USE OF ACTIVATED COAL CHAR FOR REMOVAL OF VOLATILE ORGANIC COMPOUNDS FROM WATER

P .J. Beaulieu, S .M. Fatemi, and J .B. Tumidalsky, Analytical Research and Services Division, Amoco Research Center, Box 3011, Naperville, Illinois 60566,
and
C. W. Kruse, M. Chou, and C. Feizoulof, Illinois State Geological Survey, 615 East Peabody Drive,Champaign, Illinois 61820.

Keywords: char, environmental, adsorption, mild gasification, coal

INTRODUCTION

Mild gasification is an alternative to traditional coal burning for coal utilization. Mild gasification produces gas, liquid, and substantial quantities of coke. Coal liquid and gas are being studied as alternatives to petroleum and natural gas, as sources of chemical feedstocks and fuels. This project concentrates on an alternate use for the solid coke, upgrading it to a higher value product, an activated char, and use for sorption of pollutants.

Activated charcoal is conventionally produced from a source such as coconut husk. We reported earlier on the conversion of coke to activated char by a process of controlled oxidation (1). There is a large market for activated charcoal as a sorbent for removal of organic compounds from water supplies and industrial outfalls. Presently, activated charcoal for this purpose is priced at more than $1,000/ton. If coal char can successfully compete in this arena, the value of the coke would be upgraded dramatically, and the economics of coal utilization changed substantially. In this paper, we report on successful testing of activated coal char under laboratory conditions as a sorbent for removal of volatile organic compounds from deionized water.

Organohalogens are common environmental pollutants. We reported earlier that activated coal char catalytically promoted dehydrohalogenation and other elimination reactions, producing olefins (2-5). If an overall process of sorption of organic compounds from water and their catalytic decomposition and conversion to more useful or less noxious compounds can be demonstrated, it would represent an advantage for coal derived char over other charcoal types. Last minute results of experiments testing for decomposition of previously sorbed compounds will also be reported, if ready in time for the meeting.

EXPERIMENTAL

Experimentation consisted of preparation of activated char from coal, equilibration with deionized water containing 37 organic compounds, and GC-MS analysis to measure the amounts of these compounds remaining in the water at the end of the sorption period. Details follow below.

Preparation of Coal Char Activated coal char was prepared from a blend of Illinois #5 (Springfield) and Illinois #6 (Herrin) coals using the following method. The starting material was char from a United Coal Company pilot scale, fixed bed, mild gasification reactor. This material was further devolatilized using a fluidized bed reactor at ISGS, heating in an atmosphere of pure nitrogen at a rate of 20°C/min, and holding a final temperature of 500°C for 15 minutes. After characterization, steam treatment followed. The material was heated at a rate of 20°C/min to 870°C in pure nitrogen. The atmosphere was changed to 50% steam in nitrogen, and conditions held constant for 3 hours to increase porosity. After characterization, mild oxidation followed. The material was heated at 20°C/min to 450°C in pure nitrogen. The atmosphere was changed to 10% oxygen in nitrogen, and conditions held constant for 15 minutes to activate the surface. This product, which had a surface area of 557 meter^2/gram, was used for the sorption studies described below.

Sorbates. A methanolic stock solution of 37 analytes, each at 1000 ppm, was purchased from a vendor of environmental analytical standards (Accustandard). Components are listed in Table I. This solution contains most of the volatile organic compounds (VOC) for which federal and state discharge permits usually require screening. These are also known as VOA, for volatile organic analytes. Portions of this stock solution were injected (spiked) into water as described in the experiments detailed below.

Equilibration Experiments. Samples of char were covered with deionized water, and were either spiked immediately with the stock solution (Experiment 1), or spiked after a four hour conditioning period during which the char equilibrated with the unspiked water (Experiment 2). After spiking, the char was equilibrated with the spiked water for 20 hours (Experiments 1 & 2). Sampling of the water layer for GC-MS analysis followed. To do Experiment 3, several refilled samples from Experiment 2 were used. A second 20 hour equilibration and second GC-MS analysis followed. Experimental details follow.

Experimental Details. A sample of char (either 0.100 gram or 1.00 gram) was placed in a precleaned glass 40 milliliter environmental water sample vial (VOA vial). A second vial was designated immediately as control. Each was filled with deionized water and sealed immediately with its teflon faced septum screw cap. After the unspiked conditioning times described above, each vial was opened momentarily in turn, and a syringe (or glass micropipette) used to add a spike volume (0.002 to 1.00 milliliter) of the sorbate solution to each, injecting it well below the water surface. Taking care to exclude bubbles, the vial was resealed immediately and was mixed by inverting several times.

