

## **Title Page**

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## ABSTRACT

Honeywell has completed working on a multiyear program to develop and demonstrate proof-of-concept for an "on-vehicle" desulfurization fuel filter for both light duty and heavy-duty 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 NO<sub>x</sub> adsorbers. The NO<sub>x</sub> adsorber may be required to meet the proposed new EPA Tier II and '2007-Rule' emission standards. The proposed filter concept is based on Honeywell's reactive filtration technology and experience in liquids handling and conditioning. A regeneration and recycling plan for the spent filters was also examined.

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. In the second phase of the program a light duty diesel engine test was also demonstrated. Further, technology developed under this proposal would also have application for the use of liquid based fuels for fuel cell power generation.

The program consisted of four phases. Phase I focused on developing a concept design and analysis and resolution of technical barriers concerning removal of sulfur-containing species in low sulfur fuels. In Phase II concentrated on prototype filter design and preparation followed by qualification testing of this component in a fuel line application. Phase III studied life cycle and regeneration options for the spent filter. Phase IV focused on efficacy and benefits in the desulfation steps of a NO<sub>x</sub> adsorber on both a heavy and light duty engine.

The project team included a number of partners, with Honeywell International as the prime contractor. The partners include an emission control technology developer (Honeywell International), a fuel technology developer (Marathon Ashland Petroleum), a catalyst technology developer (Johnson Matthey), a CIDI engine manufacturer (Navistar Inc. (formerly International Truck & Engine Corporation) and Mack Trucks Inc.), and filter recycler (American Wastes Industries).

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## INTRODUCTION

The goal of this program is to develop an emission control device that can enable engine manufacturers to comply with the new EPA emission standards including EPA Tier II Bin 5 for light-duty engines and the new '2007-Rule' for heavy-duty applications. The '2007 rule' also includes a new diesel fuel sulfur limit that has a maximum cap of 15 ppm. Successful integration of the sulfur-removal filter into either a heavy-duty or light duty vehicle fuel stream coupled with a post-combustion NO<sub>x</sub> adsorber catalyst device will allow these vehicles to meet these new emission regulations with a robust post emission control device.

The sulfur removal device developed under this solicitation can expedite implementation of the new emissions standards by reducing the need for diesel fuels to attain the near zero sulfur levels required to ensure optimal performance of NO<sub>x</sub> adsorber technologies under development. This should be accomplished at relatively modest cost to the end-user because the sulfur-removal device will be an add-on to the existing fuel system, and will be packaged in a conventional engineering format. It is anticipated the cost of the proposed sulfur-removal device to the consumer will represent no more than a low multiple of the current cost of a standard fuel filter.

## EXECUTIVE SUMMARY

The main objective of this program was to demonstrate proof-of-concept for a fuel desulfurization filter that is able to reduce sulfur levels in fuel to tolerable levels which enables the implementation of post-combustion NO<sub>x</sub> adsorber technology. The technology developed relied on Honeywell's expertise in reactive filtration technology. The targeted design and performance of this filter was developed based on criteria supplied by Johnson Matthey (the NO<sub>x</sub> catalyst manufacturer) Mack Trucks and Navistar Inc. (the CIDI manufacturer).

This development program incorporated the following key elements: 1) a survey of all applicable current and proposed sulfur removal approaches, 2) technical evaluation of potential technologies, 3) laboratory screening of down-selected approaches, 4) package selected technologies for on-board configuration, 5) prototype design and preparation, 6) pilot scale life-testing and efficacy testing of the filter on both a light duty and heavy duty diesel engine, and, 6) approaches to recycling/regeneration of the spent filters.

The key accomplishments highlighted in this program are, 1) over 4000 sulfur removing chemistries were screened from the broad range of published, commercial and invented scientific landscape, 1) identification of a class of sorbents which are capable removing sulfur from ULSD fuel to levels which can significantly prolong the detrimental desulfation steps in a NO<sub>x</sub> adsorber, 3) this family of sorbents function under conditions suitable for an "on board" process, 4) successfully scaled the preparation and operation of this sulfur removal process from the milligram scale to the several gallon scale, 5) integration of the sulfur filter into both a heavy duty and light duty diesel engine test, 6) successful demonstration that with the sulfur filter the NO<sub>x</sub> adsorber's NO<sub>x</sub> removal efficiency could be prolonged between 2 to 3 fold between the detrimental desulfation steps, 7) a method was found in which the spent sorbent could be regenerated to within 80% of its original sulfur removal capacity. The program has been completed and successfully met both its technical and financial goals.

## PROGRAM PLAN/SUMMARY

### Objectives

- To develop and demonstrate proof-of-concept for an “on-vehicle” desulfurization fuel filter for heavy and light duty diesel engines.

### Approach

- Phase I: Develop a concept design and analysis, and resolution of technical barriers concerning removal of sulfur-containing species in low sulfur fuels
- Phase II: Implement high throughput screening techniques for chemistry selection and dynamic testing
- Phase III: Prototype design and testing; adapt research concept into a practical filter module and test its efficacy, produce prototype(s).
- Phase IV: Life cycle studies; study life cycle and regeneration options for spent filters
- Phase V: Validation Testing; engine testing with NOx adsorber and test prototype filter on a heavy duty and light duty diesel engine for efficacy and system testing and component integration.

### Accomplishments

- A sorbent identified from screening over 4000 candidate approaches from published, commercial, and invented sources.
- Successfully scaled up preparation to operation from the milligram to several gallon scale.
- Two engine tests with both heavy duty and light duty diesel engines confirmed benefit of sulfur filter to prolong desulfation of the NOx adsorber.
- National fuel variability study carried out with “at the pump” ULSD to determine impact on sulfur filter’s performance. Modest performance variability but significant impact biodiesel has on the sulfur filter.
- A method to regenerate the sulfur filter was found which can regain 80% of its original activity.
- A study was undertaken to determine where in the USLD stream it would best be undertaken.

### Future Directions (near term 2 months)

- No further action, program has been completed as of July 2008



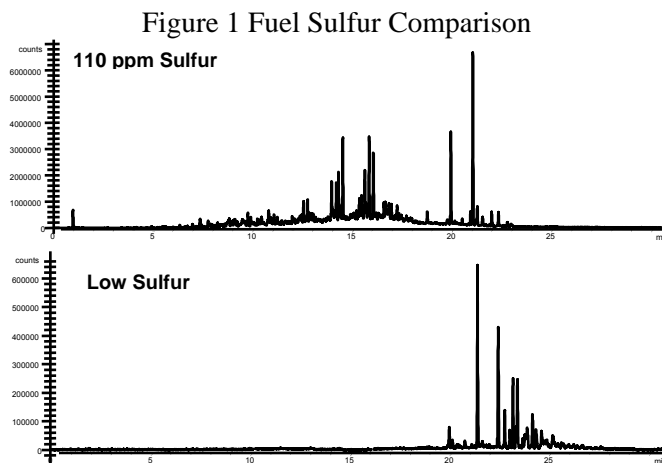
## EXPERIMENTAL

All of the studies were done with ULSD low sulfur fuel from commercial at the pump sources as indicated. Samples of retail ULSD were obtained from various locations within three major geographical areas of the country, west coast, mid-west and east coast. Two collections of fuel were obtained at different times of the year representing winter time blends and summer time blends. No special precautions were taken to treat the fuel prior to use. All temperature controlled experiments were carried out with standard laboratory equipment and were accurate to within  $\pm 2$  C. Total sulfur analysis was measured with an ANTEK Sulfur Analyzer, model 9000VLLS, which has a detectability limit of  $<1$  ppm. Speciation of the sulfur contaminants were measured using a gas chromatography technique using a methyl silicone capillary column and a SIEVERS sulfur chemiluminescence detector. Aromatics content were measured via a gas chromatographic technique. Samples analyzed for other fuel properties were carried out at Southwest Research Laboratories.

