Technology and Policy for Removal of Sulfur from Fuel

by

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ABSTRACT

The conventional hydrodesulfurization (HDS) process is sufficient for removing aliphatic and acyclic sulfur compounds, but requires severe conditions for adequate removal of benzothiophenes and dibenzothiophenes. It is not clear whether the ultra low sulfur levels required by some exhaust treatment systems can be achieved at all with HDS. New technology that operates at mild conditions without addition of hydrogen or catalysts would significantly reduce the cost and negative environmental impact of desulfurization. What is needed is technological innovation, and public policy that will speed its development and distribution.

One option that has been explored is a combination of oxidation and extraction, where the sulfur compounds are oxidized and then extracted with a polar solvent. Experiments presented in this thesis are aimed at determining whether the partition coefficient of oxidized sulfur compounds can be high enough to make oxidation and extraction a feasible alternative for achieving ultra low sulfur levels in fuel. Dibenzothiophene sulfone is used as a model oxidized sulfur compound, and the partition coefficient is determined for toluene/water and cyclohexane/acetonitrile systems. The partition coefficient calculated for the cyclohexane/acetonitrile system is large enough to validate more research into this method.

In addition to experimental work, this thesis also gives an overview of available technological options, including proven and developmental processes, as well as policy choices available to the government in the area of sulfur standards in fuel.

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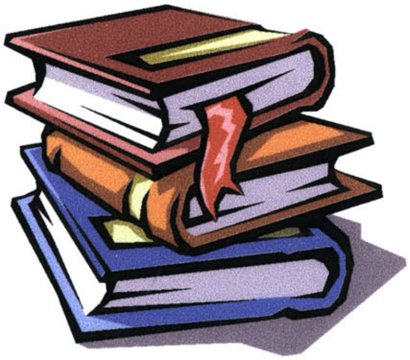

I. Introduction

Reduction of sulfur levels in fuel would benefit the environment in many ways. Particulate and CO emissions from vehicles would decrease and acid rain would be less prevalent. A decrease in sulfur content will make catalytic exhaust treatment more effective and allow new catalysts to be developed, which in turn will lower hydrocarbon, CO, and NO_x emissions.[1]

The conventional hydrodesulfurization (HDS) process is sufficient for removing aliphatic and acyclic sulfur compounds, but requires severe conditions and the use of catalysts for adequate removal of benzothiophenes and dibenzothiophenes. New technology that operates at mild conditions without addition of hydrogen or catalysts would significantly reduce the cost and negative environmental impact of desulfurization. What is needed is technological innovation, and public policy that will speed its development and distribution.

One option that has been explored is a combination of oxidation and extraction, where the sulfur compounds are oxidized and then extracted with a polar solvent. A barrier to this method is finding a solvent that will have a high enough partition coefficient. A low partition coefficient means that a relatively large amount of extraction solvent would be necessary to remove sulfur to low levels. Besides the cost of the solvent, there is also the cost of sulfur recovery and waste removal to be considered. Minimizing the amount of extraction solvent used will lower these costs. A further consideration is how much fuel is dissolved in the extraction solvent along with the oxidized sulfur compounds.

Experiments presented in this thesis are aimed at determining whether the partition coefficient of oxidized sulfur compounds can be high enough to make oxidation and extraction a feasible alternative for achieving ultra low sulfur levels in fuel. Dibenzothiophene sulfone is used as a model oxidized sulfur compound, and the partition coefficient is determined for toluene/water and cyclohexane/acetonitrile systems. Equations

In addition to the experimental work, this thesis explores available technological options, including proven and developmental processes, as well as policy choices available to the government.

II. Technical Background

In 1996, gasoline sold in the US averaged 340 ppm sulfur outside of California[2]. Untreated diesel fuel has around 4200 ppm sulfur.[3] For some time it has been known that fuel sulfur was generally undesirable because it is converted into SO_2, which contributes significantly to acid rain. More recently it was recognized that a high sulfur level in traditional diesel fuel leads to formation of sulfate particulates, a significant fraction of all man-made fine particulates in urban areas. These airborne particulates are thought to have significant health effects, and their concentration correlates with morbidity rates.

In response to these environmental problems, several years ago Sweden imposed a very tight standard on sulfur in Class 1 diesel fuel: 10 ppm.[4] However, at that time most countries decided that the environmental benefits were not worth the cost of such strict desulfurization. It was noted that most SO_2 emissions in the US come from coal, not from liquid fuels, and most particulates are made of organic compounds, not sulfates.

Very recently, it was recognized that fuel sulfur can have a major effect on vehicle emissions via more indirect mechanisms than those listed above. Sulfur is a well-known poison for many catalysts, including some of the catalysts used in current and planned exhaust control systems. As emissions standards for NO_x, hydrocarbons, and soot are tightened, it is becoming increasingly difficult to design exhaust treatment systems which work effectively in the presence of sulfur. This is particularly true for diesel engines – in the past diesels did not use exhaust treatment devices, so the high sulfur level did not matter, but in the future it is anticipated that diesel engines will employ catalytic NO_x reduction strategies which are extremely sensitive to sulfur. These developments have led the US and other countries to impose very strict sulfur standards on both gasoline and diesel fuels. The Tier II standards in the U.S. became effective on April 10, 2000.

A. Sulfur in Fuels

Sulfur occurs naturally in crude oil, from less than 0.05 wt.% to several percent with an average of 1% in the U.S. The portion of the crude oil in the gasoline boiling range typically contains only about 100 ppm sulfur, but the heavier portion in the diesel boiling range has a much higher level of sulfur, typically ~5000 ppm. While the sulfur is mostly in the heaviest petroleum compounds, the fluidized catalytic cracker (FCC) unit breaks up these heavy compounds into smaller compounds, producing 30-50% of gasoline in most refineries. This portion may contain over 1000 ppm sulfur. Over 90% of the sulfur content in gasoline comes from the FCC. The coker unit, which produces coke from the heavy fraction of crude oil, contributes a gasoline blendstock generally containing over 3000ppm of sulfur. Although this blendstock is usually less than 1% of gasoline, the high sulfur content makes it significant.[5]

Hydrodesulfurization (HDS) is the conventional method to remove sulfur from fuel. Hydrogen gas is mixed with fuel at high pressures over a catalyst to convert the organo-sulfur compounds into H_2S gas. The H_2S is separated from the fuel and converted into elemental sulfur and/or sulfuric acid, which can then be sold. The hydrogen used during this process is often produced on-site, raising costs and producing the greenhouse gas carbon dioxide. HDS can lower the sulfur content in fuel significantly, but is not very effective at removing dibenzothiophenes or some other complex organo-sulfur compounds. The sulfur atom in these compounds is bound to a carbon atom on both sides, making them difficult to remove with conventional methods without unwanted effects on the fuel.[6]

The hydrogen gas used during hydrodesulfurization can saturate olefins, having the undesirable effect of lowering the octane number. Saturating olefins also uses more hydrogen, increasing the operating costs of desulfurization. Given the disadvantages of

HDS, it would be beneficial to develop a new method that operates at milder conditions with little adverse effects on fuel.

