

## ADSORBENTS FOR THE DESULFURIZATION OF LIQUID FUELS

### The Problem

The U.S. Environmental Protection Agency announced new regulations that require refineries to reduce sulfur levels to 30 ppmw in gasoline and 15 ppmw in diesel by 2006<sup>1,2</sup>. Thus, refineries in the U.S. and worldwide face the challenge of producing very low sulfur highway and non-road fuels, even though the sulfur content of crude oils refined in the U.S. is getting higher and the feedstocks are getting heavier. The requirements for the deep desulfurization of transportation fuels may become even more stringent because of the possibility that these fuels can be used on-board or on-site to support the operation of fuel cells for mobile, portable and transportation applications. Both high and low temperature fuel cells require clean feed streams with very low levels of sulfur<sup>3,4</sup>. To use gasoline or diesel fuels, which are ideal for fuel cells because of their high energy density, ready availability, safety and ease of storage, the sulfur concentration should preferably be below 0.2 ppmw<sup>5</sup>.

Currently, deep desulfurization is achieved by a multi-step process including, hydrodesulfurization (HDS) over CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts and subsequent removal of H<sub>2</sub>S with a sorbent. However, the HDS process is not suited well to produce ultra clean (essentially sulfur free) transportation fuels, particularly for fuel cell applications. At the severe reaction conditions required for effective sulfur removal, the olefins and aromatics in the gasoline are saturated, decreasing the octane number. In addition, the current HDS process cannot adequately remove the refractory sulfur compounds present in the diesel and jet fuels. It has been shown that size of the HDS reactor needs to be increased by a factor of 7, to reduce the sulfur content of the diesel from 500 to 15 ppmw<sup>6</sup>. Clearly, more effective and affordable methods are needed to reduce the sulfur content of the transportation fuels to ultra low levels.

Recently we developed a sorbent for natural gas and liquefied petroleum gas (LPG) desulfurization, where the sorbent effectively removed sulfur-bearing odorants (e.g., thiophenes, mercaptans) with very high capacity<sup>7</sup>. The sorbent can be regenerated by applying a mild temperature swing (by heating up the sorbent bed to 250-300°C) through several consecutive adsorption/regeneration cycles were also demonstrated<sup>8</sup>. Molecular theory and preliminary findings suggest that the same family of sorbents also have the potential to remove refractory sulfur species from higher hydrocarbon fuels. The challenge is to develop effective sorbents that selectively remove the sulfur compounds. Below we summarize the initial testing of these new sorbent materials for deep desulfurization of transportation fuels.

### Experiments

Several formulations were screened to measure their physical properties, including porosity, surface area, crush strength of the pellet and active material content<sup>8</sup>. In the selection of proper active material and support, the material costs were taken into consideration. The choice of substrate materials included conventional supports, which are low-cost and have high surface area (150 to 580 m<sup>2</sup>/g measured by the manufacturers). The formulations with the desired physical properties were tested to measure their sulfur removal performance under simulated conditions.

Preliminary tests for desulfurization of the fuels were performed in a batch reactor. As reported in a similar study<sup>9</sup>, for these experiments a fixed fuel:adsorbent ratio was used to quickly screen

various sorbent candidates at a baseline conditions. In a typical test, about 2 g of sorbent was mixed with 60 ml of a model or actual fuel containing about 2,000 ppmw of sulfur compounds in a round bottom flask (corresponding to a fuel:adsorbent ratio of 12.0). After mixing, the fuel and sorbent was continuously stirred while 50  $\mu$ l liquid samples were taken out every hour for 4-6 hrs. A heating mantle and a water reflux combination provided the capability to run experiments at temperatures up to 80°C. These static experiments were used for quick screening to identify potential candidates to be tested in a flow system where the adsorbent will be tested in a tubular reactor.

## Performance of the Sorbent

The composition of the transportation fuels vary widely depending on the crude oils used in the refining process, the product demand and specifications. Branched and n-alkanes are the main ingredients of these fuels, accounting more that 70% of the total. The major normal alkanes and the main branched alkanes are C5 to C8 compounds. The aromatics content constitutes about 30% of the fuel, and the main components are benzene, toluene, xylenes and alky benzenes. Thiophene, benzothiophene dibenzothiophene and their alkylated derivatives are the major sulfur compounds remaining in the fuel after HDS.

In the preliminary screening tests, n-heptane and benzene were used as model fuels to measure sorbent's efficacy in removing the sulfur. Figure 1 shows the gas chromatograms of the liquid samples extracted from the batch reactor at different time intervals.

In this experiment, n-heptane fuel containing 1,000 ppmw of benzothiophene and 1,000 ppmw of 2-methyl benzothiophene were mixed with a sorbent sample and the sulfur uptake capacity of the sorbent was measured as a function of time. The temperature of the reactor was maintained at 60°C throughout the test. As indicated by Figure 1, the sorbent could remove potentially all the sulfur in 6 hrs and more than 98% of the original amount in less than 2 hrs.