After the 20 hours spiked equilibration, the vials were sampled for GC-MS analysis. The deionized water needed for a dilution was placed in a VOA vial. Each vial was opened momentarily, and the volume for analysis removed. Except for the vials spiked with the smaller volumes, the aliquot taken was that required to prepare a diluted solution approximating 125 ppb in concentration. The volume was removed either by syringe (or glass micropipette) or by decanting and weighing (when the desired volume exceeded 5.00 milliliters). When a syringe (or glass micropipette) was used, this aliquot was injected below the surface of the deionized water in the analysis vial. When decanted, it was poured without vortex into the water in the analysis vial. For Experiment 3, the water volume removed for the GC-MS analysis in Experiment 2 was immediately replaced with fresh deionized water. The vials were immediately resealed, and equilibrated for 20 hours more. No makeup spike was added. This brought the cumulative equilibration time for Experiment 3 to 40 hours before the second sampling. Immediately after adding the sampled aliquot to the analysis vial, 0.080 milliliter of the internal standard and surrogate solution described below was added by micropipette, the vial topped up with deionized water, resealed and mixed. The resulting solution was analyzed by GC-MS as described below.

Internal Standard Solution. A combination solution of three internal standards (20 ppm each) and three surrogate analytes (25 ppm each) was prepared by diluting methanolic stock solutions (Accustandard, Supelco, or other vendor). High purity methanol was used as solvent. Internal standards are used as GC-MS references, for locating the chromatography peaks of the analytes, and for calculation of concentrations of analytes present. Surrogate analytes are used to ascertain that the GC-MS analysis and calculation methods are in control. Compounds used as internal standards and surrogates are listed in Table II.

Method of Analysis. Concentrations of the volatile analytes remaining in solution were measured by Purge and Trap GC/MS, using an automated version of EPA Method 8240, as was specified by EPA for analysis of waste water regulated under the Resource Conservation and Recovery Act (3). This method is largely the same as the earlier EPA Method 624 for sites regulated under the Clean Water Act (4). The analysis vials prepared as described above were placed in an autosampler, where they were held until a 5 milliliter volume was transferred automatically to the purge and trap device (OI Analytical 4460A). Helium was used to purge the volatile organics from the room temperature water sample, transferring the organic vapors to a multilayer (OV-1, Tenax, Silica Gel, Activated Charcoal) trap where they were held for analysis by GC-MS. On signal from the GC, the organic vapors were thermally desorbed and transferred to the GC, which was equipped with a 2 meter glass column (1% SP-1000 on 60-80 mesh Carbopack B). The temperature programmed GC sequentially eluted the components to the mass spectrometer over a period of about 40 minutes. The mass spectrometer was a Finnigan 4500 quadrupole instrument operating in the EI, positive ion, full scan mode. Scan time was 2 seconds, mass range 34 to 340 M/Z, and tuning was to EPA specifications for the spectrum for bromofluorobenzene.

Standard Finnigan peak search software was used to locate the chromatogra-

phy peaks, integrate the EPA recommended quantitation ion for each compound, and calculate results. To calculate results, the peak area for the analyte and that for the internal standard eluting nearest the analyte peak were obtained for a series of 5 calibration standards in the range 10-200 ppb. Relative response factors ("RRFs", relating analyte area, analyte concentration, internal standard area and internal standard concentration) were calculated. EPA statistical quality control requirements were followed in evaluating the analytical range, establishing initial average RRFs, and then for checking and updating the response factors to be used for calculation on a daily basis. Concentrations were then calculated in the analysis solutions using the library of daily RRFs.

GRAPHICAL PRESENTATION OF RESULTS

Most peaks for the 37 analytes were resolved, either by effective GC separation, or by identification of a unique quantitative mass. However, in the case of two peaks, each of which contained two isomers, resolution was not possible. This resulted in 35 calculated data points to be reported for each solution, including the sum peaks for the isomeric pairs. In addition to the 35 analytes, the three surrogate compounds were determined in the same manner. The amount of methanol was not determined. A value for the amount of each analyte (the ith analyte) sorbed on the char was calculated as a percent, relative to the matching control solution, using the equation:

$$\textbf{Percent Sorbed}_i = 100 \times \frac{[\textbf{Concentration}_i \textbf{ in Control} - \textbf{Concentration}_i \textbf{ in Sample}]}{\textbf{Concentration}_i \textbf{ in Control}}$$

A typical component is illustrated in Figure I, where the data for benzene are shown. A total of 35 similar graphs resulted from the data processing. Several more graphs will be presented at the meeting, as germane to a discussion of the slight differences between sorption properties of the individual components and classes of components.