B. Diesel Standards

Effective June 1, 2006, highway diesel fuel produced at refineries must contain 15 ppm or less. Highway diesel fuel that is sold as low sulfur fuel at the terminal level must meet the same standard effective July 15, 2006, with fuel for retail stations and fleets meeting the standard on September 1, 2006.

There are flexibility provisions including a temporary compliance option that are available from June 2006 through 2009. Like the Tier 2 program (see below) there is an averaging, banking and trading program as well as credit for compliance prior to June 2006. Under these programs refineries could produce up to 20% of highway diesel fuel at the current sulfur standard of 500 ppm. The higher sulfur fuel would need to be separated from the low sulfur fuel, and would be restricted from use in 2007 and newer model year heavy-duty vehicles.

Small refiners will be given additional flexibility, as well as those within the Geographic Phase-in Area of the Tier 2 standards (see below). Refiners may also apply for a general hardship provision on an individual basis.

The EPA estimates that the new diesel standards will increase the cost of production and distribution of diesel fuel by approximately 4-1/2 to 5 cents/gallon. For more details on the standards, see reference 7.

C. Gasoline Standards

In 2004, a corporate average standard of 120 ppm S/gal with a cap of 300 ppm S/gal will be imposed on most refiners and importers. In 2005, the corporate average will be lowered to 90 ppm with a refinery average standard of 30 ppm. In 2006, the corporate average is discontinued in favor of a 30 ppm average and a cap of 80 ppm on individual refineries. Small refineries and those in the Geographic Phase-in Area (including parts of the Great Plains and Rocky Mountains, as well as Alaska) will temporarily have less stringent requirements.

According to the EPA, 15% of domestic gasoline production is already in compliance with these Tier 2 standards, or could be with little investment. However, most U.S. refineries will need to install at least one additional desulfurization unit, with many requiring installing prior to 2004 to meet the 300 ppm cap standard.

D. Vehicle Standards

EPA is implementing the sulfur standards in part to allow vehicles to be developed that will comply with Tier 2 standards. The Tier 2 program will apply the same standards to cars, light trucks, and SUVs, regardless of the type of fuel used, beginning in 2004. The

Tier 2 program will be phased in, beginning with fleet averages that meet or exceed federal and California Low-Emission Vehicle, Phase I (LEV I) standards. The Tier 2 program establishes a new class of vehicles that includes passenger vans and SUVs called "medium-duty passenger vehicles".[8]

E. Effect on Catalysts

The EPA estimates that damage by sulfur to Tier 2 catalysts used in gasoline powered vehicles will be 45% irreversible under normal driving conditions.[9] This is significant for setting caps on sulfur levels in fuel. A relatively high cap may reduce the effectiveness of emission control systems, even if the required average is low. There is a trade-off between flexibility to refiners and emission control.

III. Desulfurization Technology

A. EPA Regulatory Impact Analysis

The EPA released a Regulatory Impact Analysis (RIA) for the Tier 2 program. The technological feasibility section of the RIA described the following desulfurization technologies.[10]

1. FCC Feed Hydrotreating

One conventional method to desulfurize fuel is to use a hydrotreater or hydrocracker for FCC feed hydrotreating. This method has the additional benefits of decreasing the amount of nitrogen and some metals. However, the cost of installing these units can be over $100 million for medium to large refineries. The hydrotreating process involves high pressure and temperature, which increases the costs to the refiner.

2. FCC Gasoline Hydrotreating

FCC gasoline hydrotreating costs about half that of FCC feed hydrotreating for a medium to large refinery. Only gasoline from the FCC unit is treated in this process, and operating temperatures and pressures are lower, further reducing costs. The disadvantage of this method is that a reduction in octane value may occur along with a decrease in the gasoline yield.

New gasoline hydrotreating technologies, such as CDTech or Mobil Oil Octgain 220, limit these reductions through specially designed catalysts and milder operating conditions. Operating costs are lower for the newer technologies, with capital costs from $20 to $40 million for a medium to large refinery. While lower costs would indicate that refineries would install newer processes, comments from the oil industry to the EPA indicate that they will only use processes that have been used commercially for at least two years. This will certainly limit the options available to refiners. Many of the newer technologies would be less expensive than those that have been commercially proven.

a. Widely Used Gasoline Desulfurization Technologies

Mobil Oil Octgain 125, Exxon Scanfining, and IFP (Intitute Francais du Petrole) Prime G are fixed bed desulfurization technologies that are used commercially. Hydrogen is added to high temperature and pressure gasoline blendstock. The mixture enters a fixed bed reactor, where the fuel comes in contact with a catalyst and the sulfur is removed as hydrogen sulfide. Olefins are saturated during the process, leading to octane loss and an increase in hydrogen use. These three commercial processes reduce or offset octane loss. Following removal of the sulfur compounds, gaseous phase components are separated from the liquid phase. Hydrogen sulfide is removed and converted to elemental sulfur, which may be sold. Hydrogen may also be separated and sold, depending on volume, or may be burned with light hydrocarbons.

