LABORATORY EVALUATION OF PROMOTED ALUMINA ADSORBENT FOR FUEL DESULFURIZATION

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Introduction

Naturally occurring fuel generally contains varying amounts of sulfur compounds. Refining processes like hydrodesulfurization (HDS) work to lower the sulfur content of these fuels to environmentally acceptable levels.[1,2] The sulfur compounds in refined gasoline may include organic disulfides and polysulfides. Varying concentrations of aliphatic thiols, aromatic thiols, thiophenes and benzothiophenes are also present.[3] Sulfur species in refined fuels such as gasoline, kerosene, diesel fuel, and jet fuel are objectionable because combustion of the fuel converts sulfur species to sulfur oxides that are released to the atmosphere. The U.S. Environmental Protection Agency has proposed new industry standards limiting the sulfur content of finished gasoline to 30 ppm. This limit is scheduled to be implemented in 2004.[4] Besides the direct impact to the atmosphere, sulfur species are generally detrimental to automobile catalytic converter systems.[5] Although the technology exists to produce ultra-low (<30 ppm) sulfur fuel using tried and true HDS systems, the extreme temperature and pressure conditions of such systems are often unfeasible or economically prohibitive. Adsorption may be useful in helping refineries to meet the lowest new sulfur standard if incorporated into, for example, a fixed bed system.

Even if gasoline leaves the refinery in an environmentally acceptable state, transport of "low-sulfur" hydrocarbons through a contaminated pipeline can also introduce elemental sulfur as an impurity. Sulfur species in liquid fuels have a corrosive effect on brass parts of valves, gauges, and fuel pumps. To avoid corrosion problems associated with elemental sulfur contamination, petroleum refiners may utilize processes to convert the elemental sulfur impurities to separable organic disulfides and polysulfides. Removal of the resulting disulfide and polysulfide species would then be necessarily performed "post-pipeline" where HDS technology is not often available. A fixed bed adsorption system may be useful in these applications.

Sulfur removal is also an issue in the field of fuel cell technology. Fuel processing units are generally placed upstream of the fuel cell catalyst to prevent poisoning by various impurities and to ensure good catalyst performance. A need exists for a compact, efficient and simple sulfur trap to prevent catalyst poisoning in fuel cell applications.[6]

We have developed a regenerable alumina-based adsorbent which is highly effective in removing sulfur compounds from hydrocarbon fluids.[7] The adsorbent is macroporous promoted alumina with a surface area of approximately 200 m^2/g. A laboratory evaluation of this novel adsorbent for removal of various sulfur species from finished gasoline is the subject of this paper.

Experimental

Adsorption capacity tests. The effectiveness of the new product for removing sulfur species was assessed through a series of laboratory screening tests. Initial tests were performed to establish static equilibrium capacities of the adsorbent for specific sulfur compounds. Further testing was performed to investigate efficiency of removal from various solvents and from finished gasoline. A known weight of adsorbent spheres (1.4-2.4 mm diameter) was placed in a sealed container at ambient temperature and pressure along with a known weight of sulfur-containing hydrocarbon liquid (~100 ppmwS). Contact times were established to ensure equilibrium had been reached. Final sulfur concentrations in the liquid were measured to determine the capacity of the adsorbent for a given sulfur species.

Dynamic sulfur loadings were determined with a variation of the above test. The adsorbent was crushed and screened to a uniform size of 28x48 mesh (0.3-0.7 mm). A known weight of adsorbent (2-3 grams) was placed in a ½ inch diameter glass column. The column was mounted vertically and equipped with a metering valve at the bottom to control the rate of liquid flow. A 250 ml separatory funnel attached to the top of the column served as a reservoir to which a known weight of liquid was added. Specifically, we performed said experiments using a commercially available "sulfur-free" finished gasoline containing <1ppm sulfur. Individual gasoline samples were prepared by spiking the gasoline with known concentrations of common sulfur impurities.

