Diesel Desulfurization Filter

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Abstract:

Honeywell is working on a program to demonstrate proof-of-concept for an "on-vehicle" desulfurization fuel filter for diesel engines. Integration of the filter into the vehicle fuel system will reduce the adverse effects sulfur has on post combustion emission control devices such as NOx adsorbers. The sulfur filter's role is to reduce the sulfur levels in the fuel resulting from the various sulfur contaminants remaining in the fuel after refining or resulting from pipeline contamination.

We have chosen to develop and demonstrate this technology based on criteria set forth for a heavy duty CIDI engine system because it represents a more challenging set of conditions of service intervals and overall fuel usage over light duty systems. It is anticipated that the technology developed for heavy-duty applications will be applicable to light-duty as well.

In this paper we will describe the development activities and challenges that have gone into this development effort. The challenge underlying this program was to identify an approach which can selectively remove or capture the sulfur contaminants from the other competing components in the ultra low diesel fuel and at the same time minimize any adverse side effects to the fuel. Additionally, the approach used to remove the sulfur must satisfy other practical criteria that this "on board" device will need to meet.

We will cover the activities beginning with the massive screening studies of sulfur removal approaches through the optimization and the successful scale-up work to the 1 gallon scale. The sulfur removal approach is estimated to require a 10 gallon sorbent bed to reduce by 45% the overall sulfur load on the NOx adsorber over a 25K miles interval. A lowering of the fuel lubricity has also been observed in the processed fuel.

Several partners have participated in this program including, Mack Trucks, Marathon Ashland Petroleum, Johnson Matthey. This work has been sponsored under a contract by the Department of Energy.

Program

Goal: To develop and demonstrate proof-of-concept for an "on-vehicle"desulfurization fuel filter for diesel engines.

Project Team

- Honeywell Consumer Products Group FRAM
- Honeywell Laboratories
- Marathon Ashland LLC
- Mack Trucks Inc.
- Johnson Matthey
- American Waste Industries