Octgain 124 operates at severe conditions for octane recovery, and is good for desulfurization of high sulfur fuel. Scanfining also runs at severe conditions for deep desulfurization, where high octane loss can occur. However, the Scanfining process has minimal loss of yield. Prime G conserves octane by not saturating olefins, and operates under less severe conditions.

b. "Improved Desulfurization Technologies"

Mobil Oil Octgain 220 and CDTech are classified as "improved desulfurization technologies" by the EPA. Octgain 220 is similar to Octgain 125, but CDTech uses catalytic distillation to remove sulfur. The CDTech process uses two distillation columns packed with a catalyst. The CDHydro column desulfurizes the lighter portion of FCC gasoline while the CDHDS desulfurizes the heavier portion. The mercaptans in the CDHydro column are converted into heavy thioethers through reaction with dienes. These are collected at the bottom of the distillation column with the heavier compounds. This column operates at much milder conditions than conventional hydrotreating, which decreases olefin saturation and octane loss, and minimizes hydrogen use. The CDHDS column then hydrotreats the heavy fraction from the CDHydro reactive distillation. In May 2000, CDHDS was commercialized. In March 2001, several U.S. refiners announced that they planned to install these units at a capacity of 300 kBPSD. This appears to be a success, with the capability of reducing sulfur to 30 ppm in gasoline, with only a 0.5 loss of octane number.[11]

c. Adsorption Desulfurization Technologies

Adsorption processes are projected to be lowest cost desulfurization technology, based on an analysis by the EPA. Adsorption desulfurization technologies developed by Black and Veatch Pritchard Inc. and Phillips Petroleum Co. are quickly approaching commercialization. The process runs at milder conditions than hydrotreating, and so offers lower operating cost. IRVAD, the Black and Veatch process, uses an alumina-based adsorbent that is fluidized. The adsorbed material, approximately 4% of the treated petroleum stream, is removed in the regeneration column. The adsorbent is regenerated using hydrogen, and then recycled back into the process. There is almost no hydrogen loss and the octane number of the gasoline is increased during the process. The high sulfur stream that is separated from the desulfurized fuel during the process has to be treated before reblending. Black and Veatch expect the stream to be treated in an existing diesel hydrotreater and then separated by a stripping or splitting column into diesel fuel and gasoline.

Phillips' S-Zorb process adsorbs sulfur compounds onto the catalyst in a reaction vessel. The sulfur is cleaved from the petroleum compound, and adsorbed onto the catalyst. The catalyst accumulates sulfur and is periodically regenerated in the regeneration column using hydrogen. The hydrogen disulfide generated is converted to sulfur dioxide and is transferred to the sulfur recovery unit. S-Zorb does not require hydrotreating of a high sulfur stream, but does saturate some olefins, and therefore lowers the octane value. The first S-Zorb commercial unit, a small 6 kBPSD unit, was started in April 2001.

B. Biological Desulfurization

Another method of removing sulfur from fuel is biological desulfurization, which is under investigation by several groups. Chang et al.[12] have explored the use of Gordona sp. CYKS1 to cleave bonds between the carbon and sulfur atoms in organo-sulfur compounds at mild conditions.

Biological desulfurization has advantages over conventional desulfurization using hydrogen because it can operate at room temperature and atmospheric pressure. A further advantage is that dibenzothiophene and other unreactive molecules can be desulfurized. Aerobic or anaerobic bacteria may be used, but aerobic desulfurization does not need the additives and special equipment required for the anaerobic bacteria; it also does not need hydrogen.

Gordona sp. CYKS1 converts dibenzothiophene sulfone to 2-hydroxy biphenyl, with dibenzothiophene sulfone as an intermediate. Methyl sulfide, thiophene, phenyl sulfide, and other organo-sulfur compounds can also be desulfurized by this bacteria. Chang et al. have also investigated Norcardia sp. CKYS2, which has similar capabilities to Gordona sp. CYKS1.[13] Considerable development is required to scale these laboratory processes to the industrial scale.

C. Precipitation as Salts

Benzothiophenes and dibenzothiophenes can be methylated at room temperature by iodomethane using silver tetrafluoroborate as a catalyst, resulting in crystalline powders of S-methylated benzothiophenium and dibenzothiophenium tetrafluoroborates. These powders are polar and insoluble in nonpolar hydrocarbon solvents. Removal of benzothiophenes and dibenzothiophenes may be possible as precipitates in nonpolar light oil.

A study by Shiraishi et al.[14] examined the feasibility and selectivity of this method. They found that dibenzothiophene was removed from tetradecane (a model for light oil) with 58% efficiency at 303 K, with CH_3I and $AgBF_4$ present at 20- and 2-fold quantities respectively. When an equal amount of dichloromethane is added to tetradecane, the efficiency increased to 85%. Temperatures above 320 K resulted in decreased efficiency due to thermal decomposition of the sulfonium salts. To completely precipitate benzothiophenes, the tetradecane solution had to be cooled to 273 K.

The process was then used on straight-run light gas oil (LGO), commercial light oil (CLO), and light cycle oil (LCO) with a respective 10- and 2-fold molar excess of CH_3I and $AgBF_4$ added. A viscous liquid precipitate formed, leading to sulfur removal of 2% in LGO and CLO, and 94% for LCO. The oil could be recovered by decantation with yields of 94% for LGO, 95% for CLO, and 92% for LCO. Desulfurization increased with quantity of CH_3I and $AgBF_4$ added. The study concluded that this process could result in less than 0.005 wt % sulfur content in light oils.

Shiraishi *et al* also studied the effect of aromatic hydrocarbons on the desulfurization process. Using tetralin and naphthalene in tetradecane as a model, they discovered that the high electron densities on both molecules make substitution by the methyl groups of CH3I competitive with the desulfurization process. Alkyl substituents of high carbon number on dibenzothiophenes or benzothiophenes were also found to impede this desulfurization process.

Like biological desulfurization, further effort is required on both the chemistry and the separation for this approach to be economically feasible.

D. Oxidation and Extraction

A conversion/extraction desulfurization (CED) process for diesel fuel has been under development by Petro Star Inc. since 1996. The process works by selectively oxidizing sulfur compounds at mild conditions, and then extracting the oxidized sulfur compounds with a reusable solvent. The oxidation increases the polarity of the compound, increasing its solubility in polar solvents such as DMSO and methanol. Organo-sulfur compounds can be selectively oxidized in part because of sulfur's d-orbitals, which facilitate selective reactions with certain oxidizers. A peroxyacetic acid system is used for the selective oxidation, with dibenzothiophene as the model sulfur compound.

A stoichiometric quantity of the peracid is used at atmospheric pressure and 100°C or less to effect oxidation in under 25 minutes. Bonde et al.[15] found that DMSO could remove over 95% of the oxidized sulfur in diesel and jet fuels. Although this is promising, a much higher sulfur removal efficiency is required for this process to offer a significant advantage over existing desulfurization technologies. Also, an appreciable amount of fuel is extracted along with the oxidized sulfur compounds in the CED process[16], leading to an undesirably large waste stream. They have also been investigating mixtures of solvents that are more cost-effective than DMSO alone for the liquid/liquid extraction. These mixtures have patents in process. In the experimental section below, measurements are presented for alternative solvents to try to achieve a better separation than obtained by Bonde et al. using DMSO-based solvents.