However, it proved easier to contrast and compare the data after further manipulation. The Average Percent Sorption was calculated for each sample from the percent sorption for the individual analytes in each sample/control pair. Average sorptions are shown in Figure II.

$$\textbf{Average Percent Sorption} = \frac{\sum_{i=1}^{35} \textbf{Percent Sorbed}_i}{35}$$

Figure III shows the relative strength of sorption listed by component. The sorption for benzene can be seen to closely resemble the average sorption. This was seen earlier by comparison of Figure I and Figure II, but the comparison is easier when Figure III is considered. This data for construction of Figure III was obtained by further calculation. Using the sample average sorption described for Figure II, the relative strength of sorption for each (that is, the ith) component in each sample was calculated using the equation:

$$\textbf{Relative Sorption Strength}_i = [\textbf{Percent Sorbed}_i - \textbf{Average Percent Sorption}]$$

The average relative sorption strength for this (the ith) component in for all (j = 17) samples was then calculated and plotted in Figure III.

$$\textbf{Average Relative Sorption}_i = \frac{\sum_{j=1}^{17} \textbf{Relative Sorption Strength}_i}{17}$$

In Figure III, the analytes are listed alongside a bar graph representing the average sorptions of the analytes for all experiments. The analytes which sorb best are to the left of the vertical line. The center of the bar represents the average sorption over all experiments, the length of the bar is a measure of the precision (each bar is 2 standard deviations in length).

DISCUSSION AND CONCLUSIONS

Fresh, dry Activated coal Char can be seen to have sorbed the analytes, with efficiencies improving at lower concentrations. Some individual analytes proved to be more strongly sorbed than others, and the strong sorbency persisted to higher concentrations.

The average results for Experiment 1, as presented in Figure I, will be considered first. In experiments at or below at 100 micrograms of each analyte per gram of char, removal was essentially complete for most analytes (96% sorption at the lowest concentration level studied, 50 ppb, leaving a concentration of only 2 ppb in solution). Above 100 micrograms of each analyte per gram of char, performance degraded. In the experiment at 5000 micrograms of each analyte per gram of char, removal of the sorbates from solution was largely incomplete (approximately 60% of all 35 analytes, at an aqueous concentration of 25 ppm, leaving 10 ppm in solution).

Results for the second (pre-soaked) experiment proved somewhat more variable and the char somewhat less effective. Most of the samples showed lower sorptions (for the same spike amount) than in the case of samples which were not pre-soaked. Two exceptions were noted to lie closer to the line representing the first experiment. These two are believed to represent samples which still contained entrained air. Note was not taken of samples which did not sink, and thus might still contain air, since this was not known to represent an important variable at the time. For the several samples refilled with deionized water, and allowed to reequilibrate with the spiked solutions, the amounts of each analyte sorbed increased.

Since presoaking with water was observed to degrade performance of the char somewhat, it is proposed that water binds active sites which would otherwise be available to the analytes. A hidden component, methanol, is probably also sorbing on the char, occupying active sites. If methanol is also sorbing, the total capacity of the char for organics is then probably much higher than the sum of the 37 analytes, but further work will be needed to measure the total capacity.

Kinetics have not been characterized at this point. In the presence of presoaked char, at a spike level of 50 micrograms of each analyte per gram of char, sorption appears to be approximately 60% complete in 20 hours and increases to the about 75% in 40 hours. Since the 40 hour equilibration never produced sorptions higher than those produced by the 20 hour equilibration with dry char, it is possible that the sorption is essentially complete by 20 hours in the presence of dry char, but further experimentation will be required to be certain.

In summary, activated coal char appears to be an effective sorbent for VOCs, but the equilibrium is displaced somewhat and/or the sorption rate slowed by presoaking the char in water.

References:

1. C. W. Kruse, L. M. Lytle, M. Rostam Abadi, M. Chou, and Feizoulof (ISGS); S. M. Fatemi, J. A. Mahoney, P. L. Beaulieu, and J. O. Schreiner (Amoco) Annual Technical Report to the Center for Research on Sulfur in Coal, 1991. **Upgrading Mild Gasification Char: Evaluation of Oxidized Char as a Catalyst**
2. C. W. Kruse, G. C. Ray, U.S. Patent 3,240,834 Mar. 15, 1966.
3. J. E. Mahan, R. E. Reusser, C.W. Kruse, U.S. Patent 3,352,935 Nov.14 ,1967.
4. C.W. Kruse, U.S. Patent 3,437,695 Apr. 8, 1969.
5. C. W. Kruse, M. I. M. Chou, C. Feizoulof (ISGS); S. M. Fatemi, P. L. Beaulieu, J. O. Schreiner (Amoco); Vol 37#2, 556-563, 1992. 203rd ACS National Meeting, San Francisco, CA. **Evaluation of Oxidized Char as a Catalyst - I. Characterization**
6. United States Environmental Protection Agency; Office of Solid Waste & Emergency Response, Washington, D.C. 20460, November, 1986. **SW-846 Test Methods for Evaluating Solid Waste; Laboratory Manual; Physical/Chemical Methods; Volume IB; Third Edition.**
7. 40 CFR Part 136, United States Environmental Protection Agency **Guidelines Establishing Test Procedures for the Analysis of Pollutants.**