Program began April 2002

Fuel Sulfur Removal Filter

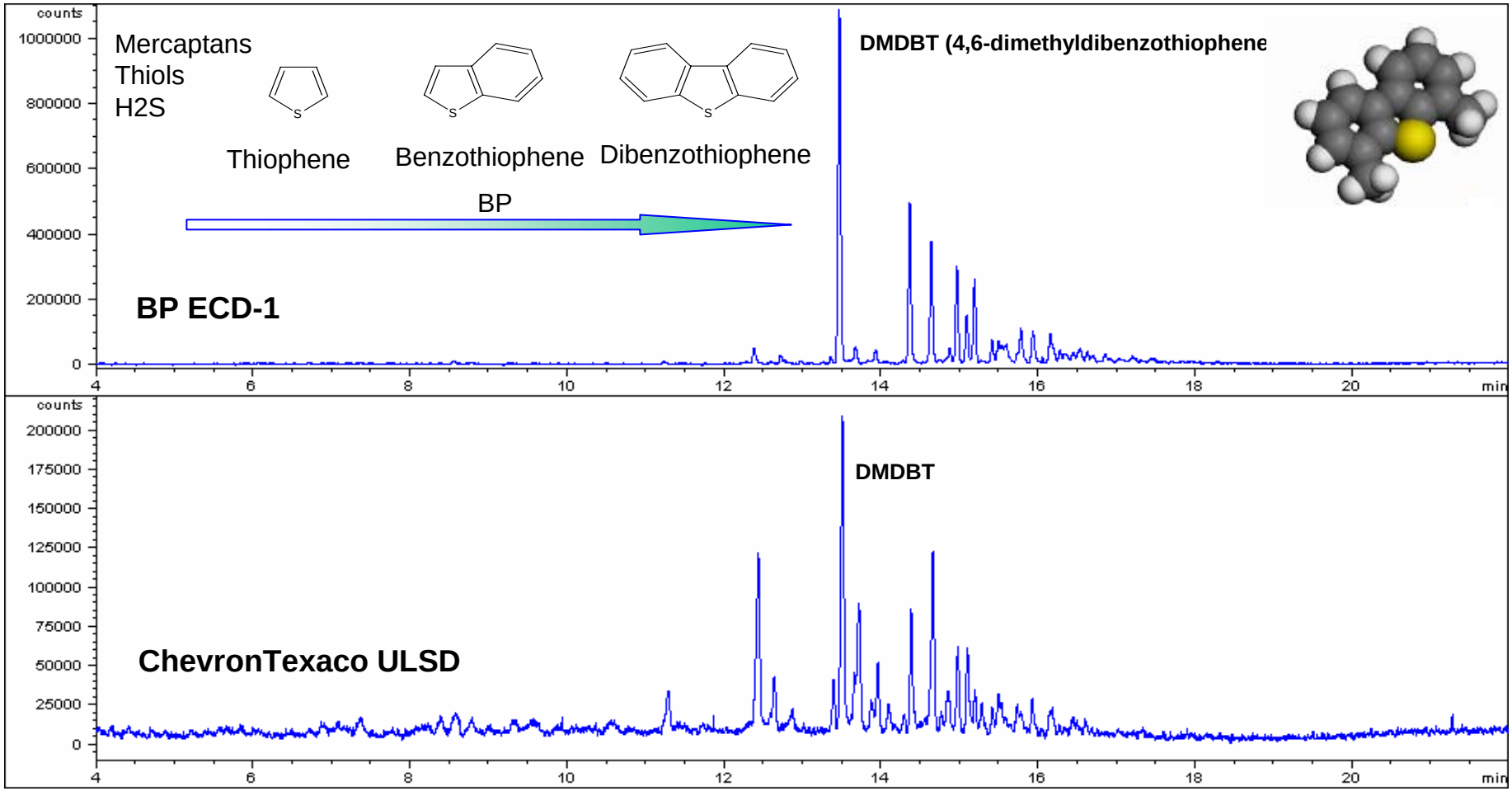
In-Going Rationale

- NOx adsorber technology sensitive to sulfur levels in the fuel
- Reduction in the number of desulfation events for NOx adsorbers can improve their life
- Refineries will face a challenge to achieve economical hydro-desulfurization to achieve levels low enough to not poison NOx adsorbers, 3 ppm or lower.
- Reduced fuel sulfur levels make point-of-use sulfur treatment feasible
    - volume required for an “on-board” sulfur trap is within reason
- Pipeline contamination will likely raise sulfur levels

Approach

- Develop fuel filter type device as an adsorption bed for sulfur removal.
- Integrate sulfur filter maintenance interval to other scheduled maintenance events

Sulfur Speciation Comparison



-Note the relative enrichment of earlier eluting components in CT vs. BP Fuel
-DMDBT is largest single component in both fuels, although only ~1/5 as much in the CT fuel
-Much more of the sulfur detector counts are in the 'weeds' in the CT fuel vs. BP fuel
-10.2 x 10^6 sulfur counts in BP vs. 8.1 x 10^6 counts in the CT fuel

Challenge

The DMDBT looks similar to and behaves like some major components in diesel fuel

Diesel Composition

- 20% 1 ring aromatics
- 3% 2 ring aromatics (30,000ppm) very similar to DMDBT
- DMDBT is at 10 ppm

3000 to 1 ratio

- Low level polar contaminants in fuel-lubricants, oxidative degradation products and antioxidants

Approaches

- Remove the sulfur contaminant directly (requires high selectivity)
- Convert it into something more easily removed
    - Create a “chemical hook”