Most polar compounds, including sulfones, are removed in CED by continuous liquid/liquid extraction, but some oxidized benzothiophenes and dibenzothiophenes that are highly substituted are not readily extracted by DMSO. To remove these compounds, Bonde et al. suggest polar solid phase polishing materials, similar to those used in the IRVAD process described above, as an adsorbent. They have successfully tested refining clay, silica gel, and alumina among others.

A high sulfur stream and a desulfurized raffinate result from the CED process. Bonde et al. have investigated different methods of desulfurizing the high-sulfur extract stream. Experiments by Bonde *et al.* have removed up to 95% of the sulfur from the organo-sulfur compounds. This stream could also be run through a conventional HDS unit. The desulfurized extract can then be blended with the raffinate or sold.

Hydrogen peroxide is used to make the peroxyacetic acid used in the CED process, and accounts for almost half of the operating costs. A further cost is the loss of up to15% of the fuel into the extraction solvent, costing up to $6/bbl, which is more than double the projected costs of the whole CED process.[17] If CED is to be used on a refinery scale, the loss would need to be reduced or at least partially recovered. By comparison, the liquid/liquid extraction is relatively inexpensive due to low temperature conditions and the ability to recycle extraction solvent. If CED is used as a supplement to HDS, less peroxyacetic acid would need to be used since there would be less total sulfur. A combination of HDS and CED could be cost effective, particularly for refineries that have HDS already installed but need to further reduce sulfur levels.

In addition to its low cost in comparison to conventional HDS, CED does not significantly alter the quality of the fuel, and actually improves API Gravity and Cetane number by decreasing the aromatic content. This process may be the only desulfurization unit used, or can complement an HDS unit to meet the Tier II standards. There are no commercial units at present, but the technology is essentially ready for commercialization.

IV. Experimental Measurement of Oxidized Sulfur Partition Coefficient

The work of Bonde et al.[18] seems to have the potential to be a relatively inexpensive method to desulfurize fuel. They achieved 99% oxidation of the organo-sulfur compounds in diesel fuel, but only 85% efficiency in removal of the oxidized compounds. One of the obstacles to overcome in the CED method is the tendency for the extraction solvent to dissolve some fuel as well as the oxidized sulfur compounds. The following equation shows the relationship between the volumes of fuel and solvent and the partition of fuel into the solvent:

$$\frac{\text{Amount of fuel lost}}{\text{Total amount of fuel}} = \frac{V_{\text{solvent}}\ \alpha}{V_{\text{fuel}}} \qquad \textbf{(1)}$$

where V_{solvent} is the volume of extraction solvent, V_{fuel} is the volume of fuel, and α is the solubility of the fuel in the solvent. Bonde observed an α value around 0.04 for diesel fuel in dimethyl sulfoxide (DMSO).

What is needed to minimize waste streams and costs is a solvent with a high partition coefficient for polar compounds (i.e. oxidized organo-sulfur compounds) that is selective (i.e. does not dissolve much of the fuel). The CED method appears to have a partition coefficient of 3 to 4. However, assuming an extraction solvent:fuel volumetric ratio of 1:100, and that all sulfur compounds were oxidized to dibenzothiophene sulfone or similar compounds, to go from 10 ppm to 1 ppm sulfur in fuel the partition coefficient would need to be greater than or equal to 900. The following equation states the relationship between partition coefficient, solvent:fuel ratio, and fraction of sulfur compounds oxidized:

$$\frac{[S]_{fuel}\,\chi}{[S]_{desired} - [S]_{fuel}\,(1 - \chi)} = \varepsilon\,(V_{solvent}:V_{fuel}) + 1 \qquad \mathbf{(2)}$$

where $[S]_{fuel}$ is the concentration of sulfur compounds in fuel stream, $[S]_{desired}$ is the desired concentration of sulfur compounds in fuel, is the fraction of sulfur compounds that are oxidized, ε is the partition coefficient, $V_{solvent}$ is the volume of solvent, and V_{fuel} is the volume of fuel.

Table 1 shows the results of these calculations for various scenarios with α and χ held constant at 0.4 and 1 respectively.

ε	[S]fuel (ppm)	[S]desired (ppm)	Vsolvent:Vfuel	% Fuel lost
4	3000	10	74.75	2990
40	3000	10	7.475	299
400	3000	10	0.7475	29.9
1000	3000	10	0.299	11.96
4	30	10	0.5	20
40	30	10	0.05	2
400	30	10	0.005	0.2
1000	30	10	0.002	0.08
4	10	1	2.25	90
40	10	1	0.225	9
400	10	1	0.0225	0.9
1000	10	1	0.009	0.36
4	3000	1	749.75	29990
40	3000	1	74.975	2999
400	3000	1	7.4975	299.9
1000	3000	1	2.999	119.96

Table 1. Result of calculations for various scenarios, with α=0.4 and χ=1.

The difference in amount of solvent needed and percent of fuel lost is dramatic between the different partition coefficients. An ε of 4 corresponds roughly to the CED method, while an ε of 40 is close to the partition coefficient measured in the experiments described below.

The table also shows the difference in amount of solvent needed and percent of fuel lost between different sulfur levels, with ε held constant. A value of $[S]_{fuel}$ of 3000ppm represents untreated fuel, while 30ppm represents fuel that has already been treated (i.e. by HDS). With a partition coefficient of 40, for example, a CED-type system installed in a refinery as the only desulfurization system would be insufficient to reduce sulfur levels to 10ppm since the calculation indicate that over 100% of the fuel would be lost. However, the same system installed in a refinery with an HDS system could reduce the sulfur level in the fuel from 30ppm to 10ppm with only a 2% loss in fuel and a $V_{solvent}:V_{fuel}$ of 0.05. If a solvent or mixture of solvents could be found with a high enough partition coefficient, the CED method could be applied economically (assuming the solvent is readily available and relatively inexpensive) at the refinery scale.