Gasoline passed through the column of adsorbent at a rate of approximately 0.5 cm^3/minute. Samples (~ 0.5 ml) were taken periodically and analyzed for sulfur content. Gasoline was continuously added to the reservoir until the contacted liquid's sulfur concentration reached that of the untreated gasoline. Chemiluminescence was used to determine the total sulfur concentration in all liquid samples (Antek model #9000NS).

For comparative purposes, all experiments were performed first with the promoted alumina adsorbent and then with unmodified activated alumina. In addition, comparative experiments were completed using an alumina-zeolite composite that is currently being offered commercially for removal of disulfides.

Regeneration Studies. Once the adsorbent column saturated, such that the sulfur content of the gasoline going in equaled the sulfur content of the gasoline coming out, the promoted alumina adsorbent was regenerated and the experiment repeated. A two-step regeneration process was employed. The adsorbent was transferred from the glass column to a ½ inch outer diameter stainless steel tube and placed in a programmable oven. In the first step, nitrogen gas (UHP grade) flowed through the adsorbent bed at approximately 1000 cm^3/minute while the temperature was increased to a temperature ranging from 290-500°C and held for two hours. In the second step, air flowed across the hot adsorbent for two hours. The regenerated material was allowed to cool and returned to the glass column for subsequent adsorption cycles.

Results and Discussion

Sulfur loading capacities were established for a variety of typical fuel impurities: thiophene, 3-methylthiophene, benzothiophene, 2-methylbenzothiophene, ethyl mercaptan, and dimethyldisulfide (DMDS). Isooctane was chosen as the initial carrier in the testing. **Figure 1** indicates the promoted alumina's excellent performance in adsorptive capability for the sulfur species investigated. In all cases, initial equilibrium loading capacities of the new adsorbent were found to be much higher than those measured for the standard adsorbents. The promoted alumina showed performance enhancements ranging from 5 -75 times that of unmodified alumina and from 5 -50 times that of the composite alumina-zeolite adsorbent. Subsequent tests revealed that adsorptive capacities were extremely dependent on the carrier fluid of the sulfur species. Capacities were found to be much lower when sulfur-containing finished gasoline was tested using the above procedure. To determine the cause of this phenomenon, a set of experiments was performed using several different types of hydrocarbon fluids and comparing to the isooctane

results. Identical tests were performed with the various sulfur components in cyclohexane, hexane, and toluene.

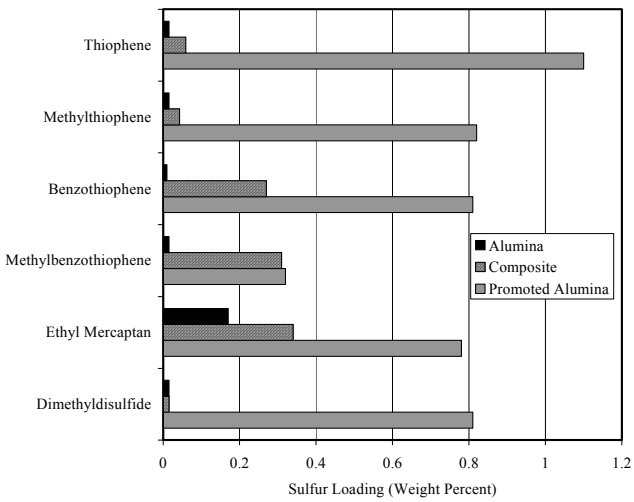

Figure 1. Sulfur loadings (weight percent) of various species on activated alumina, a composite zeolite-alumina, and promoted alumina.

Figure 2 shows equilibrium loading capacities for thiophene removal from the various hydrocarbons. Clearly, the adsorbent performs better when removing thiophene from saturated hydrocarbons than from unsaturated hydrocarbons. A typical experiment is shown in the figure below, but similar results were observed for the other sulfur species as well. Results indicate that the solvent can in some way inhibit sulfur removal by the promoted alumina. The mechanism behind this interference is not well understood. It should be noted that the interference is more pronounced for thiophene than any of the other species, and is almost negligent for ethyl mercaptan.

