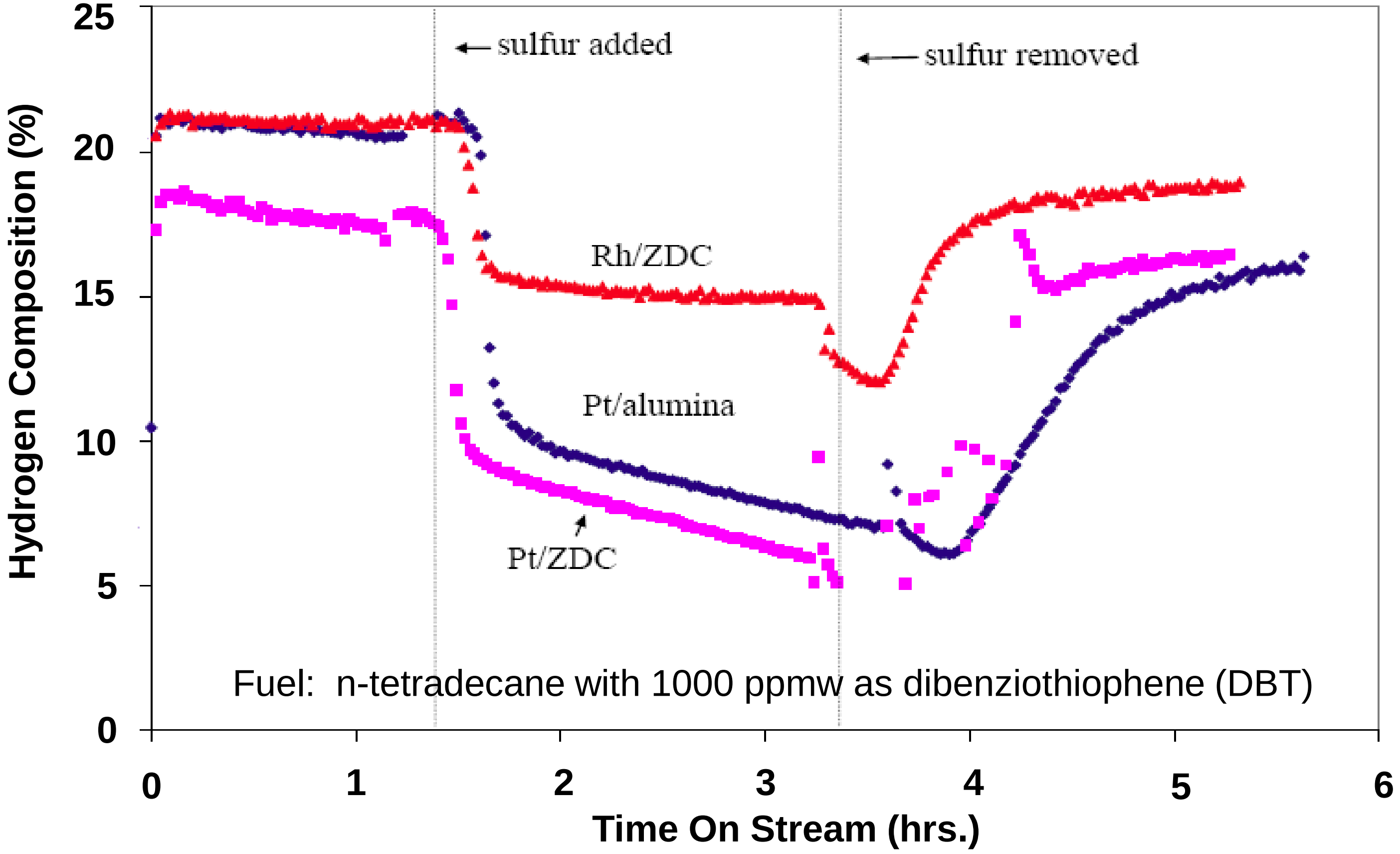
Electron Density Iso-surface

- Numerous organo-sulfur compounds can be found in JP-8.
- 2,3-dimethylbenzothiophene and 2,3,7-trimethylbenzothiophene have been suggested as best representative compounds.
- Steric hindrances present in more refractory compounds makes sulfur sorption difficult.

Subramani Velu, Xialiang Ma, Chunshan Song, Mehdi Namazian, Sivakumar Sethuraman, and Guhanand Venkataraman. Desulfurization of JP-8 Jet Fuel by Selective Adsorption over a Ni-based Adsorbent for Micro Solid Oxide Fuel Cells. *Energy Fuels*, **2005**, 19 (3), 1116-1125.

