

# Novel Oxidative Adsorbents for the Selective Removal of Sterically Hindered Benzothiophenes From JP-8 Logistics Fuel

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## Introduction

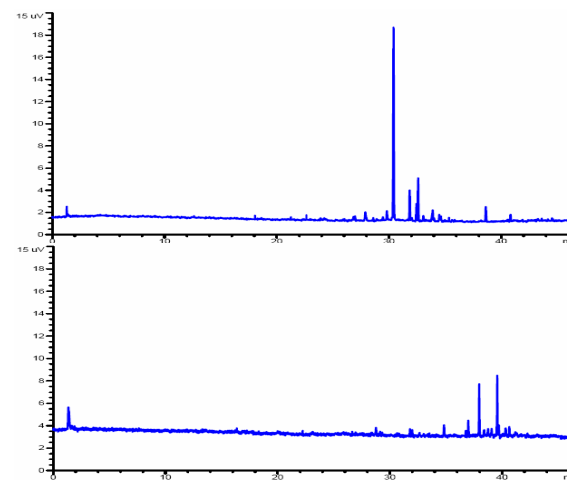
Production of hydrogen by reforming of fossil fuels for fuel cell use requires that sulfur content be very low in order to protect the reforming catalysts as well as the fuel cell. For the case of JP-8 and diesel fuels, benzothiophene and dibenzothiophene molecules having alkyl substituents in sterically hindering positions are difficult to remove by simple adsorption [1]. These are the same sulfur-bearing molecules that are most difficult to remove by hydrodesulfurization. Selective oxidation of these sulfur-bearing molecules provides an alternative and complementary method to dealing with these sulfur compounds. Multiply-substituted aromatic thiophenes appear to be activated toward oxidation at the sulfur position, generating sulfones that can be subsequently removed by adsorption or extraction. The primary oxidants employed in this approach are peroxides, either hydrogen peroxide (in a two liquid phase process) or organic peroxides that are soluble in the organic phase [2]. Solid catalysts such as Ti-containing zeolites [3] or Ti-containing mesoporous silicas [4] appear to accelerate the oxidation step, although deactivation of these latter catalysts was apparent. Moreover, the requirement to provide hydrogen peroxide or organic peroxides results in a relatively high cost for the process and in some cases results in complicated product workup. The use of supported solid phase materials in the absence of peroxide-based oxidants does not appear to have been reported. We have found a class of solid materials that are capable of converting tri- and tetra-substituted benzothiophenes present in hydrodesulfurized JP-8 to heavier species via an oxidative process, and in some cases achieving full removal of the sulfur with the co-production of sulfates. Because these materials are stoichiometric reagents, their application appears to be best in removing low concentrations of difficult-to-remove sulfur species following an initial treatment such as hydrodesulfurization.

## Materials and Methods

The oxidative adsorbents were prepared by impregnation methods. The majority of experiments were carried out with a low sulfur JP-8 fuel, generated from a JP-8 fuel (from BP Tacoma refinery) having an initial content of 1225 ppmw sulfur via a hydrodesulfurization process in which syngas was employed in place of hydrogen [5]. The desulfurized fuel contained 6.5 ppm residual sulfur, comprising benzothiophenes predominantly substituted by methyl or other alkyl groups in sterically hindered 2- and 7- ring positions. Adsorption experiments were carried out in batch mode, using a heated shaker bath. Typically, 1g of the solid was mixed with 30 ml of low sulfur fuel at a selected temperature (ambient to 87°C) for a period of 1-4h. Analysis of the hydrocarbon liquid for sulfur content was carried out using an Agilent 6890 gas chromatograph equipped with a sulfur chemiluminescent detector and a DB-5 column. Post analysis of the solid oxidant for sulfur concentration and speciation was carried out by SEM/EDS and X-ray Photoelectron Spectroscopy.

## Results and Discussion

Figure 1 shows the result of exposing 30ml of the low sulfur JP-8 to 1g of the oxidative oxidant. The top trace shows sulfur distribution in the starting hydrocarbon, the lower the sulfur species following treatment with the solid oxidant. Although the total sulfur has only been decreased from 6.5 to 4.5 ppmw, the amount of sulfur species remaining that correspond (by retention time) to the initially present species is less than 200ppbw (98% conversion). These new sulfur species are compounds having a higher molecular weight than the starting sulfur compounds. The detection of sulfate on the spent solid indicates that an oxidative process has occurred, suggesting that these new species are oxidized products of the substituted benzothiophenes. Identification of these new sulfur species is ongoing, it does not appear that they are the same as those produced by peroxide oxidation. The majority of these new sulfur species can be subsequently removed by inexpensive adsorbents.



**Figure 1.** Effect of solid oxidative treatment of low sulfur JP-8: initial sulfur distribution (6.5 ppmw S, top); following oxidative treatment (4.5 ppmw S, bottom)

## Significance

A novel oxidative method using low cost materials has been identified to convert multiply substituted benzothiophenes to heavier products that can be subsequently removed.

## References

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