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REMOVAL OF SULFUR CONTAMINANTS IN METHANOL
FOR FUEL CELL APPLICATIONS

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INTRODUCTION

Fuel cell power plants are being developed for transit bus and passenger car applications that use methanol as the on-board fuel. Commodity methanol by itself contains very little sulfur; however, it may occasionally be contaminated with up to about 1% diesel fuel or gasoline in current liquid-fuel distribution systems, leading to the presence of sulfur in the methanol fuel. This sulfur must be removed because of its deleterious effect on the reforming catalysts. International Fuel Cells has set the allowable sulfur limit in the methanol fuel at less than 1 ppm.

RESULTS AND DISCUSSION

Sulfur compounds present in a typical diesel fuel were identified by a gas chromatograph coupled to a mass spectrometer (GC/MS) and a gas chromatograph with a flame photometric detector (GC/FPD) operated in the sulfur mode; they were found to be essentially C1-C4 alkyl-substituted benzothiophenes, 0-C3 alkyl-substituted dibenzothiophenes, and their isomers. Table 1 summarizes the estimated relative amount of each sulfur group in diesel fuel. The totals are 33~35% benzothiophenes and 65~67% dibenzothiophenes.

Table 1. Estimate of Relative Amount of Sulfur Groups in Diesel Fuel

Compound Class	Approximate Percentage of Total Organic Sulfur	
	GC/MS	GC/FPD
C1-Benzothiophenes	6.4	1.3
C2-Benzothiophenes	9.9	9.7
C3-Benzothiophenes	11.8	14.9
C4-Benzothiophenes	6.9	7.4
Total Benzothiophenes	35.0	33.3
Dibenzothiophene	7.8	8.1
C1-Dibenzothiophene	19.9	27.4
C2-Dibenzothiophene	24.4	21.9
C3-Dibenzothiophene	12.9	9.3
Total Dibenzothiophenes	65.0	66.7

Next, activated alumina, activated bauxite, activated carbon, attapulgite clay, and diatomaceous earth were experimentally evaluated for their sulfur adsorption capabilities from methanol that had been doped with 1 vol% diesel fuel (containing 0.29% S). Activated carbon (AC) was found to be the most effective. Subsequently, several commercially available activated carbons (Table 2) made with different starting materials and activation processes were screened. In general, the coconut-based carbons activated by high-temperature steam were found to be more effective than the coal-based activated carbons in removing sulfur compounds from the contaminated methanol.

Table 2. List of Activated Carbons Tested for the Adsorption of Sulfur in Methanol

Carbon Type	Raw Material	Activation Process	Surface Area, ^a m ² /g
Filtrisorb 400 ^b	Bituminous Coal	High Temp. (HT) Steam	950-1050
Type ADP ^b	Bituminous Coal	HT Steam and Acid Washing	1500
Centaur ^b	Bituminous Coal	Patented Process	800-850
Type CPG LF ^b	Bituminous Coal and Binder	HT Steam	950-1050
Type PCB ^b	Coconut Shell	HT Steam	1150-1250
Type MI ^c	Coconut Shell	HT Steam	1300
Type SE ^c	Coconut Shell	HT Steam	1200
Type COC/AW L60 ^d	Coconut Shell	HT Steam	1150-1200
Type COL/P L60	Bituminous Coal	HT Steam and Acid Washing	950-1000
Nuclear SA-20 ^e	Wood	HT Steam	1400-1800
Ambersorb No. 572 ^f	Ion Exchange Resin	Patented Process	1100

^aMeasured by the N₂ BET method.

^bCalgon Carbon Corp., P.O. Box 717, Pittsburgh, PA 15230.

^cBarnebey & Sutcliffe Corp., P.O. Box 2526, Columbus, OH 43216.

^dCarbon Activated, 1662 W. 139th Street, Gardena, CA 90249.

^eWestvaco Corp., Carbon Department, Coventon, VA 24428.

^fRohn and Haas Co., 5000 Richmond Street, Philadelphia, PA 19137.

The adsorption capacity of an adsorbate on activated carbon is related to the adsorbate's concentration in solution. Equilibrium adsorption isotherm tests were conducted to determine the relationship between the concentration of sulfur in methanol and the activated carbon dosage. These tests used the coal-based Calgon Filtrasorb 400 AC and three coconut-based carbons: Calgon Type PC and B&S Types SE and MI. As expected, the sulfur concentration in the AC-treated methanol decreased with increasing dosage. At 1-g carbon per 100-mL methanol, AC removed approximately 45% of the benzothiophenes and approximately 97% of the dibenzothiophenes. This value increased to 97-99% for benzothiophenes and essentially 100% for dibenzothiophenes at a dosage of 4-g AC/100-mL methanol.