Effects of Sulfur on Catalysts Performance

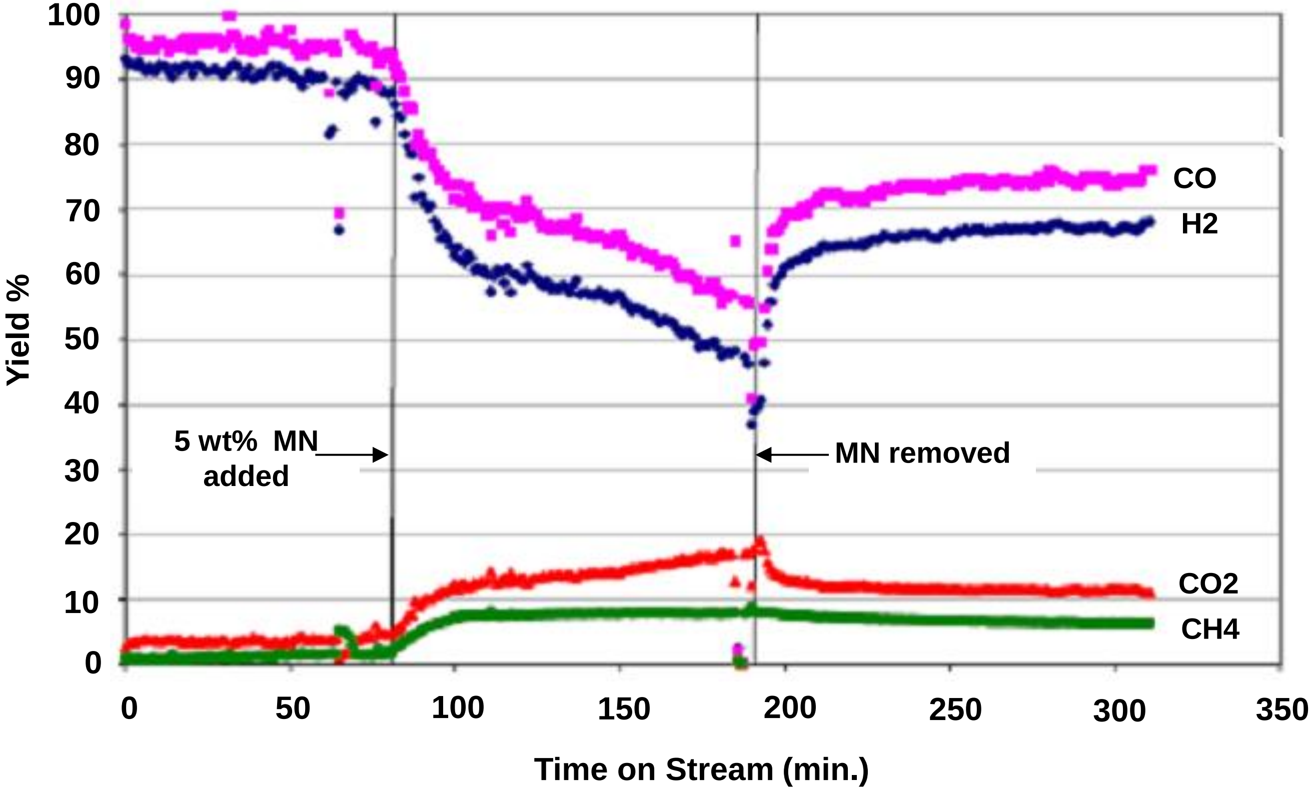
- Some catalysts exhibit good “sulfur tolerance”, but most, if not all catalysts perform better with low or no organic sulfur content.



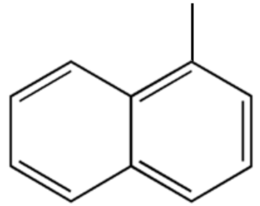
Source: Spivey, J, Haynes, D, Salazar-Villaphando, M., Berry, D., Shekawat, D., Gardner, T, “Evaluation of fuel reforming catalysts for logistics fuel cell applications,” *6th Annual Logistics Fuel Reforming Conference*, May 15-16, 2006.

Effects of PAH on Catalysts Performance

- Poly-aromatic content in fuels has been shown to result in irreversible deactivation in CPOx/ATR reformers.



Step response of LRZ after addition of 5 wt% MN (O/C = 1.2, 0.23 MPa, 900 ^{o}C and 50,000 scc/gcatalysts/hr.



1-methylnaphthalene (MN)

- **CPOx at O/C = 1.2; Fuel = n-tetradecane w/ 5% 1-methylnaphthalene.**
  - **Significant negative effect with permanent catalysts deactivation.**

Source: Haynes, D., (2007), "The Catalytic Partial Oxidation of N-tetradecane on Rh and Sr Substituted Pyrochlores," M.S. Thesis, Louisiana State University, May 2007.

Introduction

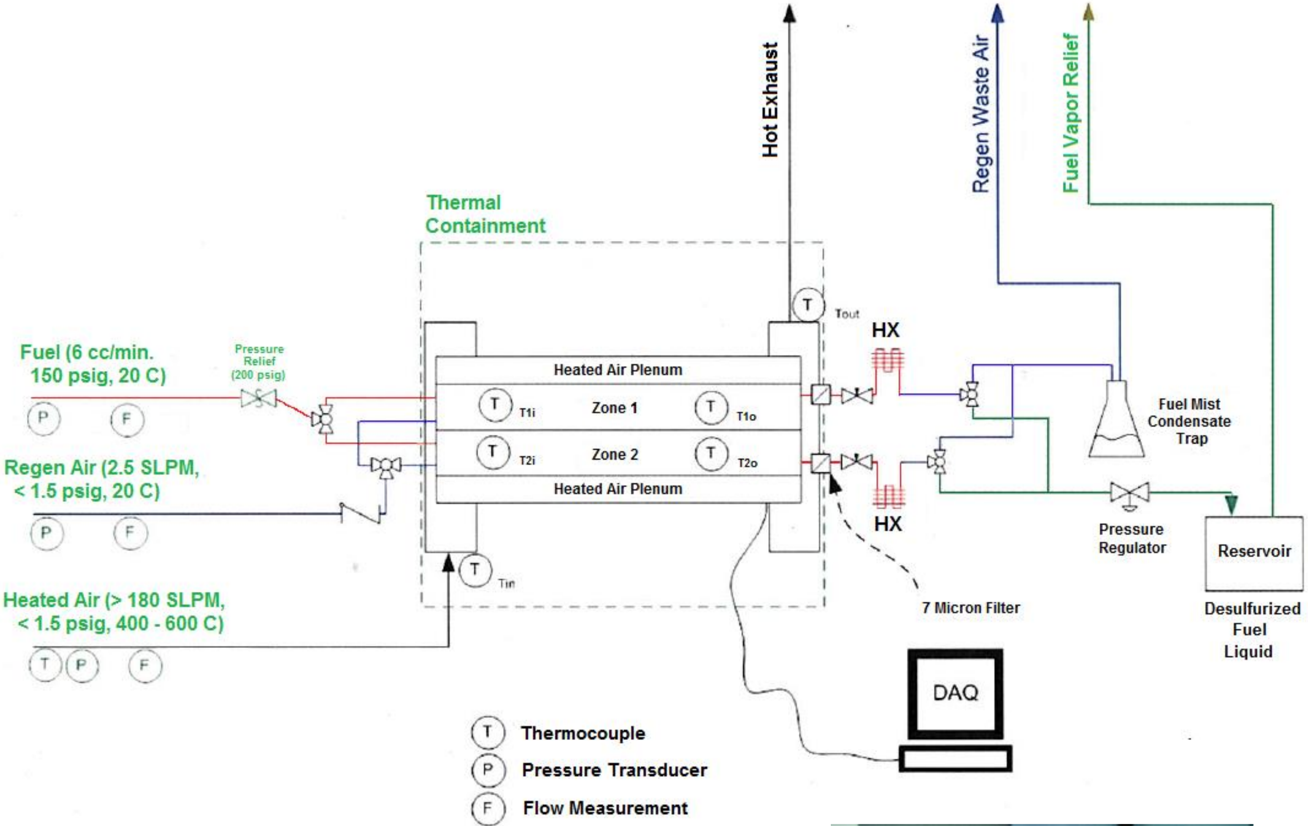
Objective:

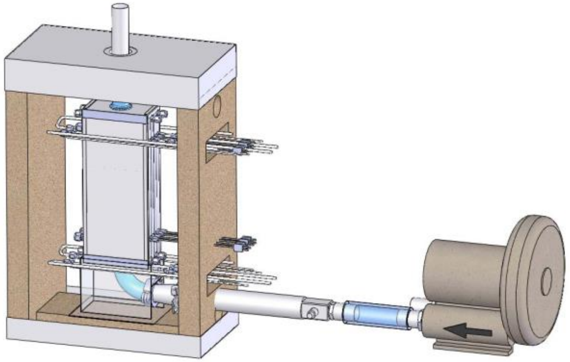
Evaluate mixed metal oxide compounds for air regenerable JP-8 desulfurization.

- JP-8 fuel: desulfurization to ≤ 10 ppmw with 1000 ppmw JP-8 input fuel.
- Single pass yield ≥ 90%.
- Lifetime of ≥ 1000 hrs.

Fuel (Diesel/JP-8)	Objective	Threshold
Production Rate (ml/min.)	12	6
Organic sulfur content (ppm)	1000	400
Aromatic (%)	25	20
Start-up		
Lab Demo (@21 ^{o}C, min.)	≤20	≤30
Thermal Cycles	100	60
Lifetime (hrs.)	1000	800
Turn down ratio	10:1	5:1
Acoustic signature (dBA @ 7m)	50	55

Experimental Setup





- Dual Bed Design
- Absorbent: mixed metal oxides and some catalytic materials
- Bed Volume = 0.80 L/bed
- Absorbent mass = 680 gm/bed
- Operating Pressure = ~150 psig
- Nominal adsorption temperature = 450 °C
- Power Consumption:
  - Ctrl = 15.1 W
  - Fan = 40.8 W
  - Bed Heater = 1500W

Analytical Methods

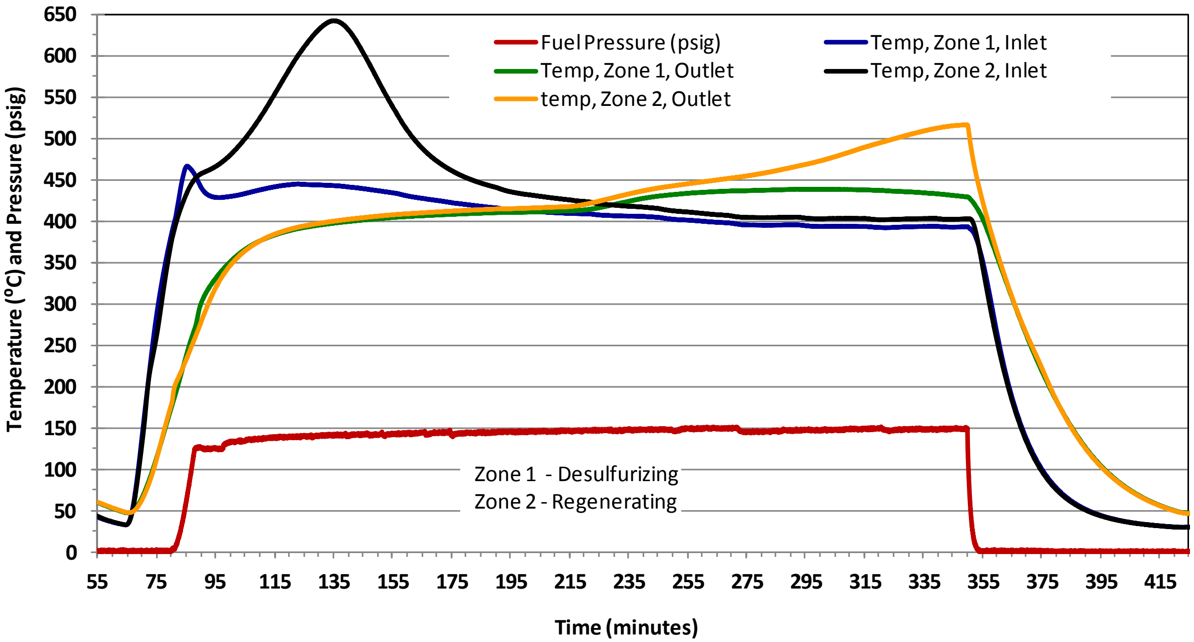
- Elemental Analyzer - Analytik-Jena Ea3100
  - Sulfur – ultraviolet (UV) fluorescence
    - Calibration Range: 0.2 ppmw S to 1000 ppmw S
  - Carbon – nondispersive infrared sensor (NDIR)
    - Calibration Range: 84 wt% to 90 wt% carbon

- Gas Analysis
  - Agilent Micro GC 3000 (2 channel)
  - Columns:
    - (i) molecular sieve column (10 m x 0.32 mm)
    - (ii) Plot U column (8 m x 0.32 mm)

  Multiple level calibration curves were used for all compounds with the calibration gases at ±1 % blend tolerance and 0.02% analytical tolerance.