Chemical Approaches/Down-Selection

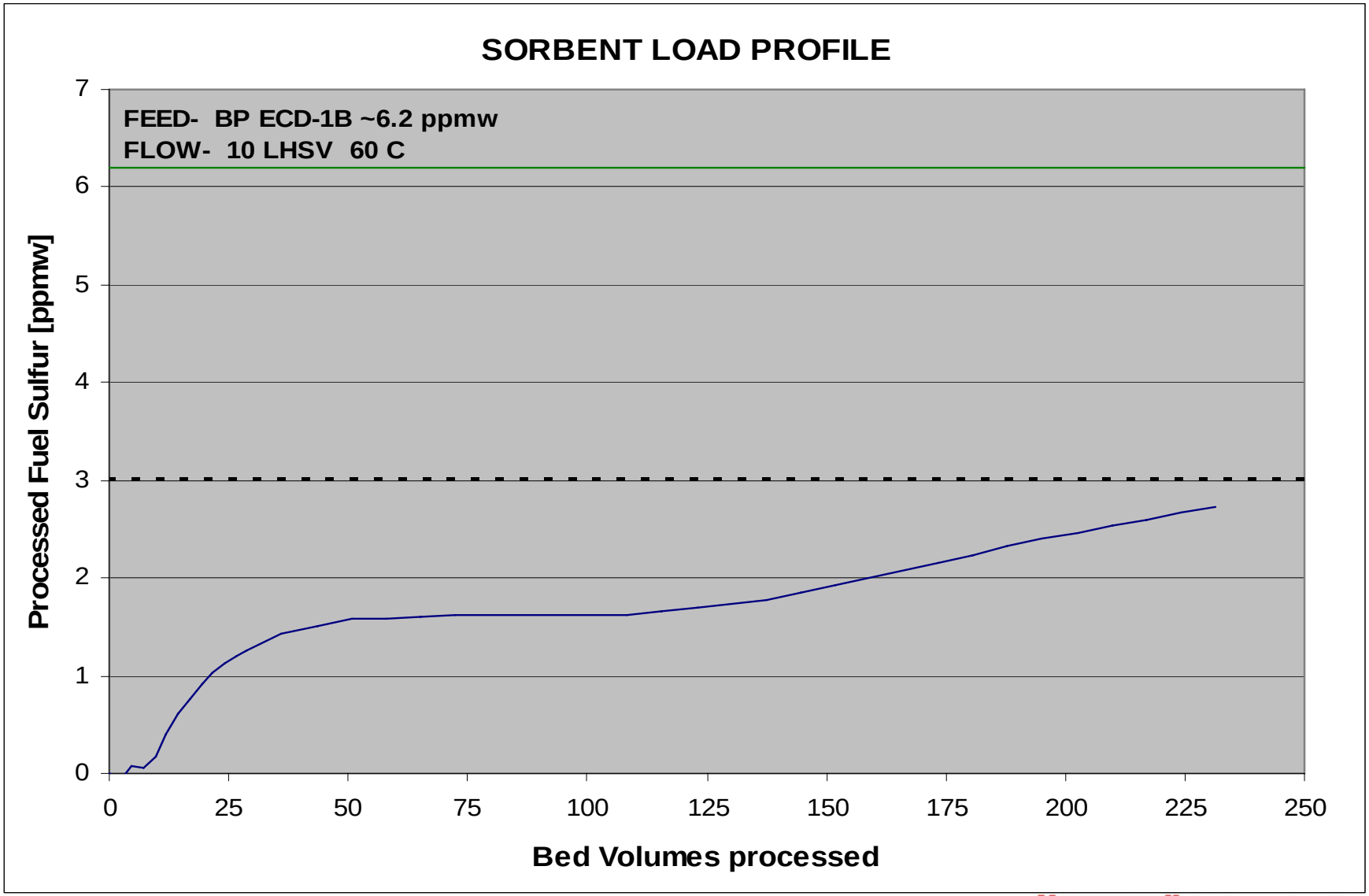
13 Categories – Over 4000 candidate approaches screened

- Ionic liquids
- Metal oxides
- Oxidation
- Photochemical
- Reduction
- Solvent Extraction
- Sorption
- Biochemical
- Catalytic
- Chemical derivatization
- Electrochemical
- Complexation
- Misc (membranes)

- 13 categories tested, 1 most promising
  - Adsorption

- Remainder of short list have been eliminated for further study
  - adverse fuel effects
  - operating parameters
  - design issues
  - health, safety or environmental issues
  - too low capacity

Sulfur Uptake Profile



Fuel Properties

How does the sulfur removal effect fuel properties

Chemistry	Notebook Ref	Copper Corrosion D130	Viscosity @40C D445 (cSt)_	Cetane No. D613	Bromine No. D1159	Cloud Point D2500(deg C)	Total Aromatics in Diesel D5186 (mass %)	Mono Aromatics (mass %)	Poly A (mass %)	Lubricity D6079 (mm)	Thermal Stability D6468 (%)
Control (BP ECD1)	40065-13	1A	2.446	55.6	0.4	-6	23.3	20.7	2.6	0.465	98
Sorbent A	40059-24	1A	2.451	50.5	0.41	-6	22.9	20.4	2.5	0.625	100

Loss of lubricity observed, removal of additive identified

Reintroduction of 50 ppm lubricant additive, carboxylic acid, brings lubricity back to spec 0