## RESULTS AND DISCUSSION

### ULSD FUEL

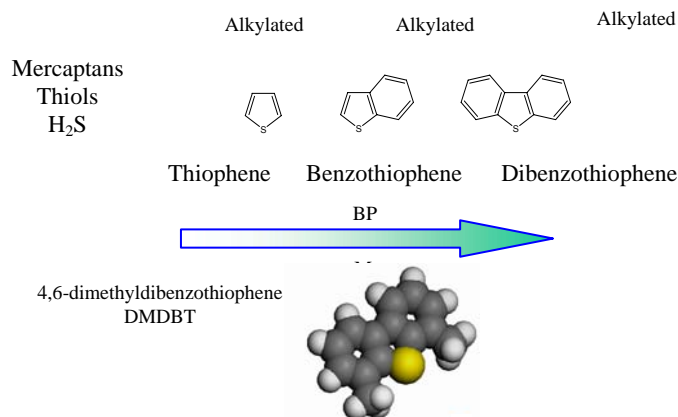
ULSD fuel will become commercially available in September/October 2006. In order to meet this low sulfur specification, fuel will have to be extensively hydrosulfurized, leaving behind only a small fraction of higher molecular weight sulfur containing species. Some of these sulfur species are considered recalcitrant for further treatment<sup>(3,4)</sup>. Figure 1 shows two gas chromatographic elution profiles of the sulfur species in two diesel fuels, one a 110 ppm sulfur diesel fuel and the other a ULSD fuel. Typically in gas chromatography, components elute from the column progressively with increasing boiling points. Also as the molecular weight increases, to some degree, so does their boiling point. One can see that in ULSD fuel the sulfur species elute with higher retention times, with higher boiling points and higher molecular weights. Speciation with known standards shows the main component to be DMDBT, 4,6-dimethyl dibenzothiophene and various alkylated isomers. The two methyl groups on the dibenzothiophene ring are responsible for the steric hindrance for the molecule to in contact with the catalyst surface, making it recalcitrant to catalytic hydro treating.



There are large numbers of families of sulfur compounds present in fuels. They range from simple inorganic sulfur species such as hydrogen sulfide to various organosulfur compounds ranging from simple mercaptans and thiols to multi-ring sulfur heterocycles. These are described

in Figure 2 below. The boiling points increase as the complexity and size of the organo sulfur species increases.

Figure 2 Sulfur Species



In addition to the more recalcitrant nature of the DMDBT and its derivatives, the chemical and structural nature of the substituted benzo thiophenes are similar to some major components in the fuel, particularly, the polynuclear aromatics. In a typical ULSD fuel there can be 20% by weight of one ring aromatics and up to 3% two ring aromatics. The two ring aromatics chemically behave very similar to the DMDBT. To further complicate the separation the 2 ring aromatics are present at a ratio of 3,000 to 1 to the DMDBT. The challenge was to identify a selective sorbent which could distinguish the DMDBT from the polynuclear aromatics which would be present at several orders of magnitude excess and resemble the DMDBT both chemically and structurally.

#### CHEMICAL REMOVAL SCREENING

Two generic approaches were envisioned as separation strategies for the DMDBT removal; 1) find a selective environment which could directly remove the DMDBT or 2) alter the DMDBT to make the subsequent separation easier. Separation of DMDBT and sulfur in fuels has been widely published with separation techniques as diverse as membranes to photochemical oxidation. The first task, knowing there would very such different techniques and conditions, was to establish a standard test protocol in which all the different techniques could be tested and compared under a similar set of conditions.

To this end a comprehensive screening program was undertaken in which samples and approaches were obtained from universities, companies, inventors, patent literature and published literature<sup>(5,6)</sup>. Additionally, a combinatorial investigation of sorbents was undertaken at UOP. Overall over 4000 candidate systems and approaches were tested. Molecular modeling assisted in narrowing down the potential candidates. The list of 13 different families of approaches investigated are listed in List 1

#### List 1 Sulfur Removal Approaches

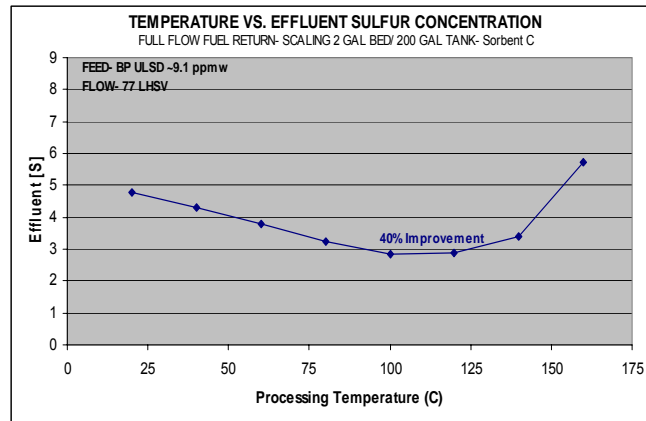
- Ionic Liquids
- Metal Oxides
- Photochemical

- Reduction
- Solvent Extraction
- Sorption
- Biochemical
- Catalytic
- Chemical derivatization
- Electrochemical
- Complexation
- Membranes
- Combinatorial Discovery

The 4000 chemistries were studied under a common set of testing conditions. The combinatorial study undertook a large sorbent/metal space including >165 sorbents with 21 metals in single, binary and tertiary combinations in their reduced, oxidized and sulfided states. From the large data base resulting from the screening operation, statistical methods using six sigma tools were employed for the down selection process to help identify the most promising candidates. From over 4000 candidate systems one approach was chosen which met the requirements for an “on board” vehicle filter. These included overall sulfur uptake capacity, operating parameters commensurate with those found on the vehicle, kinetics of uptake consistent with fuel flows in the fuel train, and effects on fuel quality. Many of the runner up approaches suffered from either having adverse effects on the fuel, operating parameters outside the useful range for an “on-board device”, complex design issues, health safety and environmental issues, or too low of capacity.

One approach was chosen which met the system requirements; it relied on an adsorption mechanism to remove the sulfur. The operating parameters associated with this approach were next studied. The parameters which could be controlled were; particle size of the sorbent, operating temperature, aspect ratio of the column. The goal was to see if any of these parameters could be varied to improve the sorbent’s overall sulfur uptake and kinetics of adsorption, thus reducing the size of the column and its footprint. A series of column flow tests were conducted in which the temperature of the sorbent bed was varied between 25 C and 160C. It was found that the sorbent uptake and capacity increased as the temperature was increased above room temperature. It showed an optimum from 100C to 120C. However after this temperature the capacity again declined. Figure 3 shows this temperature profile.