- Functional Group Analysis via GC-FTIR
  - GC: Thermo Scientific (Trace 1310)
    - The GC column used was an RTX1 15 meters, 0.53mm ID, 1um dimethyl polysiloxane stationary phase
  - FTIR: Thermo Scientific (Nicolet iS50)

Operating Characteristics
(Temperature/Pressure)



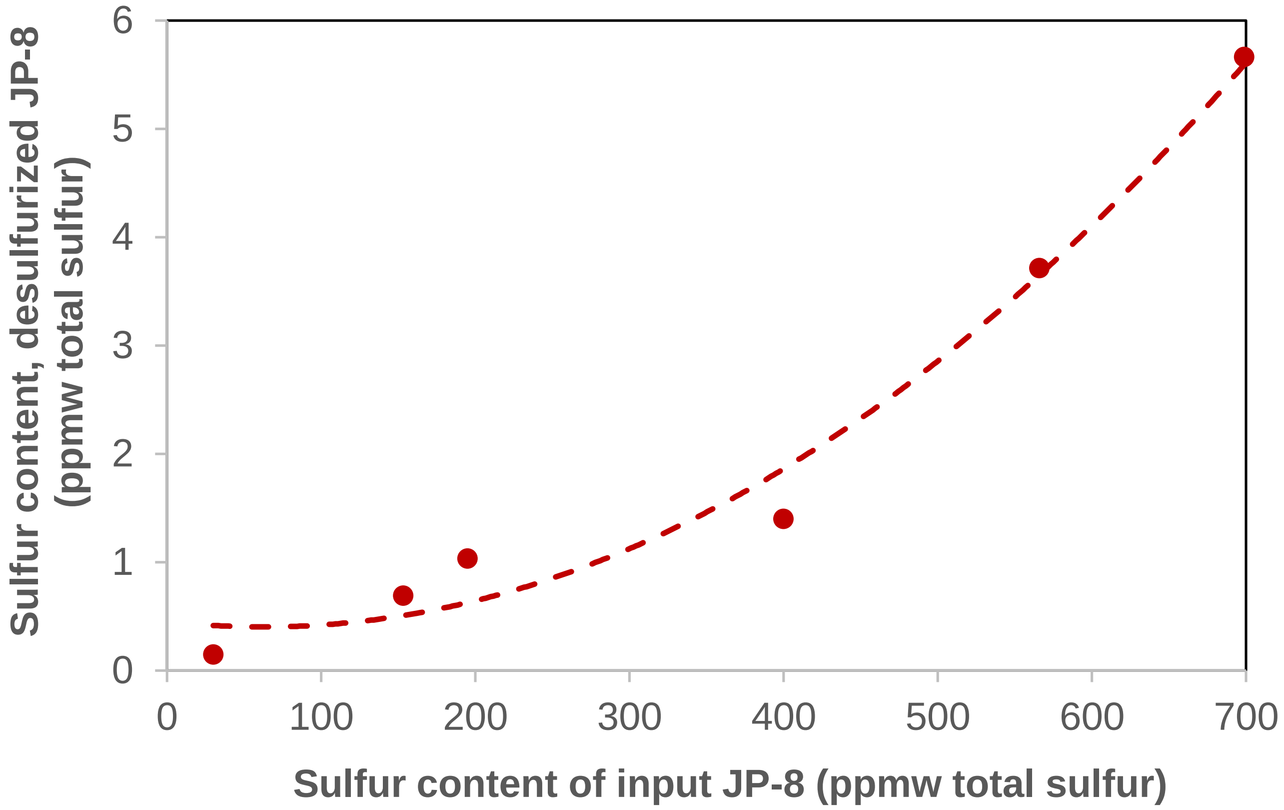
- A thermal wave within the beds can be seen for both desulfurization and in regeneration.
- Cycle time and regeneration air flow are largely dictated by the regeneration cycle and the need to control exothermic reactions.

Fuel: JP-8 w/ 314.3 ppwm total sulfur
Hours Ops: 28.9
Desulfurized JP-8 @ <1 ppmw total sulfur

JP-8 input fuel at 6 ml/min. JP-8 feed; 450 °C adsorption temp., 150 psig bed pressure

Desulfurized JP-8, sulfur content as function of input fuel

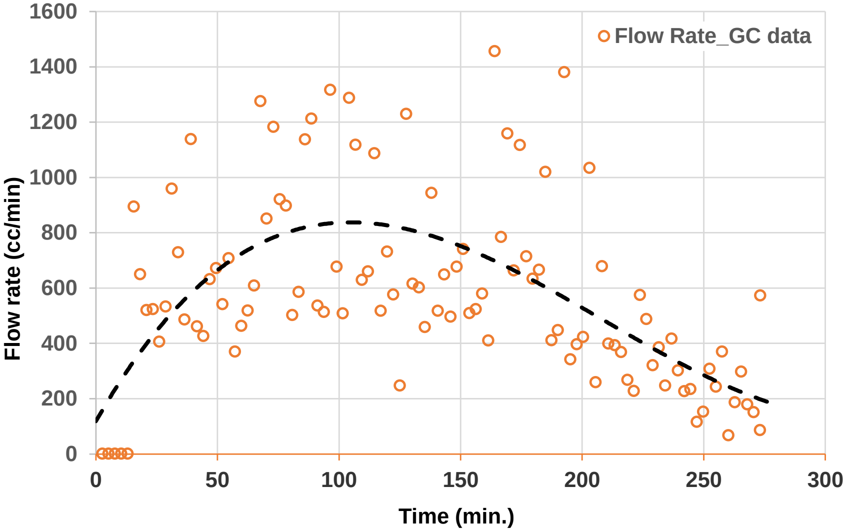
6 ml/min. JP-8 feed; 450 ℃ adsorption temp., 150 psig bed pressure