A. Experimental Procedure

To further explore the extraction portion of the CED method, experiments were conducted to find the partition coefficient for dibenzothiophene sulfone in two different solvent systems. Analysis for this procedure was performed using a Hewlett Packard 5890 Series II Plus Gas Chromatograph and Hewlett Packard 5972 Series Mass Selective Detector. The GC capillary column was an HP-50+ (crosslinked 50% PH ML Siloxane, HP Part No. 19091L-433). It had a 30m × .25mm × .25μm film thickness. Chemicals used were from Aldrich and consisted of 99.9+% HPLC grade Cyclohexane (CAS 110-82-7), 99% optical grade Pyrene (CAS 129-00-0), and 97% Dibenzothiophene Sulfone (CAS 1016-05-3). Toluene and acetonitrile were also used as solvents. The autointegration function of the GC/MS software was used to calculate the area under the peaks of the total ion chromatography traces. See Appendix 1 for data.

1. Internal Standard Calibration

Dibenzothiophene sulfone was calibrated in toluene using pyrene as the internal standard. The response factor for the internal standard was determined through a calibration curve. The pyrene concentration was held constant at 0.25mg/mL while the concentration of the sulfur compound was varied. Figure 1 shows the calibration curve for dibenzothiophene sulfone, with the ratio of the areas under the peak on the gas chromatography trace plotted against the concentration of DBTS. All chemical solutions for the calibration were made with toluene as a model fuel.

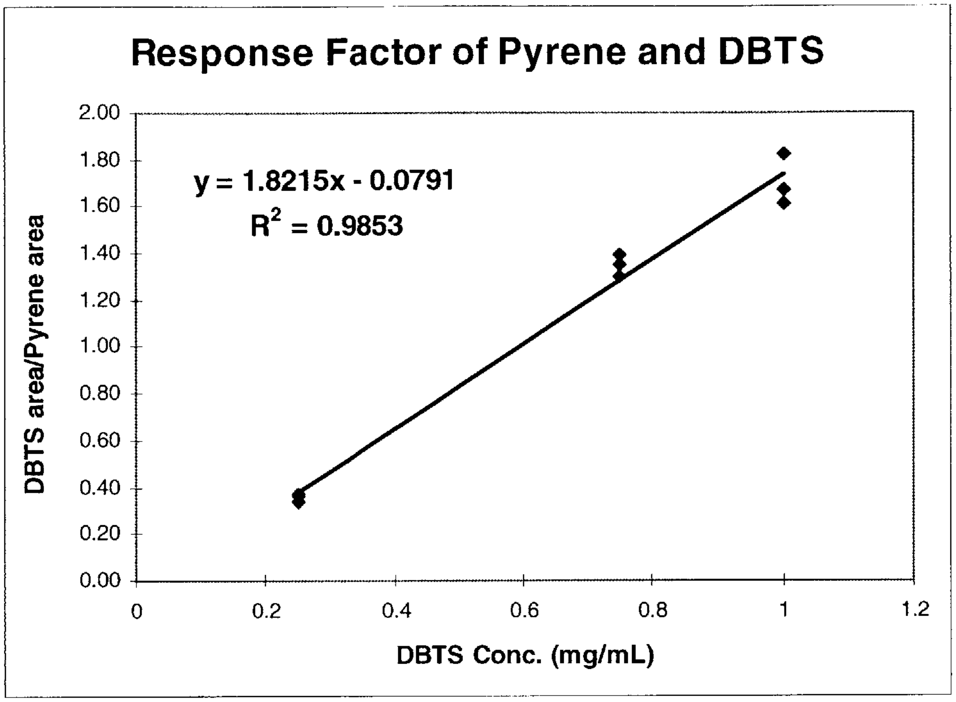

Figure 1. Calibration curve for Dibenzothiophene Sulfone.

2. Extractions

Extractions were carried out using both toluene/water and cyclohexane/acetonitrile systems.

a. Toluene/Water

Dibenzothiophene sulfone was dissolved in toluene at 1.5 and 0.6 mg/mL. Extractions were carried out at each concentration using water as the extraction solvent. Equal volumes of sulfone solution and deionized water were added to a 60mL separation funnel. The funnel was shaken vigorously for 10 seconds followed by venting. This shaking procedure was repeated four times. The solutions were allowed to separate, then 200μL of 0.50 mg/mL pyrene solution was added to 200μL of the extracted toluene solution, effectively halving the concentration of both. The pyrene/toluene solution was then run on the GC/MS.

b. Cyclohexane/Acetonitrile

15 mg of dibenzothiophene sulfone was dissolved in 20mL of acetonitrile. 10mL of this solution was added to a 60mL separation funnel along with 10mL of cyclohexane. The same extraction procedure as above was used. 200μL of 0.50 mg/mL pyrene solution was added to 200μL of the cyclohexane solution, and 1μL injected into the GCMS. No

dibenzothiophene sulfone was detected. 3mL of the cyclohexane solution was evaporated to dryness, then 200μL of 0.50 mg/mL pyrene solution and 200μL of toluene was added to the same vial. 1μL of this solution was injected into the GCMS, and dibenzothiophene sulfone was detected. Another run was performed with similar results.

B. Results and Discussion

The calibration curve generated during the internal standard calibration was used to determine the concentration of sulfur in solution after extraction (see Table 2). The partition coefficient for the cyclohexane/acetonitrile system is 41. This number was calculated by dividing the concentration of DBTS in acetonitrile after extraction by the concentration of DBTS in cyclohexane after extraction. The amount of sulfone in cyclohexane following extraction was too small to be detected by the GCMS. 3mL of the cyclohexane solution was evaporated, leaving a visible residue on the vial. 200μL of .5 mg/mL pyrene solution in toluene was added to the vial. An additional 200μL of toluene was added so that the concentration of pyrene would be identical to that used for the calibration curve. Toluene was used because the pyrene solution had been made for the toluene/water system experiments, and because toluene and cyclohexane are miscible it was not necessary to make a new pyrene solution. The solvent does not affect retention time on the GCMS.

DBTS init. conc. (mg/ml)	**DBTS conc. after extraction**		
Toluene/Water	*Run #1*	*Run #2*	*Run #3*
1.5	**1.589**	**1.702**	**1.863**
0.6	**0.618**		
Cyclohexane/Acetonitrile			
0.75	**0.018**	**0.018**	

Table 2. Concentration of DBTS after extraction.