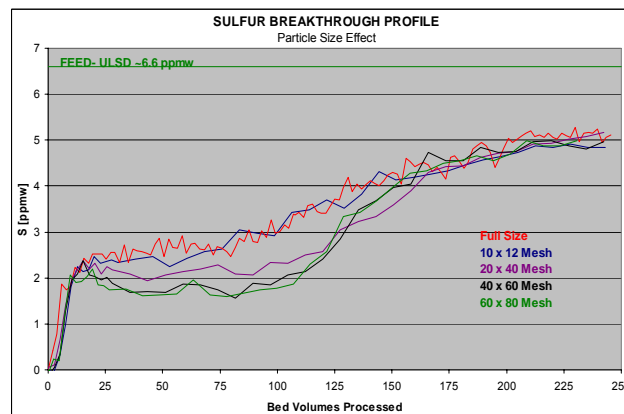
Figure 3 Temperature Profile



It was recognized that this optimum temperature would be outside the practical operating range for a vehicle application. However we chose to conduct further testing at 60C. Fuel temperatures frequently rise well above room temperature in “return” fuel systems and heat from exhaust or coolant could be used to preheat the fuel to 60C. Thus operating at a reasonable elevated temperature could be feasible.

The decrease in the sulfur uptake at temperatures above the optimum is consistent with an adsorption process with an exothermic heat of adsorption. Later studies in attempts at using this desorption effect to regenerate the sorbent were unsuccessful due to the parallel irreversible degradation of the polynuclear aromatic hydrocarbons on the sorbent. In order to assess whether any diffusional resistances were playing a role in sulfur uptake, a series of experiments were carried out measuring both internal and external diffusion. The sulfur uptake was measured as a function of particle size. Within an optimum particle size range, various column aspect ratios were tested in which the linear velocity of the bed was varied. Figure 4 is a plot of the sulfur breakthrough profiles at various particle sizes of sorbent.

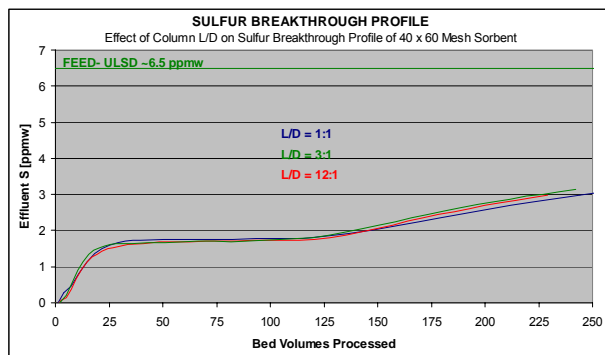
Figure 4 Sulfur Uptake versus Sorbent Particle Size



As can be seen in Figure 4 there is an improvement in sulfur uptake by going to smaller particle sizes. There is no benefit going to particle sizes below 40 x 60 mesh. Pressure drop calculations and an experimental verification were done with this particle size in the full scale column and found to be within the normal operating range. It was therefore assumed that the sorbent was not experiencing any pore diffusion resistance below this particle size range.

The next diffusion barrier studied was that of external diffusion. In this case a series of different columns were constructed in which their aspect ratio varied from 1:1 to 12:1. The residence time was kept constant and the different uptake profiles measured. Figure 5 describes the results from this study.

Figure 5 Sulfur Uptake at Various Column Aspect Ratios

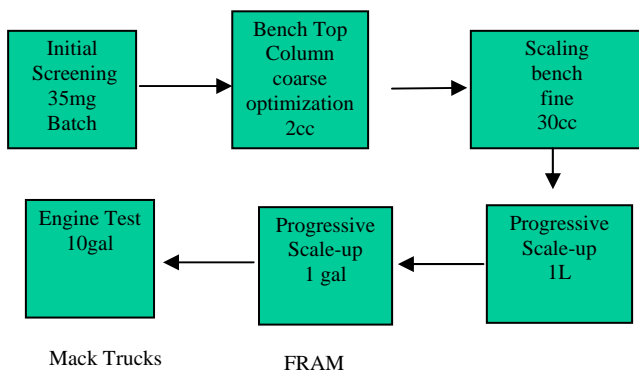


As can be seen in Figure 5 very little difference in sulfur uptake profile was seen between the different column configurations. It appears that film diffusion is not controlling the rate of the sulfur uptake. Therefore a wide range of length to diameter ratios in column design could be used without affecting performance.

#### SCALE-UP

All the initial screening work was carried out at the mg level. A progressive series of scale-up steps was undertaken which ranged from the mg level to the 40 liter level. These steps included both the production of the sorbent and also in the column testing. The system has scaled well and performed as expected up to the 40 liter level throughout all the stages, Figure 6.

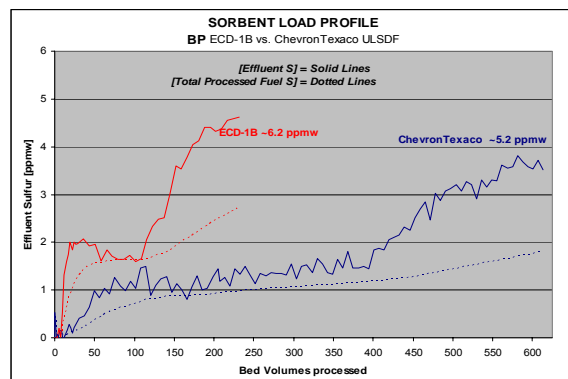
Figure 6 Scale-up Stages



#### PRECOMMERCIAL FUEL VARABILITY

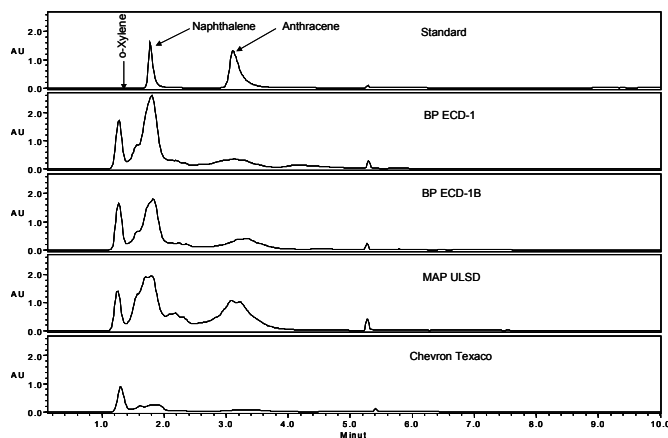
In the course of this study several precommercial and commercial ULSD fuels have been studied. The sorbent when tested with these different fuels showed a range of sulfur uptake capacities. The two extreme fuel samples are plotted in Figure 7.

Figure 7 Fuel Variability



All the ULSD fuels tested show a range of sulfur levels ranging from 5 ppm to 9 ppm sulfur. It was important to understand what in the fuel, beyond sulfur level, was responsible for the sorbent's ability to remove the sulfur. Earlier work showed that if one plotted a quotient made up from the concentration of sulfur in the effluent divided by the initial incoming sulfur level, all the sorbent showed the same uptake profile independent of sulfur level. However there was an additional component in the fuel which appears to affect sulfur uptake. A correlation was found between the polynuclear aromatics content in the fuel and the ability of the sorbent to remove the sulfur. Earlier studies demonstrated a strong competitive binding of both 1 ring and 2 ring aromatics with the DMDBT for sites on the sorbent. Figure 8 are gas chromatograms of various fuels and the PNAs present along with standards for retention time identification.

Figure 8 PNA Content in ULSD Fuels



A correlation has been found between the PNA content of the fuel and the ability of the sorbent to remove the sulfur. In sizing calculations for the engine test we based the sorbent load with that for the fuel which showed the lowest sulfur uptake.

### HEAVY DUTY MACK TRUCKS ENGINE TESTING

In order to validate the concept that reducing the sulfur level in the fuel will lengthen the time between desulfation steps and hence lengthen the NOx adsorber life a full scale engine test was undertaken with the appropriate aftertreatment devices. The sulfur filter adsorbent bed was sized to achieve a level of below 3 ppm in the fuel for the length of a typical service interval of 25,000 mi

(40,000 km). The size of the column used was 38 liters and operated by an external heater at 60 C. The engine test was carried out at Mack Trucks.