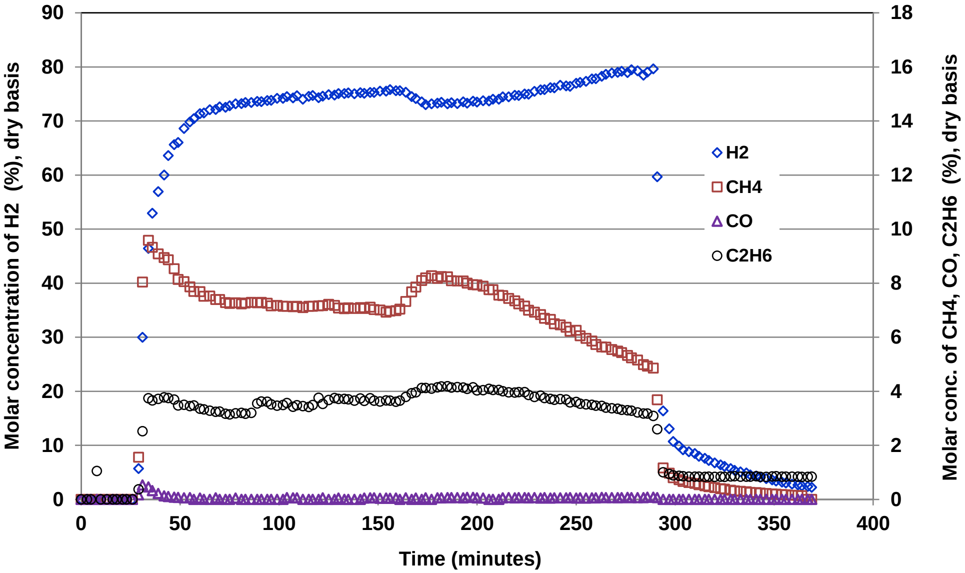


- The input fuel does affect the sulfur content of the desulfurized fuel.
- Relationship appears to be nonlinear.

Desulfurized JP-8
Gaseous Component

6 ml/min. JP-8 feed; 450 ℃ adsorption temp., 150 psig bed pressure

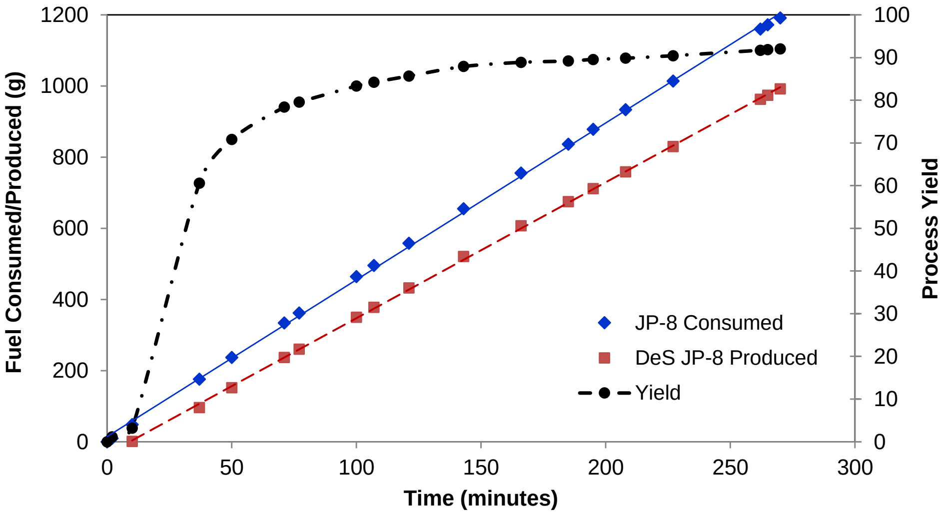


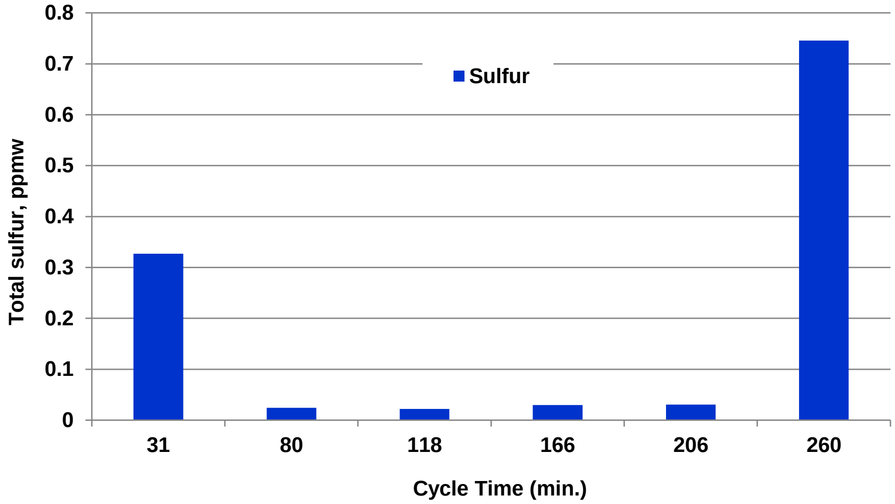


- In addition to desulfurized fuel, the desulfurization process results in a significant amount of hydrogen (70-80 mol%) and methane (5-9 mol%).
- Total gaseous component flow peaks at 110 minutes with a flow of approx. 820 cc/min.
- For a desulfurizer integrated into a power system, the hydrogen and methane would be retained and would contribute the overall efficiency and yield of the process.