The concentration of DBTS in toluene following extraction was actually somewhat higher than the initial value. This is likely the result of some toluene being dissolved in the water phase, as well as experimental error. It is evident that the partition coefficient for the toluene/water system is very low. Bonde attempted experiments using water as a solvent and also discovered that dibenzothiophene sulfone is not soluble enough in water. He found that polar, immiscible organic solvents such as acetonitrile were much more successful.[19]

While extraction with water was not very successful, the cyclohexane/acetonitrile system worked well. A partition coefficient of 41 indicates that at equilibrium, there will be 41 times the concentration of dibenzothiophene sulfone in acetonitrile than in cyclohexane. This means that the amount of acetonitrile used could be small in comparison with cyclohexane and still extract a significant amount of DBTS. Using a small solvent stream has many advantages. It is cheaper to recycle, there is less fuel extracted (see Eqn. 2), it may be cheaper to treat the waste stream, and there is the potential to use a smaller, less expensive extraction unit.

Acetonitrile is often used in industrial processes, and so would be easy for refiners to work with. Still, even if acetonitrile is very selective for polar compounds, a volumetric ratio of 1:4.6 for acetonitrile:fuel would be needed to reduce the sulfur level from 10 ppm to 1 ppm given the partition coefficient of 41.

The experiments described here are certainly not comprehensive, but they provide more evidence that an oxidation/extraction technique could be viable for desulfurization of fuel to meet or exceed Tier 2 standards. Oxidation and extraction appears to be a promising and relatively inexpensive method of reducing sulfur in fuel. In conjunction with other methods, such as the polishing technique under investigation by Petro Star, oxidation/extraction may be able to achieve sulfur levels below 10 ppm at a relatively low cost. More research is needed to determine if this is possible.

V. Technology Forcing and Environmental Regulation

A. Overview

Many developed countries are setting more restrictive standards for sulfur in fuel, recognizing that low sulfur fuels will allow for more efficient exhaust systems. In Japan and Europe, for example, the maximum sulfur level in diesel fuel is .05 wt%, with the expectation that this will be lowered to .005 wt% in the near future. This is in comparison to the 2006 U.S. standard of 0.0015 wt%.[20] The sulfur standards are about 5,000 times lower than the typical sulfur level in crude oil, and about 100 times lower than the typical sulfur level in today's fuels. More than 99% of the sulfur in fuel needs to be removed to meet the new standards – a challenging goal! A large part of these reductions are feasible using existing HDS technology, but it is not clear whether today's technology is capable of producing fuel containing only a few parts per million sulfur.

Alternatives to HDS must overcome an established technology with a huge installed capital base. This situation discourages research into alternatives in two ways:

1) It is quite unlikely that any alternative could achieve shut-down economics over the established HDS technology, so it is hard to make an economic argument for investing in this sort of research. Also, the barriers-to-entry are considerable in the refinery business, reducing the incentive to have the best technology available.

2) Most of the technically capable R&D organizations in this area also have a significant amount of capital invested in HDS, so they are even more reluctant than others to push an alternative which might force them to write off their large HDS investments.

Note also that a breakthrough in catalyst technology (to make the catalytic system less susceptible to sulfur) could erase the value of the new technology. Even the benefit to society from the research is rather indirect: improving sulfur removal technology increases the chances that improved exhaust catalysts will be commercialized, which would result in cleaner air, which would probably improve human health.

In this section we consider methods governments can use to force these sorts of socially desirable but commercially unappealing technology developments.

B. Technology Forcing

The ultimate goal of environmental regulation is to reduce the emission of harmful substances into the environment. The means of achieving this goal are often changes in technology, or "technology forcing". There are two types of technology forcing: 1) forcing the dissemination of technology that has already been developed but has not yet been commercially tested, and 2) providing an incentive for long-term research that will develop new technology to meet future needs. Technology forcing refers to a range of technology changes, from the development of new technology ("innovation") to the diffusion of a technology standard[21]. So-called "command and control" regulation can be very successful in technology forcing, and can encourage innovation. Other regulatory options can also bring about technological change, but seem to be less successful.

Specification standards, which prescribe the use of a certain technology, are a form of command and control regulation that forces the diffusion of a technology standard. An example is the "best available technology" requirement under the Clean Water Act (Section 301(b)). All firms within an industry are required to use the best technology that is economically achievable. While specification standards certainly force changes in technology and reduce pollution, they tend to stifle any innovation because there is no advantage in developing new technology.

Another form of command and control regulation is to set a standard that industry must meet. This promotes innovation by allowing industry flexibility in how they reach the prescribed standard. The disadvantage is that it may be more difficult to verify emission levels in some cases. It is generally easier to check if certain equipment is installed than to measure emissions.

Permit trading programs are another option for policy makers. The government releases only enough permits to allow an acceptable level of pollution. If each firm is charged for the number of permits it wants, or can buy and sell their permits, then there should be an incentive for innovation. The less pollution the firm emits, the less permits it needs to buy or the more permits it has to sell. Permit programs do not always work to promote technological innovation, however. For example, SO_2 trading in the electricity industry has been successful in reducing the costs of emission reduction[22], but no significant innovation has been noted.

Another alternative is innovation waivers, which allow noncompliance with regulations during the development of new technology. The Clean Air Act, for example, provides for innovation waivers under Section 111(j) for new sources. This is a direct way to encourage new technology, but many refineries would find this to be a risky proposition because there is no guarantee that the new technology will work. To offset this, the implementing agency may use a "fail-soft" strategy where they would not strictly enforce environmental regulations against firms that have made a good faith effort to develop new technology.[23] Innovation waivers do work, which is evident from the case of Monsanto v. EPA.[24] Monsanto received an innovation waiver to install a water scrubber as their pollution control system. This innovative design was intended to allow for recovery of benzene and other hazardous chemicals. The equipment was anticipated to achieve the 95% reduction required by the EPA, but instead reduced the benzene level by only 80%. The CAA provides for up to a two year extension on the innovation if this is necessary for installation of pollution control technology. EPA did not initially grant this extension, but the District Court overturned their decision and Monsanto received the extension so that it could install a supplemental carbon adsorption system. Admittedly, there were problems involved in this case, but the outcome was new technology and less pollution.

Negotiation can be used to encourage new technological development. It brings relevant parties together and sometimes innovative options that produce less pollution at a lower cost are discovered. Negotiated implementation, such as innovation waiver opportunities, focuses on technological change. A new regulatory standard, either threatened or in place, is the motivation for firms to negotiate for time to develop an "innovative compliance alternative". Thus far the innovation waiver program has not been as successful as expected, but this may be due to administrative failure rather than a flaw in the program itself.[25]

Command and control regulation can be used effectively to achieve technology forcing. In addition to direct results (through specification standards, for example), it can promote innovation through the threat of stricter regulations in the future. Refineries can gain an advantage over their competitors by anticipating future environmental control requirements and acting early to achieve them (OECD 1997).[26] Control equipment manufacturers may also respond to anticipated regulations by developing new technology. The threat of future regulations is also a motivation for industry to participate in negotiations. Alternative approaches, such as fees, can also be successful but appear to be less effective than command and control regulation.