The engine test was carried out at Mack Trucks (Volvo Powertrain) and the aftertreatment was configured in a duel leg mode, Figure 9. The exhaust from the engine passed through a series of treatment devices starting with an oxidation catalyst (DOC), soot particulate filter (CSF) and finally a NOx adsorber (NAC). We used in this test a 2002 Mack AC-427, 12 L engine with a cooled EGR (exhaust gas recirculation). The dual leg exhaust setup used a value switching and multiple injection of fuel upstream of the oxidation catalyst. The engine was operated in a steady-state duty cycle at 1800 rpm under a load of 407 Nm. Periodic soot regeneration of the particulate filters was started when the change in pressure of the CSF exceeded 190 cm-water, (2.7psi). During the soot regeneration steps, care was taken to ensure that the temperature of the NOx adsorbers was below the desulfation threshold. Oxygen and NOx sensors were placed before after the aftertreatment train. Total system performance was continually monitored through these sensors and attempts were made to run at a constant NOx out from the engine. The NOx adsorbers were undersized by almost half in order to accelerate the time necessary to see degradation due to sulfur. The fuel used in this test was commercial ULSD fuel having an average sulfur level of 6 ppm. The sulfur filter was externally temperature controlled at 60C and used in a fixed bed-single pass operation. It was plumbed into the fuel train between the storage tank and engine.

Figure 9 Aftertreatment Configuration

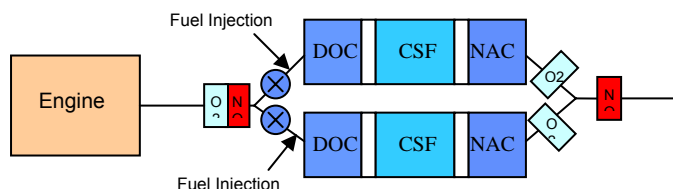
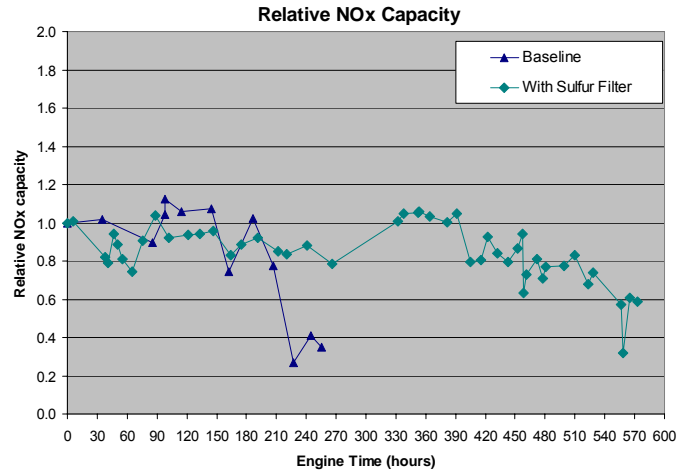


Figure 10 is plotted the NOx adsorber performance for both the baseline test without the sulfur filter and with the sulfur filter. In this plot the normalized relative storage capacity at 50% trapping efficiency is shown. The baseline test was run until 250 hours, at which point soot regeneration resulted in high temperature exposure of the NOx adsorbers. The data from 150 hours onward suggests that storage capacity had been reduced prior to this event. A typical desulfation step would have likely been initiated well before this precipitous drop. At 255 hr there was a sulfur exposure of 2.52g/l to the NOx adsorber which would have caused the NOx adsorber to lose capacity based on prior testing.

The next leg of the test was with the sulfur filter incorporated into the system and shows an improvement in the sulfur durability of the NOx adsorber. This leg was run for over 550hr. Degradation in the performance of the NOx adsorber began around 380 hr. Comparing the sulfur exposure between these tests, in the baseline test the NOx adsorber had a sulfur exposure of 41.2 g at 255 hr and with the sulfur filter test it had 40.0 g at 522 hrs. A post mortem is being done on both NOx adsorbers (baseline and with the sulfur filter) for sulfur content to confirm the sulfur loading.

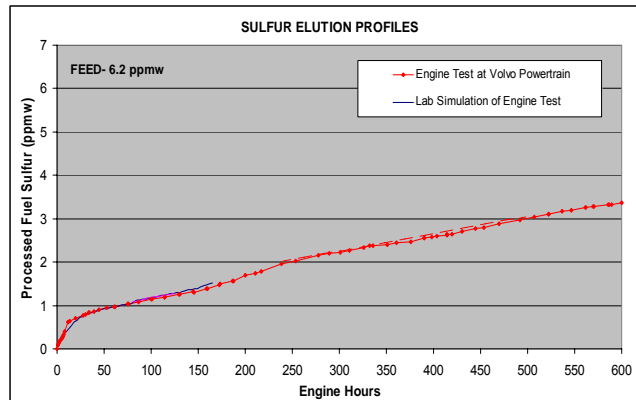
Figure 10 NOx Capacity Profile



#### PERFORMANCE OF THE SULFUR FILTER

The sulfur filter was monitored for performance throughout the run. Periodic samples of the effluent from the sulfur filter and the fuel holding tank were taken and analyzed for sulfur content, cetane number, lubricity and aromatics. Parallel to this a retained sample of the sorbent was tested on a smaller scale test rig in our laboratory to compare its performance to the larger column. In Figure 11 is plotted the performance of the sulfur filter in the engine test with time. Along with that is plotted the performance of the retain sample of the sorbent tested in our laboratory. As can be seen the larger column's performance is very similar to that of the small column testing.

Figure 11 Performance of the Sulfur Filter

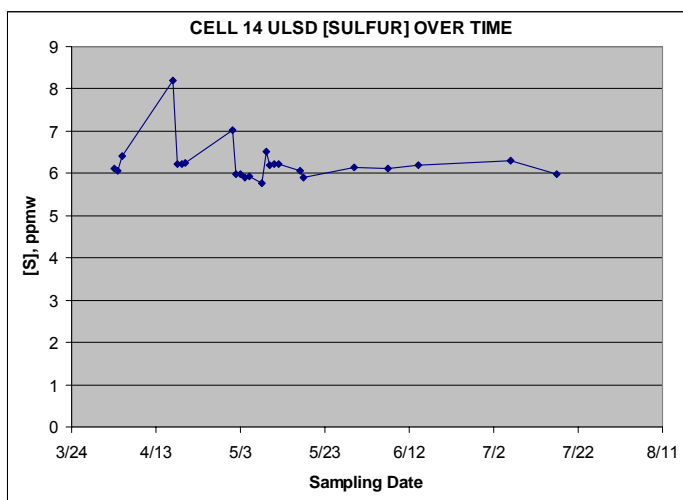


The targeted performance criterion for the sulfur filter was to be able to reduce the fuel sulfur levels to below 3 ppm for an equivalent of 25,000 mi (40,000 km). The sulfur filter achieved the target performance under real life conditions using a commercial fuel. Five hundred hours engine time is equivalent to 25,000 mi (40,000 km).

In Figure 12 is plotted the raw fuel sulfur level over time. There were only small changes in the raw fuel over the course of the run due to batch to batch variability in the fuel.