Performance throughout a Sorption Cycle

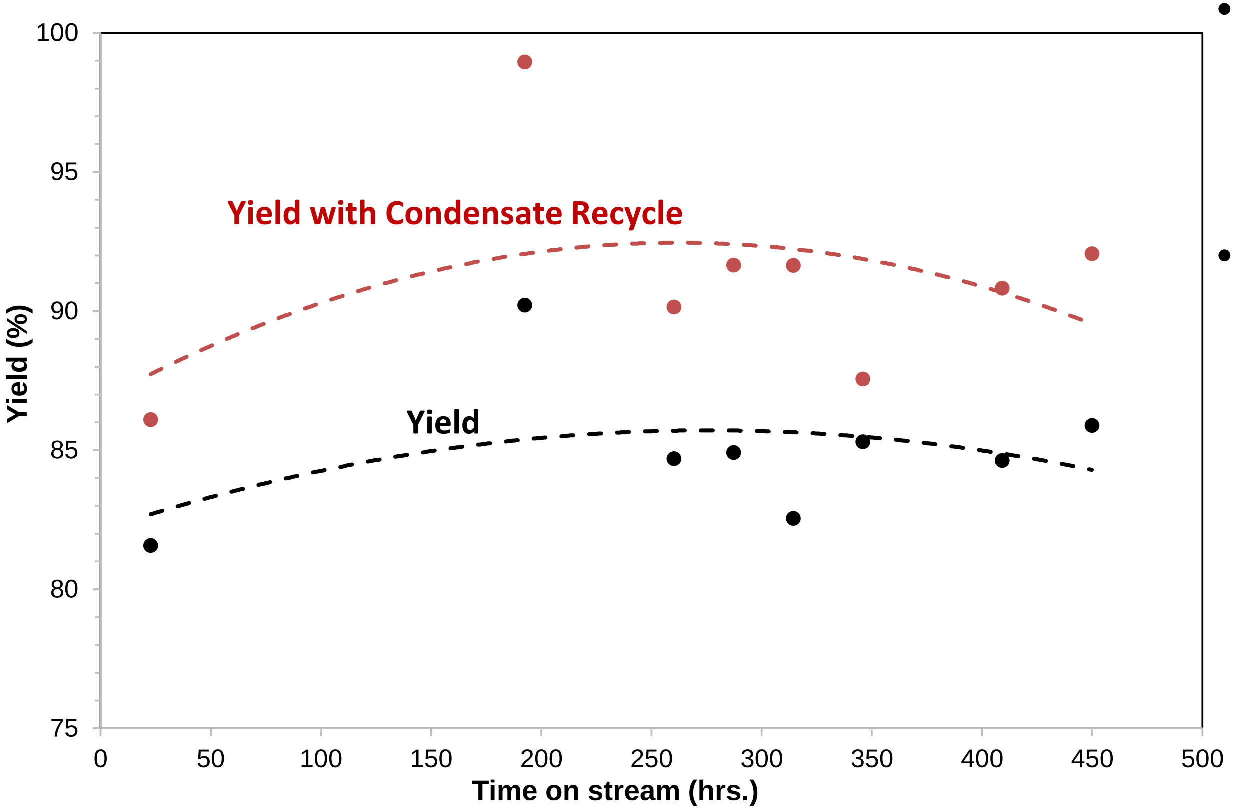
6 ml/min. JP-8 feed; 450 ℃ adsorption temp., 150 psig bed pressure





- System warm-up time ~17 – 18 minutes. Desulfurized fuel begins to flow ~9 minutes into the desulfurization cycle.
- Desulfurized fuel production is linear (mass basis). Desulfurization appears to be less efficient at the beginning and end of each cycle.
- With every cycle approximately 60 g of fuel is captured as “condensate” representing fuel purged from the bed during transition to regeneration.

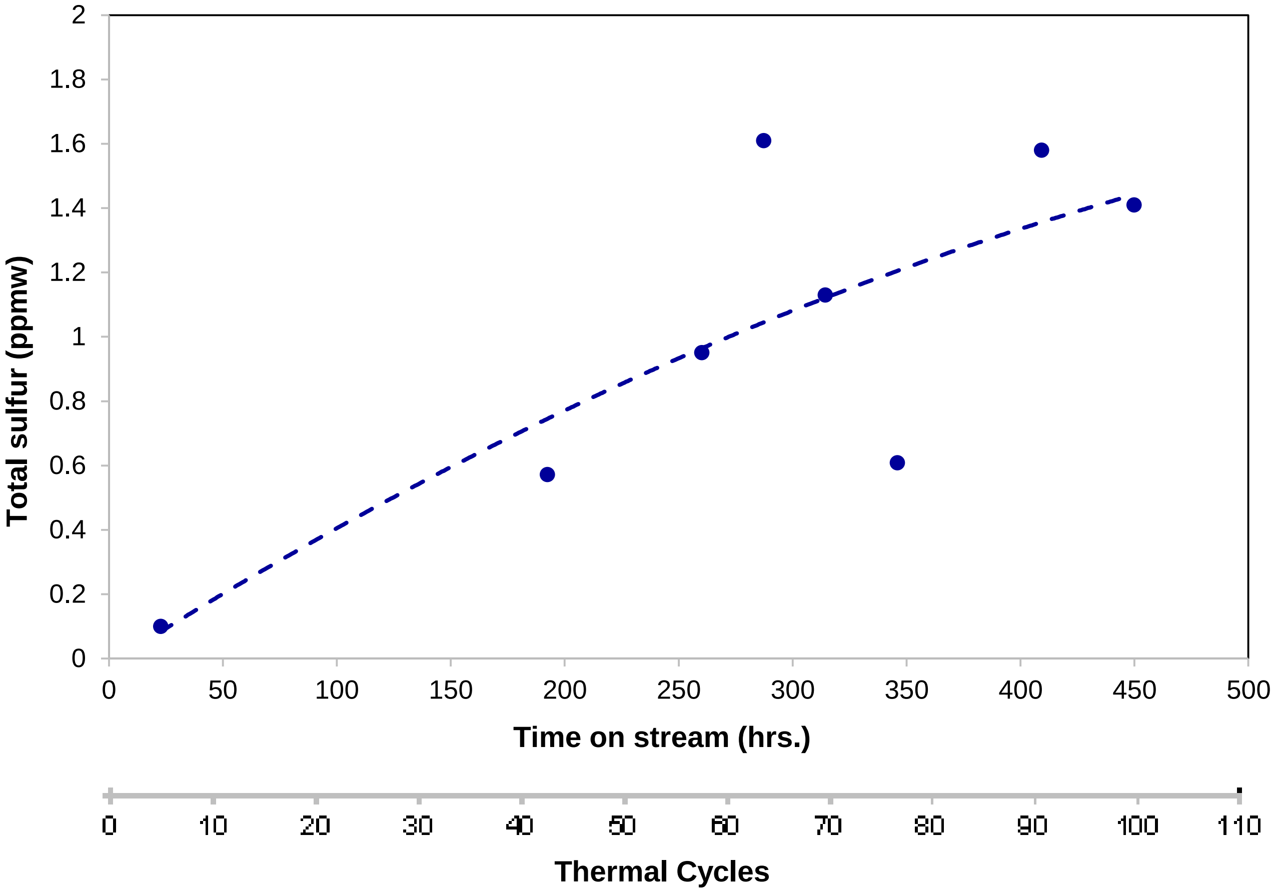
Process Yield



JP-8 input fuel at 400 ppmw total sulfur. 6 ml/min. JP-8 feed; 450 ℃ adsorption temp., 150 psig bed pressure

- *Yield with and without condensate recycle. (JP-8 input fuel at 400 ppm total sulfur).*
- *The Yield, as shown, is mass based and liquid content. The condensate is fuel that has not been fully desulfurized fuel contained in the beds during transition from desulfurization to regeneration. Condensate JP-8 typically contains 15 – 25 ppmw total sulfur and within a system would be recycled back to the fuel tank or used directly.*