1. Sulfur Averaging, Banking, and Trading (ABT) Program[27]

The Tier II Program predominantly uses regulatory standards (see Technical Background above), but makes use of permit programs as well. The ABT Program was developed to give flexibility to refiners, increase environmental benefits, and provide an incentive for technological innovation. Refineries can earn sulfur allotments in 2003 by producing gasoline that contains less than 60 ppm S/gal on an annual-average basis. In 2004 and 2005, refiners or importers (not individual refineries) can earn allotments by producing gasoline with sulfur levels below the corporate average standard for that year. These allotments may be traded between refiners/importers, and can be used towards compliance with the corporate and refinery standards. Any allotments held over from

2004 are discounted by 50% for use in 2005. Allotments may be turned into credits (see EPA Tier II rule).

Sulfur credits can also be earned. A sulfur baseline for conventional and reformulated gasoline was established for individual refineries based on 1997 and 1998 data. Credits are earned from 2000-2003 when a refinery produces gasoline with a sulfur level at least 10% below its baseline. In 2004 and beyond, credits are earned by producing gasoline that is below 30 ppm. These credits can be used towards compliance with the 30 ppm average refinery standard starting in 2005. In 2005 and 2006, refineries can use credits banked during 2000-2003 or purchased from other refineries. The ABT Program is discontinued for 2007. Because sulfur can poison catalysts in emission systems, it is important for the automotive companies to know that the sulfur cap applies to all gasoline during the design phase. If the ABT Program remained in effect in 2007, vehicles in that model year may not be able to meet Tier II standards because they would have to design the exhaust system assuming that the fuel used may be higher in sulfur than the cap.

2. Recommendations

While the Tier 2 program has many provisions for flexibility, it does not allow for corporate averaging starting in 2005. Each individual refinery must meet the standards unless they take advantage of the ABT program. The problem with this is that a corporation would not be able to blend gasoline from different refineries, even if the resulting blend would meet the standards. An individual refinery may be just above the per gallon cap, so the parent corporation would have to install additional equipment. If blending were allowed between refineries, it would lower costs and the standards would still be met. Blending between different corporations would also have the potential to lower costs. The problem is in enforcement, because it would be more difficult to keep track of fuel moving between refineries. However, a paper trail may be sufficient for enforcement of the standards.

Comments to the EPA included concern that refineries would be unable to meet sulfur caps during turnarounds (scheduled maintenance resulting in closure of processing units) or upsets (unplanned closure of processing units). A suggested solution was to allow higher sulfur gasoline to be produced during those times, but that the corporate average would still have to be met. The EPA would not allow for that flexibility because it would result in gasoline exceeding the sulfur cap that could damage emission controls in vehicles. They suggested that maintenance could be performed during periods of reduced gasoline production, or that high sulfur gasoline could be stored until the units are back on line or shipped to other refineries for desulfurization.[28] This is a situation where blending between refineries could be the solution; the sulfur cap would still be met, and the cost to refineries would be reduced.

While four years lead time seems like a long time, in terms of installation of new desulfurization equipment the time goes by quickly. This is not enough time to develop new techniques, and is barely enough time for developed but unproved technologies to be accepted by refineries. Methods such as CED are not far enough along in the research process to be ready by 2004. It may be possible for some refineries who are able to gain or buy credits through the ABT program to wait another year or two before installation, allowing more time for processes such as adsorption to be commercially proven. If the EPA had moved the Tier 2 timeline back a few years, more research and development could have been accomplished and perhaps more economical and more efficient processes would have been ready for use by refineries.

VI. Conclusion

The CED process appears to be an economical way to desulfurize fuel to very low levels, if appropriate extraction solvents are found. It is unlikely to be used to meet Tier 2 standards except perhaps in Alaska, where Petro Star is located, and perhaps in other GPA refineries that have extra time to comply with regulations. Experiments by Bonde on both diesel and gasoline with the CED process have been successful in removing sulfur. When/if the EPA decides to tighten the regulations further, the CED process—perhaps in conjunction with previously installed desulfurization equipment—will probably be a major contender. In terms of diesel standards, the CED process will likely be used in Alaska but will probably not be widely used elsewhere when the new diesel standard goes into effect in 2006. As for gasoline, CED may be viable for refineries identified as being in the GPA.

Nevertheless, oxidation and extraction has the potential to be an economical and effective method for desulfurization of fuel to 10 ppm or less. Bonde et al. have achieved over 99% oxidation of organo-sulfur, and the extraction has been successful on the laboratory scale. The partition coefficient measured in experiments outlined here (41) was much higher than the coefficient calculated by Bonde for DMSO (3-4). Further research may produce an extraction solvent or combinations of solvents with a sufficiently high partition coefficient for use in industry.

Research can be encouraged by the government and result in technology forcing. There are two types of technology forcing: 1) forcing the dissemination of technology that has already been developed but has not yet been commercially tested, and 2) providing an incentive for long-term research that will develop new technology to meet future needs. The first type is relatively easy, and mainly consists of the EPA or the relevant government agency putting forth a ruling that a certain technology must be used or a certain standard must be met. The second is more difficult, but the most obvious way is to make it clear that a certain standard will be promulgated 10 to 15 years ahead. Corporations will then invest in the research required to meet the coming standard. If there is no threat of stricter regulations, there is little incentive for a firm to invest in developmental research. It may even be detrimental to do so, since once the technology exists, the standards would then be tightened to account for it.

One problem with threatening to promulgate a new standard ahead of time is that it gives interest groups more time to fight it. Another is that the political environment 10 years in the future is likely to be quite different from today's. Firms know that it is far from certain that the threatened action will actually be carried out, reducing the incentive to prepare for it. Still, warning of a proposed rule would likely be incentive enough for many firms to fund some research. For example, Petro Star, Inc. has a relatively small budget for research, but was willing to provide Steven Bonde's salary while he worked on a new desulfurization technique that had no guarantee of feasibility on the industrial scale. The motivation for his research, which began in 1997, was the expectation that Alaska would lose its exemption from the current 500 ppm sulfur standard for diesel. Alaska is currently still exempt from the 500 ppm diesel standard, but will be subject to the new diesel standards, with special provisions.