Figure 12 Fuel Sulfur Variations



### FUEL PROPERTIES AFTER PROCESSING

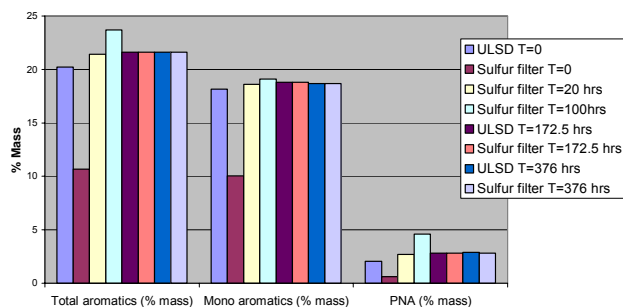
In order to determine what effects if any the sulfur filter had on other fuel properties, several properties of the fuel were measured periodically over the course of the run. Figure 13 is a plot of the cetane number measured from samples collected from the effluent of the sulfur filter throughout test. One can see that there was an initial higher cetane number collected after the first bed volume of fuel passed through the column but this was within the 2 sigma error bar of the technique. After this time the cetane number fell within the range of the starting fuel.

Figure 13 Cetane Number



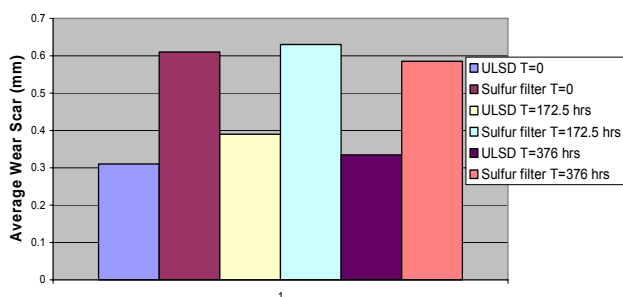
The next fuel property measured was for the aromatics content with time. In Figure 14 is plotted the total aromatics, mono-aromatics and polynuclear aromatics. Again there is very little change over time in these components in the fuel.

Figure 14 Aromatics



The final property measure was for the lubricity of the fuel. In Figure 15 is plotted the lubricity of the fuel with time.

Figure 15 Lubricity Change After Desulfurization



The fuel lubricity has decreased throughout the run to levels beyond the lubricity specification of ULSD fuel of 0.34 mm. either the loss of sulfur components in the fuel which contribute to lubricity or adsorption of the lubricity additive are the cause for this loss. There are two sources of lubricity contributing components in ULSD diesel, those naturally occurring and additives which are added after refining. It is a common practice to add lubricity additives to the fuel to make up for the loss of natural lubricants in the fuel which are lost or altered during the fuel processing. Most of these additives have some polarity in their molecular structure and can be derived from aliphatic amines, carboxylic acids, and esters. The sorbent would most likely have an affinity for these polar components. It will be necessary to bring the lubricity property back to within the specification. Work is underway to incorporate a additive release function to the filter.

#### SIZING LIGHT DUTY APPLICATIONS

Calculations based on the performance on the Mack engine test and sulfur removal data were done in order to estimate the size for a light or medium duty diesel vehicle. In Table 1 is the calculated size in liters for the sulfur filter for different maintenance intervals and km / liter fuel consumptions.

Table 1 Light/Medium Duty Sulfur Filter Size

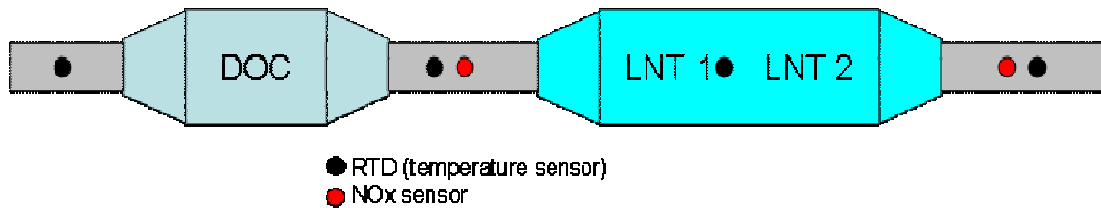
	Maintenance Interval (km)		
km/L	8125	12188	16250
6.5	2.54	3.79	5.07
8.6	1.89	2.84	3.79
10.8	1.51	2.27	3.03

#### LIGHT DUTY NAVISTAR ENGINE TESTING

The engine test was performed at the Navistar, Inc., facilities at Melrose Park, IL. A 4.8L V6 with HPCR (high pressure common rail) fuel injection was used for all the light-duty testing reported here. The engine is targeted towards the light pick-up and SUV markets. Sulfur accumulation mode was run using a steady-state duty-cycle at 1600 RPM and 210 ft-lbs load during both the baseline leg (no sulfur filter) and the sulfur filter leg of the testing. Periodically, the engine was programmed to run hot FTP simulations during which time the NO<sub>x</sub> trapping efficiency was determined. Efforts were made during the two legs of the testing to maintain, as nearly as possible, reasonably constant engine-out NO<sub>x</sub> levels.

The aftertreatment layout and sensor placement are shown in Figure W. The diesel oxidation catalyst (DOC) selected for use in this testing was appropriate for Lean NO<sub>x</sub> Trap (LNT) catalysts and was located upstream of the LNT catalyst section. The LNT catalyst was designed for low temperature applications consistent with the light-duty test. Both the DOC and LNT were supplied by Johnson Matthey. The LNTs were pre-aged and undersized in order to accelerate degradation due to sulfur accumulation.