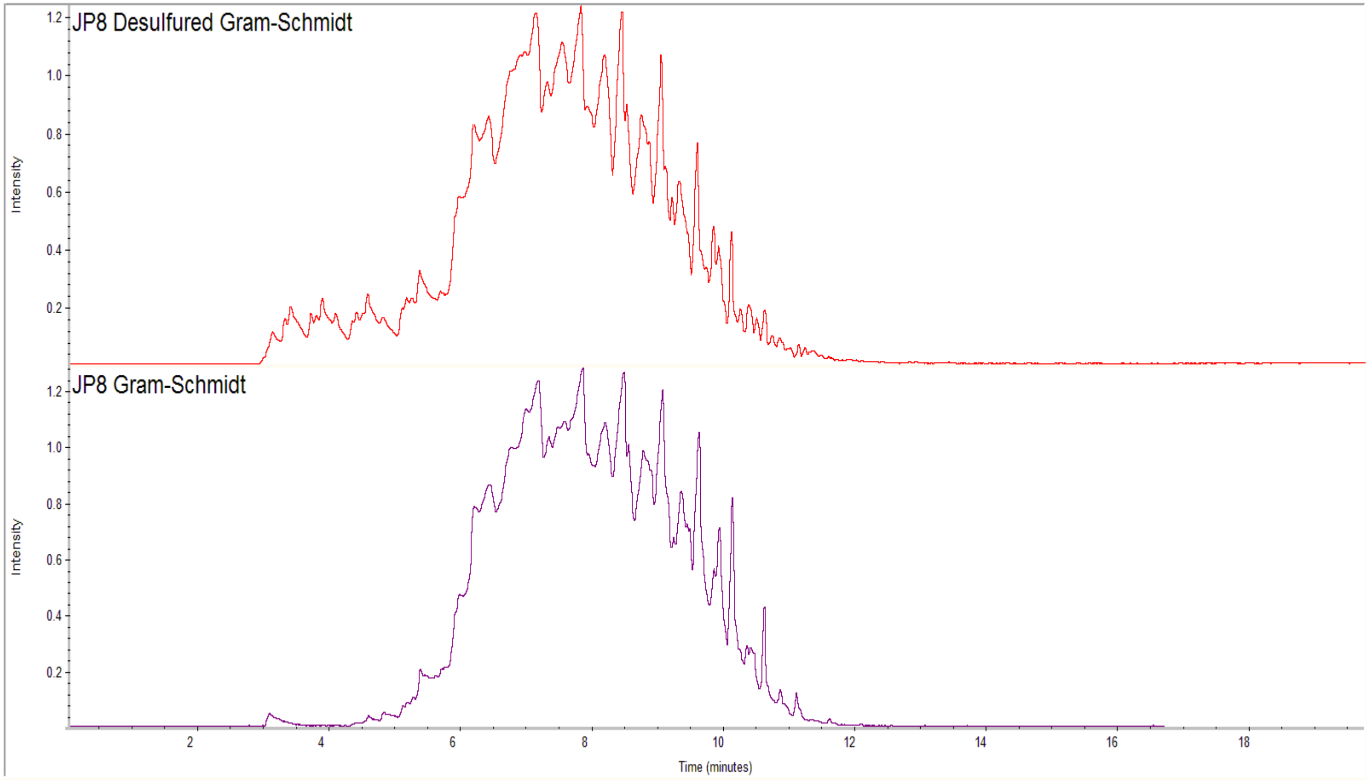
Impact of TOS and Thermal Cycling



- *Sulfur content of desulfurized fuel as a function of time-on-stream. (JP-8 input fuel at 400 ppmw total sulfur)*
- *Achieved ≥ 475 hrs/bed and ≥ 100 thermal cycles/bed.*
- *Some degradation in performances is seen, but operation is well within goals of ≤ 10 ppmw total sulfur.*

JP-8 input fuel at 400 ppmw total sulfur. 6 ml/min. JP-8 feed; 450 ℃ adsorption temp., 150 psig bed pressure