The data obtained from the equilibrium adsorption isotherm tests were interpreted by using the empirical Freundlich equation (1):

$$X/m = KC^{1/n}, \text{ or } \log (X/m) = \log K + 1/n \log C$$

where X = amount of sulfur impurity adsorbed, g

m = mass of activated carbon, g

C = sulfur concentration in methanol after equilibrium, mg/L

K, n = constants

All four adsorption isotherms (Fig. 1) in the plots of $\log (X/m)$ versus $\log C$ show two linear regions. Adsorption characteristics of a solution containing two solutes measured by a gross concentration parameter are reflected in an isotherm plot consisting of two straight lines (2). The adsorption isotherms in Fig. 1 suggest that the benzothiophene group in methanol has different adsorptivity on activated carbon from the dibenzothiophene group, and the two types of sulfur species compete for adsorption sites in the pore structure of the activated carbon.

Figure 1 also shows that the coal-based Filtrasorb 400 AC has higher sulfur adsorption capacities than the coconut-based ACs for methanol solutions that have sulfur concentrations greater than about 4.0 mg/L (5 ppmW). However, the reverse is true for sulfur concentrations less than 4.0 mg/L. Among the three coconut-based ACs tested, B&S Type MI has the highest sulfur adsorption capacity.

A preliminary assessment of the dynamic performance of these ACs was obtained in a bench-scale, dynamic batch test. In this test, Calgon Filtrasorb 400 and B&S Type MI activated carbons were packed in a Pyrex glass column of 1.77-cm ID x 91.44-cm length (0.5-in. ID x 36-in. length). The carbon has a particle size of 1.64 x 0.84 mm (-12 +20 U.S. Standard Testing Sieve No.) and was tested with diesel-fuel-contaminated methanol (containing 30 ppmW sulfur) at a flow rate of 5 mL/min. The empty bed contact time was 24 min. A 5-mL effluent sample was collected at the end of the column for every time interval tested. The test with Filtrasorb 400 lasted 16 hours, and the test with Type MI lasted 30 hours.

The sulfur breakthrough curves for both tests are shown in Fig. 2. Within experimental and analytical errors, both ACs behave similarly in terms of their breakthrough characteristics. During the first 3.0 h of continuous flow testing, they removed 100% of the 30 ppmW sulfur in the methanol feed. The breakthrough curve levels off at an effluent sulfur concentration of 24 ppmW, which is 80% of the sulfur concentration in the methanol feed. Apparently, the sulfur compounds in the feed had not totally broken through the column after the 30-h test (i.e., the column has not reached dynamic equilibrium with the feed). A GC/MS analysis of the effluent sample collected at 29 h showed approximately 89% of total benzothiophenes and approximately 29% of total dibenzothiophenes in the methanol feed.

The breakthrough data shown in Fig. 2 were mathematically analyzed by the LUB/equilibrium section concept (3). On the basis of this concept, the dynamic adsorbate loading (or adsorption capacity) of the activated carbons was estimated to be 0.79 mg S/g AC for the 80% adsorption capacity level. By extrapolation, the dynamic adsorption capacity of these two ACs would be 1.0 mg S/g AC if these activated carbons were tested until the complete breakthrough of sulfur from the column. Figure 1 indicates that the equilibrium isotherm adsorption capacity for Calgon Filtrasorb 400 and B&S Type MI activated carbons is 3.5 and 2.8 mg S/g AC, respectively. Therefore, the dynamic adsorption capacity of 1.0 mg S/g AC for these two activated carbons is about one-third of their equilibrium isotherm adsorption capacities.

Fig. 1. Adsorption Isotherm of Activated Carbon for Sulfur in Methanol

Fig. 2. Breakthrough Curve of Activated Carbon for Sulfur in Methanol

CONCLUSION

The equilibrium adsorption isotherm and breakthrough data were used to assess the feasibility of developing a granular activated carbon (GAC) adsorber for use as a sulfur removal subsystem in transportation fuel cell systems. Results of this analysis suggest that an on-board GAC adsorber may not be attractive due to its size and weight constraints. However, it may be feasible to install this GAC adsorber at methanol distribution stations, where space and weight are not a critical concern. A preliminary economic analysis indicated that the GAC adsorber concept will be attractive if the spent AC can be regenerated for reuse. It should be emphasized here that these preliminary analyses were made on the basis of the very limited breakthrough data obtained from the bench-scale testing. More detailed optimization on the dynamic testing parameters and the study on regeneration of the spent AC are needed.

ACKNOWLEDGMENTS

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