Figure 16. Navistar Light-Duty Engine Test Aftertreatment Configuration



DOC = 7.5x5", 300 cpsi

LNT = 7.5x5" (x2), 300 cpsi

LNT was designed for low temperature applications

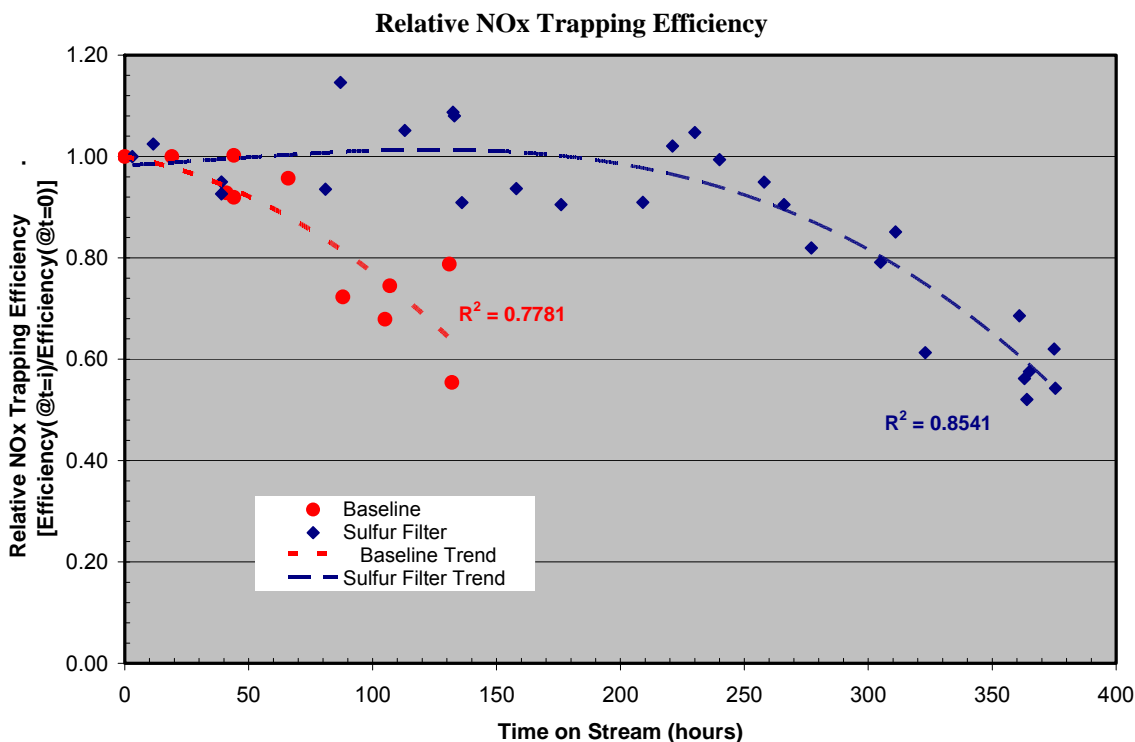
DOC selected was appropriate for LNT

Fuel used for the light-duty testing reported here was commercial ULSD fuel. The average sulfur level in samples of the feed fuel was about 8.6 +/- 0.24 ppmw (Mean +/- SD) of 9 samples collected over the entire duration of the study. These values were obtained using an ANTEK 9000LLS sulfur analyzer using procedures described elsewhere in this report. The sulfur filter was temperature controlled at 60 C using external heaters and fuel was processed in the up flow direction to avoid accumulation of any trapped air in the fuel loop. The filter was located in a low pressure recirculating fuel loop and all of the fuel consumed by the engine during both the steady-

state and FTP cycles was processed through the sulfur filter. Fuel samples were collected immediately following FTP test cycles at a sampling port located immediately downstream of the sulfur filter. Periodically, samples of the feed fuel were also collected for analysis.

The relative NOx trapping efficiencies measured during the baseline (no sulfur filter) leg and the sulfur filter legs of the testing are shown in Figure 17. The baseline data are shown in red and the sulfur filter data in blue, along with their respective trend lines (polynomial fits). Some data collected during known EGR rate excursions or cooler fouling were not included in this analysis.

Figure 17. NOx Trapping Efficiency Profiles

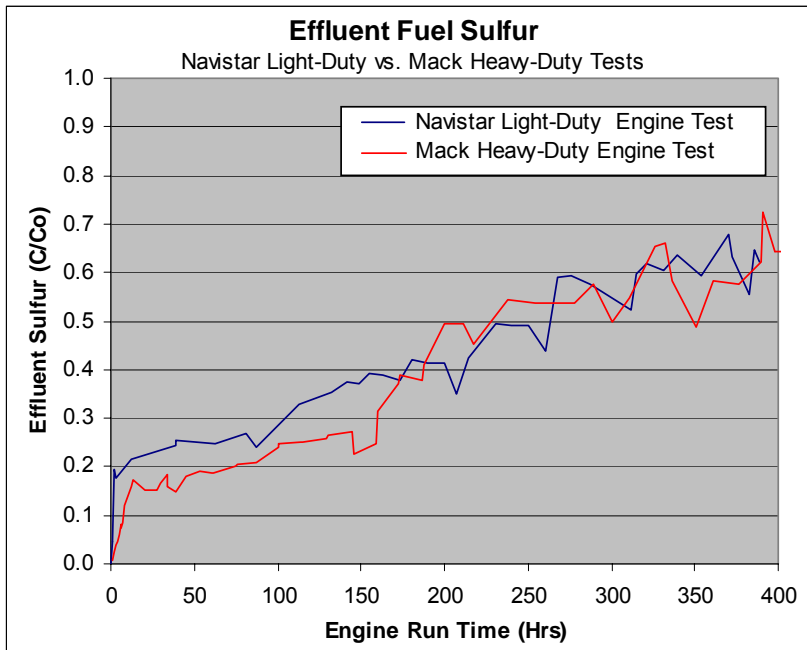


The presence of the sulfur filter resulted in a ~2.8-fold increase in the time required to reach a similar degradation level in LNT NOx trapping efficiency. During the baseline leg, the LNTs maintained a near 100% trapping efficiency until about 66 hours into the run. A relatively sharp fall-off in LNT efficiency was evident beyond this point, and by 132 hours, the NOx trapping efficiency was as little as 55%. Data from the sulfur filter leg indicated that near original performance was maintained until about 240 hours, after which the NOx trapping efficiency declined more gradually than in the case of the baseline leg. In the case of the baseline leg, the period of decline from near original performance to about 55% required only 66 hours compared to the 136 hours required with the sulfur filter present.

The sulfur levels in the fuel samples collected from the sulfur filter (filter effluent) are shown in blue in Figure 18 along with corresponding data from the heavy duty test performed at Mack Trucks (red). The results are plotted as a ratio of the feed ( $C/C_o$ ) in order to allow a comparison of results with fuel containing different sulfur levels. The sulfur breakthrough profiles are generally similar between the two runs, despite the different sources and sulfur levels in the fuel used by the

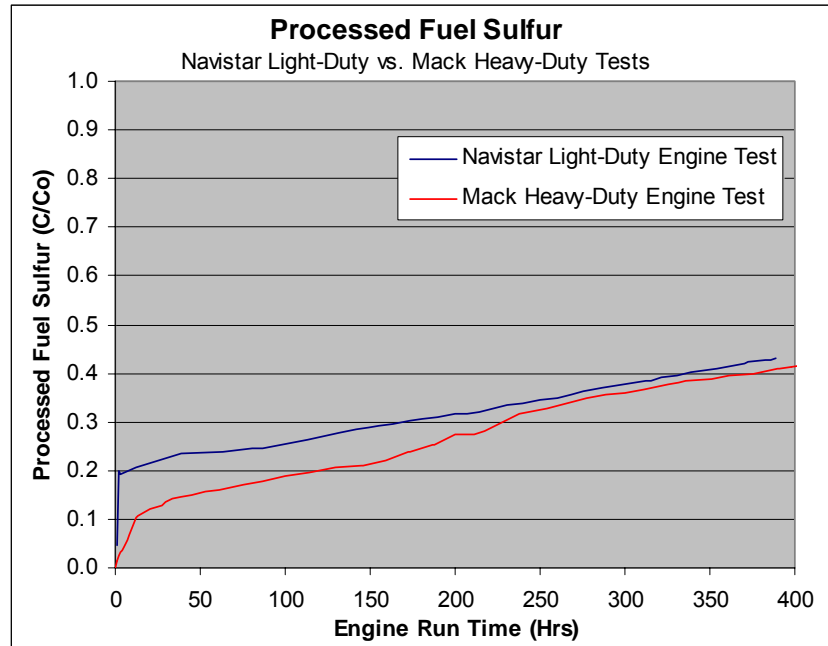
two engine manufacturers. The effluent sulfur in the Navistar light-duty run did increase more rapidly at the very beginning of the run, an effect most likely caused by differences in the filter set-up between the two runs. In the case of the Navistar light-duty run, the filter was set up in a higher filter-specific flow environment, i.e. in a fuel recirculating loop, compared to the lower specific flow single-pass set up used in the heavy-duty test at Mack Trucks. Differences in fuel composition are also known to impact performance of the sulfur sorbent used in this study. Sulfur levels were generally similar between the two tests at engine run times of >175 hours when expressed as C/Co.