IR Spectral Results

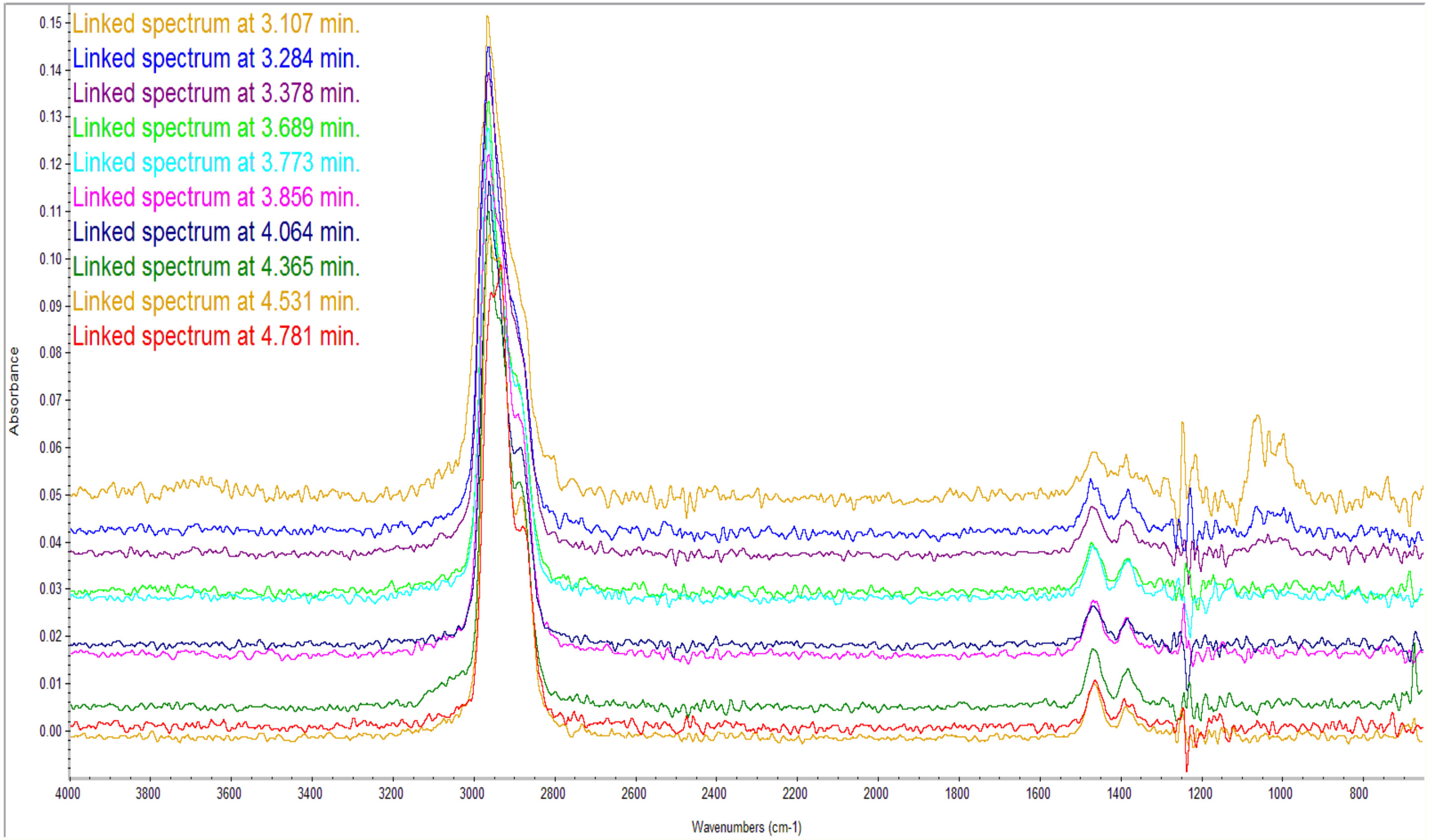


- JP-8 versus desulfurized JP-8
- Significant changes in Gram-Schmidt from 3 to 5 minutes and at 10 to 12 minutes, but little change elsewhere.

IR Spectral Results (con't)

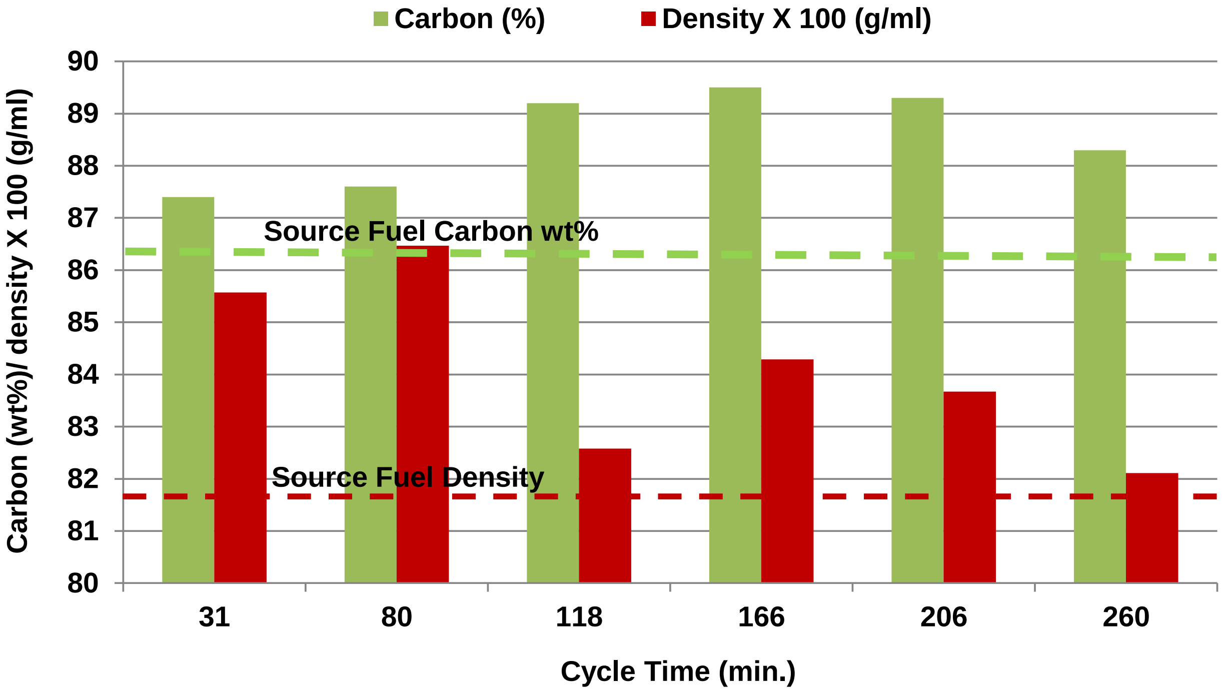
Desulfurized JP-8

Selected spectra collected at 3 to 5 min. retention times



- The desulfurizing process has increased the number of branched alkanes in JP8. Note increase in CH3 bands at 2954 and 1388cm-1.

Desulfurized JP8 Carbon Content and Density



- JP-8 Fuel specification:
  - Carbon max (wt%)* 86.6
  - Density (g/ml) 0.775 – 0.840
- Desulfurization process alters fuel density and increases amount of carbon.
  - May be increasing mono-aromatic content.

* Based on minimum hydrogen specification

Summary
JP-8 Fuel Desulfurization

- Successful operation of an air regenerative JP-8 fuel desulfurizer has been demonstrated.
- JP-8 fuel with organic sulfur content up to 700 ppm total sulfur was desulfurized to levels below 7 ppmw total sulfur.
- Very good absorbent durability has been demonstrated, achieving > 950 hours on-stream operating hours and > 105 thermal cycles.
- Yields of greater than 90% can easily be achieved.
- The desulfurized fuel is altered a bit with increased lower molecular weight hydrocarbons, increased branched hydrocarbons, and possibly increased aromatic content.

<u>Fuel Work</u>

- Continued characterization of desulfurized fuel.
- Evaluate changes in operation parameters (bed residence time, operating pressure and temperature, etc.) on performance.

Acknowledgement

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Questions