Fuel Effects

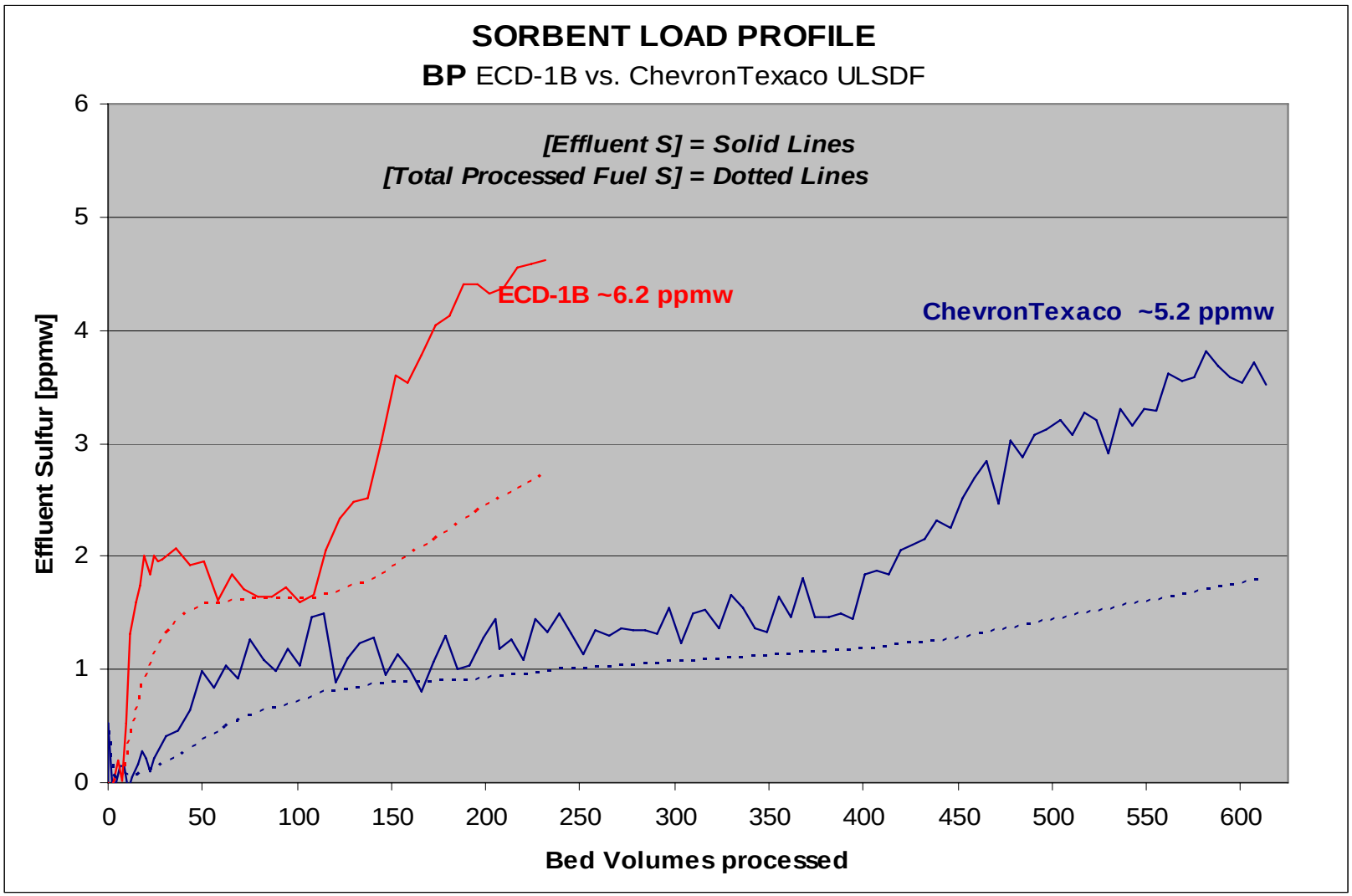
Variation in performance seen with different fuels

Comparison 3 fuels, Marathon Ashland, BP and Chevron Texaco ULSD fuels. 3 Fold difference in working capacity