Figure 18. Sulfur Profiles in the Effluent



The sulfur levels in the processed fuel were also determined from the effluent sulfur data. Results from both the Navistar light-duty and the Mack heavy-duty tests are shown in Figure 19. These values represent the sulfur that would be present in all the fuel processed at each point during the run. Results expressed this way are a better indication of the overall sulfur trapping efficiency than can be immediately appreciated from the effluent sulfur data alone. The results for the light-duty test indicate that at the end of testing, 50 – 60% of the sulfur had been removed from the 1447 gallons of fuel processed by the sulfur filter during the test period. The amount of fuel processed during the light-duty test is equivalent to nearly 29,000 miles of highway use assuming an average fuel economy of 20 MPG.

Figure 19. Total Processed Fuel Sulfur



#### COMMERCIAL ULSD FUEL VARIABILITY STUDY

Now that ULSD diesel is commercially available at retail suppliers throughout the country, it was considered important to understand the variability of “at the pump” properties of the fuel, particularly as to how it would affect the sulfur filter’s ability to remove sulfur. Additionally, fuel variability will play a central role in determining the size of the filter to accommodate any range in performance. It was recognized that it will be important to determine regional variations resulting from refinery/crude oil sources, processing variations along with seasonal variations due to the addition of specific fuel additives. Early work with precommercial ULSD from various refiners which employed pilot operations to semi commercial processing showed a wide range in the sulfur level of the product and considerable variation in the sulfur filter’s sulfur uptake.

In earlier work with the precommercial ULSD fuels, various properties of the fuels were measured in order to try to correlate the sulfur filter’s performance to these properties. The variables studied included sulfur level, polyaromatics content, water level, lubricity level and nitrogen level. A statistical method “design of experiments, (DOE)” was used to evaluate the impact and magnitude all of these properties on the sulfur filter’s performance in both single and a combined manner. However many of these precommercial fuels may not have been representative of a lined out refinery fuel nor have been additized to the same degree as the present commercial fuels that are available today.

Samples of pump fuel were collected at various retail pumps in the west coast, mid-west and east coast to sample any regional variation which might occur. The first set were collected during the winter months, January through February 2007, while the second set were collected during the summer months, June to July 2007, to determine if there were any seasonal variability. Table 2 contains the data for the sulfur levels on each fuel.

Table 2 Regional and Seasonal Sulfur Levels ULSD Pump Fuels

		WINTER	SUMMER
Fuel	Region	[S] ppmw	[S] ppmw
BP	East Coast	5.4	5.4
ExxonMobil	East Coast	5.8	7.4
Sunoco	Midwest	1.3	2.4
BP	Midwest	3.2	3
Marathon	Midwest	7.5	6.6
BP/Arco	West Coast	1.9	-
Shell	West Coast	1.1	1.0
Valero	West Coast	2.4	-
Chevron	West Coast	-	4.7
Mobil	West Coast	-	6.3

These fuels were then desulfurized using the sulfur filter to determine how the different sources of ULSD affected sulfur uptake and also how seasonal variation affected the sulfur uptake. In all of these studies a packed bed continuous feed approach was used to test the sulfur filter's ability to remove sulfur. In these studies the effluent from the column was periodically measured along with the incoming sulfur level of the fuel feed. A quotient of instantaneous/initial sulfur level was calculated and the cumulative sulfur removed was plotted against volume of fuel processed. Figures 20 through 22 are plots of from three different retail sources comparing sulfur uptake and seasonal variation.

Figure 20 East Coast ExxonMobil (Winter vs. Summer)

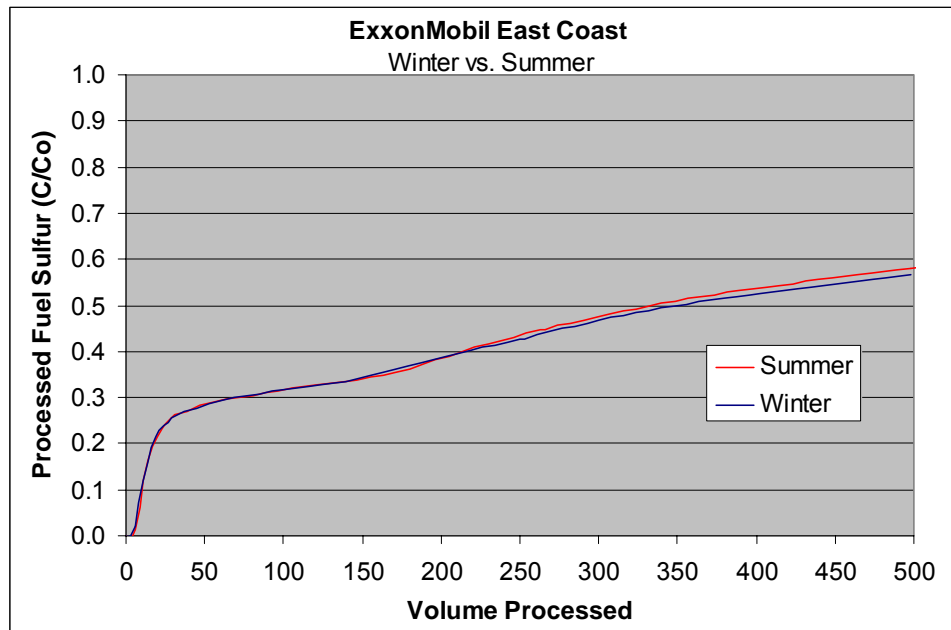


Figure 21 Midwest Marathon (Winter vs. Summer)

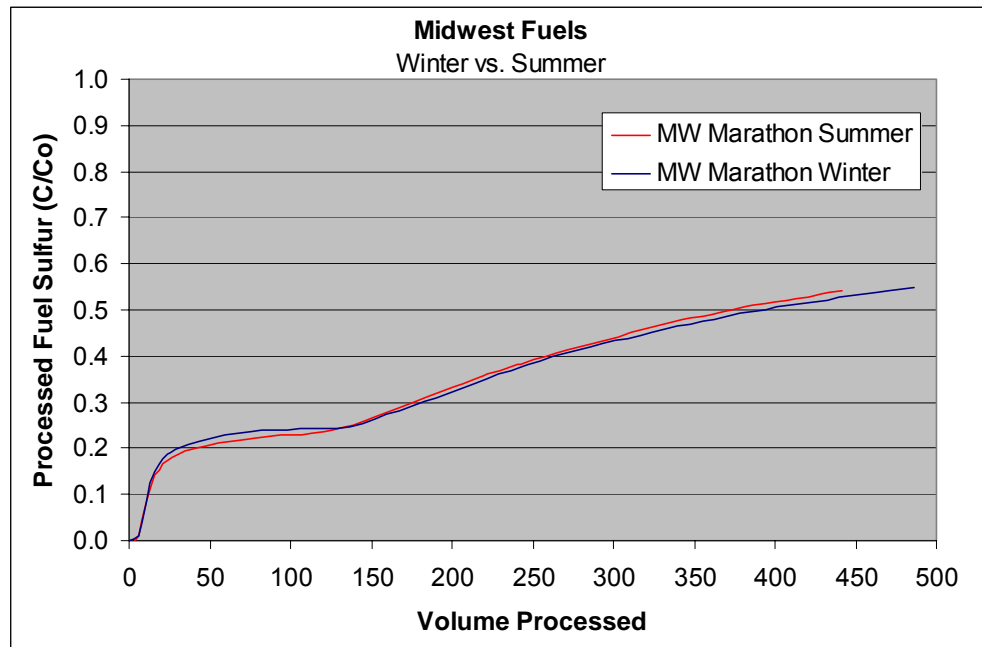
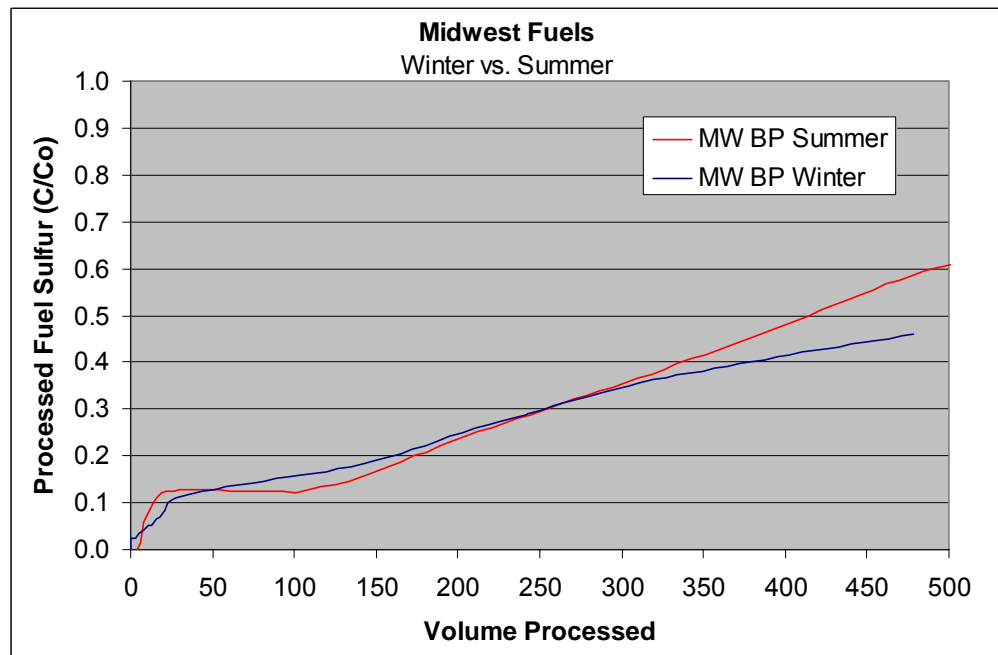