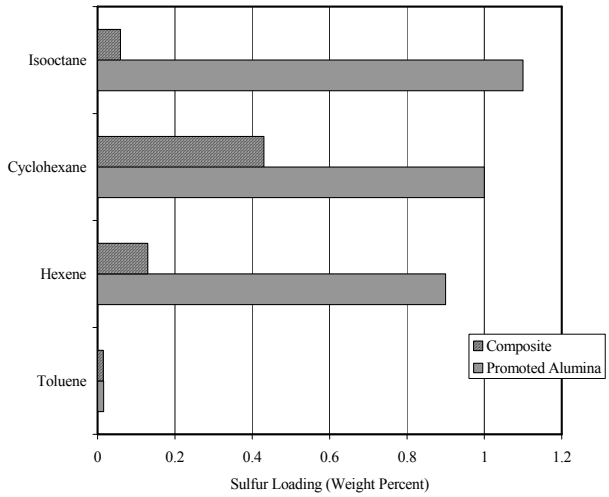

Figure 2. Sulfur loadings (weight percent) for thiophene removal from various hydrocarbons.

Dynamic adsorption tests described previously were performed on a finished gasoline stream to which known concentrations of the various sulfur species were added. At this point, the regenerability of the adsorbent was also investigated. **Table 1** presents the actual regenerative loading capacities for the promoted alumina adsorbent for the various sulfur species. The adsorbent retains approximately 70% of its adsorptive capacity for ethyl mercaptan and 30% of its adsorptive capacity for DMDS upon regeneration at 290 C. Higher regenerative capacities can be achieved at higher temperatures. As expected, removal of thiophene and benzothiophene are more difficult given the aromatic nature of the carrier fluid.

Table 1. Dynamic Loading Capacities for Various Sulfur Components on Promoted Alumina

Sulfur Species	Adsorptive Capacity (Weight % Component)		
	Initial Adsorption	Oxidative Regeneration	
		290 C	340 C
Ethyl Mercaptan	2.5	1.9	2.0
Dimethyl disulfide	1.1	0.3	0.8
Thiophene	0.03	N/A	N/A
Benzothiophene	0.08	N/A	N/A

The regeneration process requires an oxidative step to re-oxidize the promoter on the alumina. **Figure 3** displays a breakthrough curve for the adsorption of DMDS from finished gasoline. The data is presented by plotting the liquid concentration as a function of grams of sulfur added per gram of adsorbent. Loading capacities were determined by integration of the curve. The graph demonstrates the need for the promoter to be in the oxidized state to be effective.

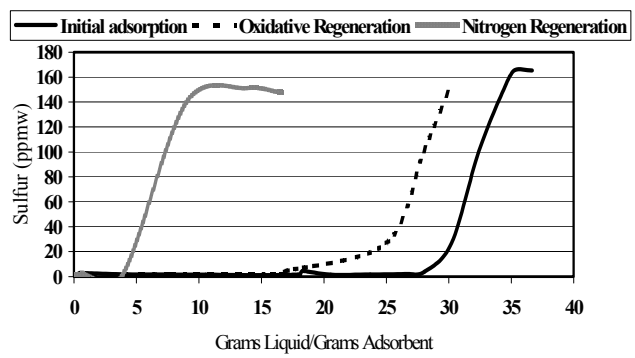

Figure 3. Breakthrough curves for DMDS adsorption by promoted alumina adsorbent. The Y-axis represents sulfur concentration in the effluent of the adsorption column.

Conclusions

Results presented here indicate the effectiveness of the promoted alumina adsorbent in removing sulfur compounds from hydrocarbon fluids. Clearly, adsorption capacities for sulfur contaminants vary greatly depending upon the hydrocarbon feedstream. This finding has serious implications given the nature of the sulfur adsorption market. As discussed previously, the applications that may benefit from a sulfur adsorbent such as this are numerous.

Additional test work is underway to quantitatively establish the adsorbent's effectiveness in removing sulfur compounds from other hydrocarbon streams. Further work is planned, which will allow us to better understand and overcome the problems of interference by unsaturated hydrocarbons on the adsorption process.

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