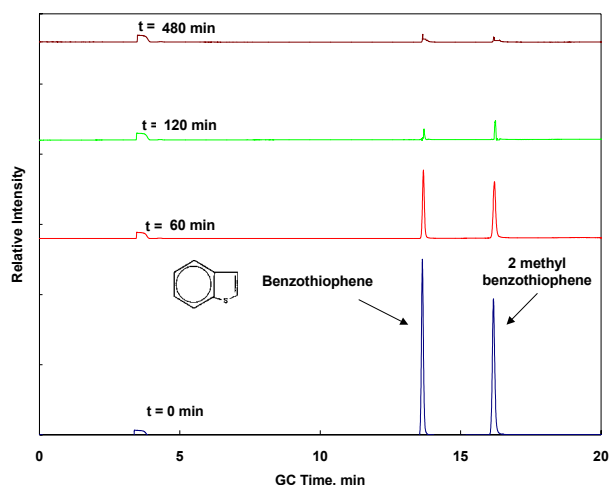


Figure 1. GC-FPD chromatograms for a model fuel sulfur analysis during a static experiment. 1,000 ppmw benzothiophene and 1,000 ppmw of 2-methyl benzothiophene in n-heptane. T=60°C.

Once a promising candidate was identified, more tests were performed to evaluate its effectiveness in different fuel environments. Figure 2 shows the change in the 2-methyl benzothiophene concentration in the batch reactor as a function of time. The removal rate and the overall sulfur uptake capacity of the sorbent were reduced when benzene was used as the model fuel instead of n-heptane. However, even with benzene as the fuel, the sulfur adsorption capacity of the sorbent exceeds 0.85% on weight basis (based on 3 hr adsorption), where the adsorption capacity is defined as lb of sulfur removed per lb of sorbent.

The regeneration potential of the sorbent was evaluated by applying a mild temperature swing. In these experiments, the sorbent was first exposed to n-heptane fuel containing 1,000 ppmw of benzothiophene and 1,000 ppmw of 2-methyl benzothiophene at 60°C. After the sorbent is saturated with sulfur, the solution was filtered to recover the sorbent. The tested sorbent was then heated to 300°C under 200 ml/min nitrogen flow overnight in a tube furnace. It was anticipated that this mild thermal treatment was sufficient to drive off the physically adsorbed sulfur species from the sorbent. The sorbent was then cooled to room temperature in nitrogen flow and then placed into the batch reactor again to test its performance using an identical sulfur-laden fuel. The comparison of the sorbent performance for removing 2-methyl dibenzothiophene from n-heptane fuel in two adsorption cycles are presented in Figure 3. In both cycles, the sorbent also removed all the benzothiophene.

These results suggest that the sulfur can be driven off from the sorbent by a simple thermal process heating the sorbent to 300°C. It is also suggested that the regenerated sorbent may maintain a stable cyclic capacity.

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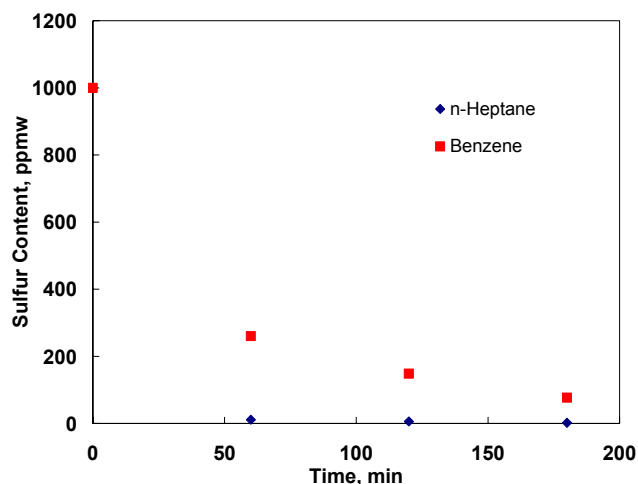


Figure 2. 2-methyl benzothiophene removal performance of the sorbent in different model fuels. 1,000 ppmw benzothiophene and 1,000 ppmw of 2-methyl benzothiophene in n-heptane and benzene. T=60°C.

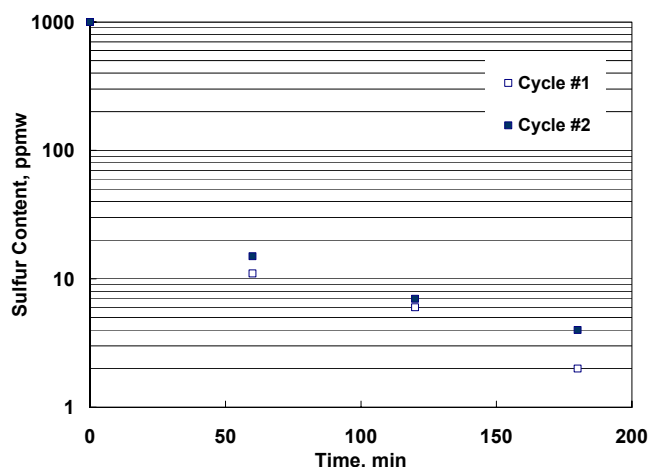


Figure 3. The sulfur removal performance of the fresh sorbent and the sorbent regenerated at 300°C in N<sub>2</sub> flow. 1,000 ppmw benzothiophene and 1,000 ppmw of 2-methyl benzothiophene in n-heptane. T=60°C.

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