Figure 22 Midwest BP (Winter vs. Summer)





## EXTRACTION OF VALUE OF SPENT SORBENT

An analysis of the life cycle of the sorbent reveals that a large volume of material will be generated during the course of the life of a vehicle since this product will be considered a replaceable and maintainable item. Several ideas were explored in order to determine how to best minimize the impact on the environment and also how to capture any residual value this sorbent might have. Typically end of life oil and fuel filters for both heavy and light duty are either, after suitable period of drainage of the fluids, recycled in metal reclamation or landfilled. However, given the latent value of this material, approaches were explored to seek ways to recapture any intrinsic value. Its greatest and most natural value would be if it could be regenerated and reintroduced into the same application. There are two ways to consider regeneration, 1) while integrated within the engine and 2) off line, removed from the engine. Both of these approaches were studied.

The first of these, “in situ” regeneration was explored in which one is looking for a set of conditions in which the adsorbed sulfur could be released from the sorbent which would bring the sorbent back into a working condition while on the vehicle. The first issue which needed to be dealt with was what would one do with all the released organic sulfur on the sorbent. To this end studies were undertaken at Southwest Research Labs in conjunction with Johnson Matthey with ultra high sulfur diesel fuel. One would anticipate that the regeneration would produce a stream of diesel fuel which would contain the released organic sulfur at an extremely high level, well over a 1000 ppm. There is possibly one scenario on the engine operation in which such a high level of sulfur in the fuel could be tolerated. During the NO<sub>x</sub> desulfation step the adsorber is operated under reducing conditions to release the bound sulfur on the adsorber using a rich fuel condition. Thermodynamically sulfur prefers to be in the unbound state. The question we asked was whether during this operation one could use extremely high levels of sulfur fuel to desulfate the NO<sub>x</sub> adsorber. In order to study this, small cores samples of a NO<sub>x</sub> adsorber were subjected to gas stimulants for this situation which was done at Southwest Research Labs. It was found that the NO<sub>x</sub> adsorber could be successfully desulfated by using this high level of sulfur in the fuel for the regenerant.

The next task was to determine if we could under “on board” conditions regenerate the sulfur filter while on the vehicle. Since most adsorption processes are exothermic and we had previously shown that there is an optimal temperature for adsorption for this particular sorbent, a temperature swing could be considered a viable approach for regeneration. Studies of the temperature/regeneration profiles were undertaken. One could achieve some level of repetitive regeneration by using a higher temperature swing, however the level of regeneration was well below any practical value. The cause for this was explored and found to be the result of parallel degradation pathways in which other components in the fuel were generated and competed irreversibly with the sulfur binding sites on the sorbent. Various ways were explored to minimize this but were unsuccessful. This approach to regeneration was abandoned as technical not practical.

The other approach studied for regeneration was for an “off line” approach. In this approach the sorbent would be removed from the vehicle and the spent sorbent collected and subjected to a much more rigorous regeneration process. In this case temperature was again used but at a much higher level. We found a set of conditions in which we could regenerate the sorbent and regain 80% of its original sulfur removing capacity. It was also anticipated that this process could be done several times without degradation of the base material. This is the approach that would be considered viable for any commercial system.

## WHERE BEST TO DESULFURIZE FUEL?

There are a number of places within the production, distribution and use of ULSD where one might consider carrying out the desulfurization process. All of these points of opportunity were evaluated based on logistics of maintenance, cost and infrastructure. As one proceeds back from

the engine into the distribution and production facility, the size of the filter progressively becomes larger. Given the desire to minimize the maintenance and service intervals the size becomes too prohibitive for the logistics of desulfurizing at distribution points. However it does become a possibility to be used within a refinery as a possible “polishing operation” where transportation and closeness to related processing of regenerant could be facilitated. Therefore the “on board” approach was considered as one of the viable places to desulfurize the fuel.

## CONCLUSION

A chemical filtration approach has been identified which can selectively remove sulfur components in a ULSD fuel to levels below 3ppm. And has sufficient capacity to be effective over a useful period of time commensurate with an oil change interval. The sorbent’s operating conditions have been optimized and are within practical operating limits for on “on vehicle” device. The sorbent preparation and performance have been scaled from the milligram level to the 40 liter level without a diminution of performance. The lowering of the sulfur in the fuel has been demonstrated to extend the length of time of the desulfation step for the NOx adsorber by at least two fold. The fuel properties after the sulfur has been removed have not changed with the exception of the lubricity which has decreased. A readditization of lubricity additive will be necessary to bring the fuel back into this specification. The commercial ULSD fuels available at the pump for both seasonal blends and from various regions shows a smaller variation in the sulfur filter’s performance then what was seen in the precommercial fuels. Testing with biodiesel B-5 showed poorer performance than any of the pure petroleum derived diesel fuels. This is the result of the fatty acid methyl ester competing for active sites on the sorbent. An approach was found in which one could regenerate the sorbent’s capacity to a useful level, albeit a lower one, which could reclaim value for the spent sorbent, thereby minimizing the environmental impact and capturing more value from the sorbent.

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#### LIST OF ACRONYMS AND ABBREVIATIONS

BT	Benzothiophene
DBT	Dibenzothiophene
DMDBT	Dimethyl dibenzothiophene
LLS	Low Level Sulfur
ULSD	Ultra Low Sulfur Diesel
GC	Gas Chromatography
CIDI	Compression Ignition Direct Injection
MAP	Marathon Ashland Petroleum