Often what sparks research is a large event that grabs the public interest. One example is CAFE standards, which were promulgated during the energy crisis of the 1970s. The shortage of energy resulted in a spike in gasoline prices and long lines at gas stations. The public was very aware of the situation, so politicians decided to force the Big 3 (General Motors, Ford Motor Co., and Chrysler) to meet standards for gas mileage and emissions.

While predicting such events is difficult, current research may point to an impending event and provide an incentive for funding of future research. An example of this is the discovery of the hole in the ozone layer. Mario Molina and F. Sherwood Rowland predicted the hole in 1974, but the satellite picture didn't provide direct evidence until 1985. In 1977, Congress included a provision for the regulation of substances "reasonably anticipated to affect the stratosphere." The U.S. banned chlorofluorocarbons (CFCs)—which were the major cause of the destruction of ozone—in spray cans soon after, and in 1987, CFCs were phased out in many countries around the world by the Montreal Protocol.[29] A substitute for CFCs were suddenly needed. Forward-looking companies aware of Molina and Rowland's research could have foreseen the need for the substitute in 1974 and started development, giving them an edge over competition.

Current research in desulfurization technology indicates the likelihood that a technique could be developed to economically reduce sulfur levels below 10 ppm. As research progresses, the EPA could reasonably lower standards for sulfur in fuel. If this occurs, oxidation and extraction techniques such as CED could be the preferred desulfurization method for refiners.

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Appendix 1

Integration Data

Peak 1 is pyrene, Peak 2 is dibenzothiophene sulfone.

Toluene

TIC: 30HAFA.D (Run #1)

200uL 30mg (init.) DS + 200uL 10mg/20mL pyr

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	26.679	VB	0.054	82546520	26.555	27.022
2	28.103	BB	0.095	112946731	27.729	28.703

TIC: 30HAFA2.D (Run #2)

200uL 30mg (init.) DS + 200uL 10mg/20mL pyr

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	26.690	PB	0.048	78611269	26.566	26.998
2	28.107	BB	0.103	115620708	27.826	28.618

TIC: 30HAFA3.D (Run #3)

200uL 30mg (init.) DS + 200uL 10mg/20mL pyr

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	26.679	PB	0.055	76775482	26.561	27.029
2	28.109	BB	0.102	124209562	27.833	28.600

Cyclohexane

TIC: CYCLO3.D (Run #1)

200ul tol+200ul 10mg pyr after extr&evap

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	26.670	VB	0.056	72619986	26.539	27.065
2	27.991	BB	0.100	12334556	27.845	28.503

TIC: CYCLO4.D (Run #2)

200ul tol+200ul 10mg pyr after extr&evap

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	26.680	VB	0.061	74858097	26.533	27.102
2	28.002	BB	0.101	12632088	27.820	28.576

Appendix 2

A. Extraction and Handling of Samples

Toluene/Water

After the separation funnel was shaken, the phases were allowed to separate for approximately 20 minutes. A glass Pasteur pipette was used to draw some of the toluene phase from the top of the funnel into a vial. Then an automatic pipette was used to draw 200μL of the toluene phase, which was emptied into a v-vial. The same automatic pipette with a fresh tip was used to draw 200μL of 0.5 mg/mL pyrene solution (in toluene), which was placed into the same vial. The vial was shaken, and a sample was drawn and injected (see GCMS procedure below). The same sample was used for all runs. While the sample was also run on the same day as the extraction, the data used in this thesis (and listed in Appendix 1) was from the following day. This is because the first run was far off from the others, and the peak was cut off on the second run, so it was decided to repeat the GCMS runs the next day.

Cyclohexane/Acetonitrile

After the separation funnel was shaken, the phases were allowed to separate for approximately 60 minutes. Cyclohexane and acetonitrile are more difficult to separate due to their similar densities. After that time, the phases appeared to be separated, so a Pasteur pipette was used to draw about 4mL of cyclohexane from the top of the funnel into a 5mL v-vial. Bubbles were noticed in the pipette, and were visible in the v-vial. These bubbles were almost certainly acetonitrile. The cap of the vial was wrapped with Teflon tape, and the vial was wrapped in aluminum foil and left in the freezer for two days. After that time, the sample was frozen solid. After thawing, the acetonitrile had settled mostly to the bottom. The acetonitrile phase was drawn out via Pasteur pipette. To settle the remaining suspended acetonitrile, the solution was centrifuged. The cyclohexane solution was removed from the vial via Pasteur pipette, and placed in a different vial. Then an automatic pipette was used to draw 200μL of the cyclohexane solution, which was emptied into a v-vial. The same automatic pipette with a fresh tip was used to draw 200μL of 0.5 mg/mL pyrene solution (in toluene), which was placed into the same vial. The vial was shaken and the sample was drawn and injected. The same sample was used for both runs, and both runs were performed on the same day.

GCMS Procedure

A syringe was used to draw and inject 1μL of the solution into the GCMS. Each run takes 44 minutes, with additional time to cool down from the ending temperature of 310 °C to the starting temperature of 50 °C. In between runs, the cap of the vial was wrapped in Teflon tape, and the vial was wrapped in aluminum foil and placed in the freezer.
One problem with the GCMS data was reproducibility. The lower the concentration of dibenzothiophene sulfone, the more reproducible the results appeared to be. For the data

used in this thesis, care was taken to try to inject the same amount of sample each time (1 μL). Also, each sample had the same concentration of pyrene as the internal standard.

Solution Preparation

The following bulk solutions were prepared: 0.5 mg/mL pyrene in toluene, 3 mg/mL dibenzothiophene sulfone in toluene, and 0.75 dibenzothiophene sulfone in acetonitrile. Dibenzothiophene sulfone is difficult to weigh out. I attempted to measure it directly into a Teflon bottle, but there was too much static. When it was measured onto weighing paper, it clung to it and was difficult to rinse off into a vial. Finally, I measured the dibenzothiophene sulfone into a glass vial, made the solution in the same vial, and then transferred it into a Teflon bottle. Teflon bottles were used for all of the bulk solutions to prevent evaporation of toluene or acetonitrile, and also to prevent water from condensing into the solutions. Because the cap and bottle are made out of the same material, differential thermal expansion is not a problem.

Solvents

Dibenzothiophene sulfone dissolved in acetonitrile, toluene, and dichloromethane. It did not dissolve appreciably in heptane or cyclohexane. Dibenzothiophene dissolved in cyclohexane.