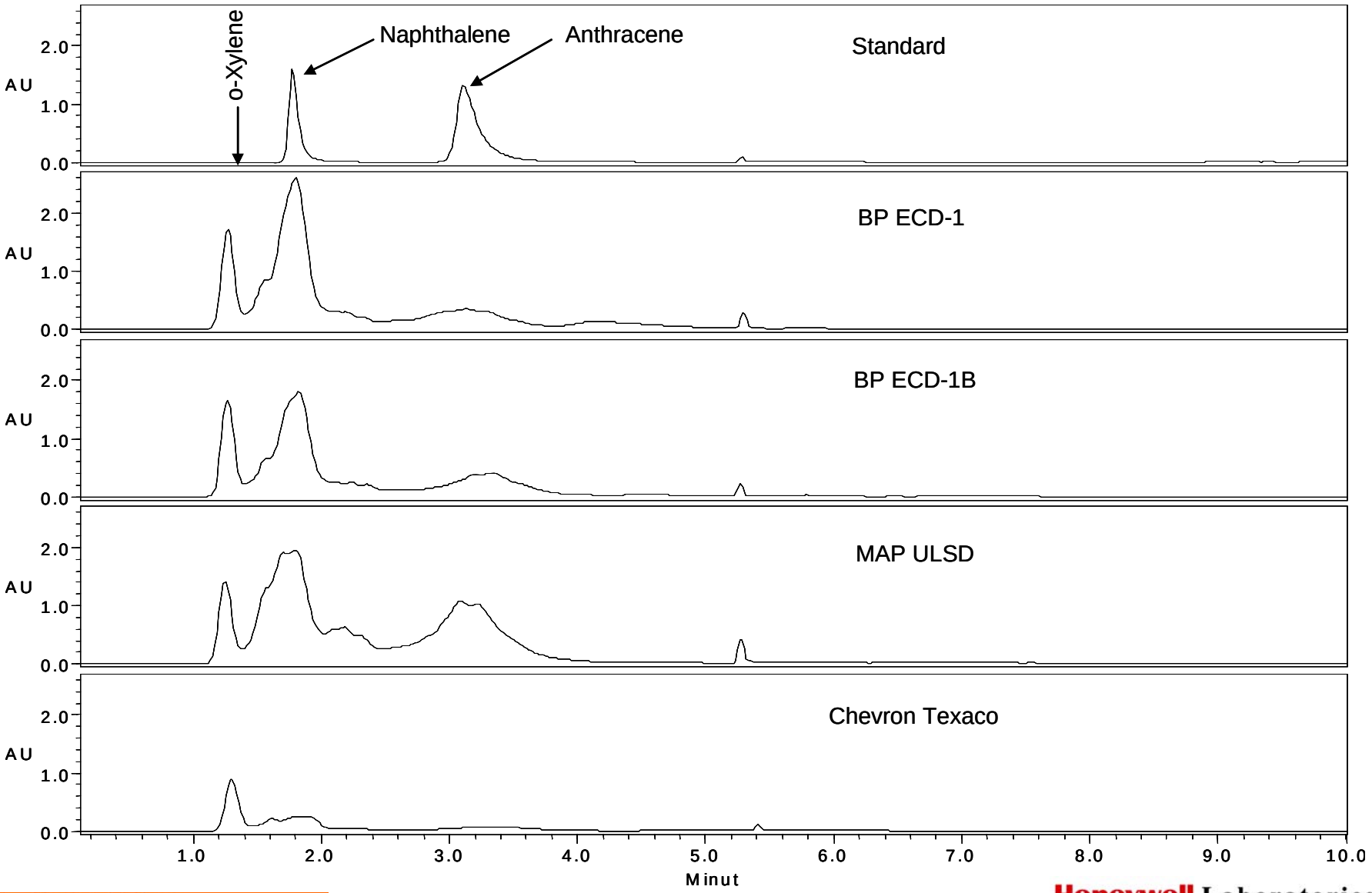
CONCLUSIONS

- Chevron Texaco ULSD shows highest sulfur removal capacity 3X greater then MAP or BP fuels
- Differences in higher (3 ring) PNA's appear to be root cause
- Size sulfur filter for worst case fuel, highest 3 ring PNAs

Fuel Effects



PNA Comparison



Mack Engine Test

TBD Aug 2005

Objective

- To monitor the sulfur level in the exhaust and NOx adsorber efficiency during a 500 hr run to determine sulfur filter performance

Requirements

- Sulfur filter (10 gallon)
- Mack MD engine with integrated NOx adsorber
- ULSD fuel (<15ppm sulfur)
- NOx monitor for exhaust

Desired result

- Increased NOx adsorber efficiency over time and reduced number of sulfur regeneration cycles required for NOx adsorber efficiency to remain at desired levels