TABLE I. COMPONENTS OF SPIKE SOLUTION
(each at 1000 Micrograms/Milliter, Except Methanol = Balance)

	HALOGENATES	
C-1	C-2 (Unsatd.)	C-3 (Unsat'd.)
Chloromethane	1,1-Dichloroethene	Vinyl Chloride
Bromomethane	Cis-1,2-Dichloroethene	Cis-1,3-Dichloropropene
Methylene Chloride	Trans-1,2-Dichloroethene	Trans-1,3-Dichloropropene
Bromodichloromethane	Trichloroethene	
Dibromochloromethane	Tetrachloroethene	
Chloroform		
Bromoform	C-2 (Satd.)	C-3 (Sat'd.)
Carbon Tetrachloride	Chloroethane	1,2-Dichloropropane
	1,1-Dichloroethane	
	1,2-Dichloroethane	
	1,1,1-Trichloroethane	
	1,1,2-Trichloroethane	
	1,1,2,2-Tetrachloroethane	
	OXYGENATES	
Methanol (Solvent)	Acetone	
Vinyl Acetate	Methyl Ethyl Ketone (2-Butanone)	
	4-Methyl-2-Pentanone (MIBK)	
	2-Hexanone (MBK)	
	AROMATICS	
Benzene	Ortho-Xylene	Styrene
Toluene	Meta-Xylene	Chlorobenzene
Ethylbenzene	Para-Xylene	
	MISCELLANEOUS	
Carbon Disulfide		

TABLE II. COMPONENTS OF INTERNAL STANDARD & SURROGATE SOLUTION

	SURROGATES	
1,2-Dichloroethane-D4	Toluene-D8	4-Bromofluorobenzene
	INTERNAL STANDARDS	
Bromochloromethane	2-Bromo-1-Chloropropane	1,4-Dichlorobutane

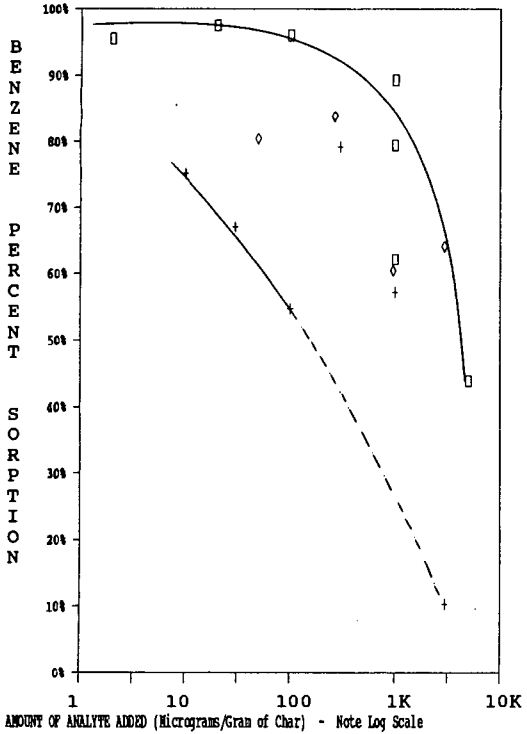


FIGURE I. EFFECTIVENESS OF ACTIVATED COAL CHAR FOR REMOVAL OF BENZENE FROM WATER
[] Experiment 1. + Experiment 2. ◇ Experiment 3.

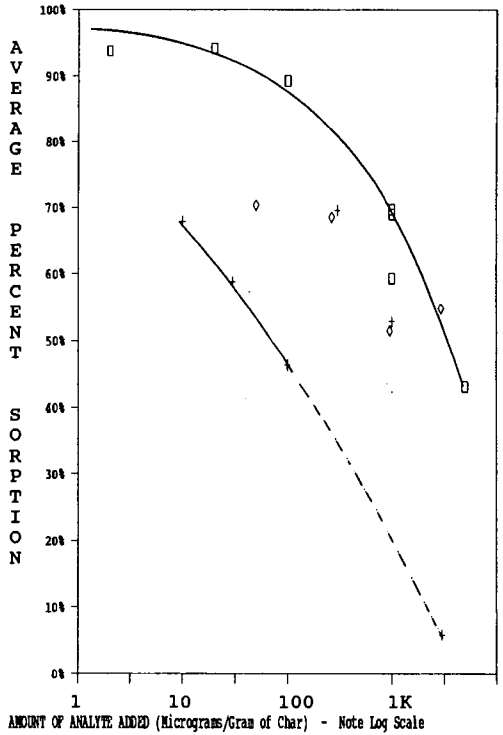
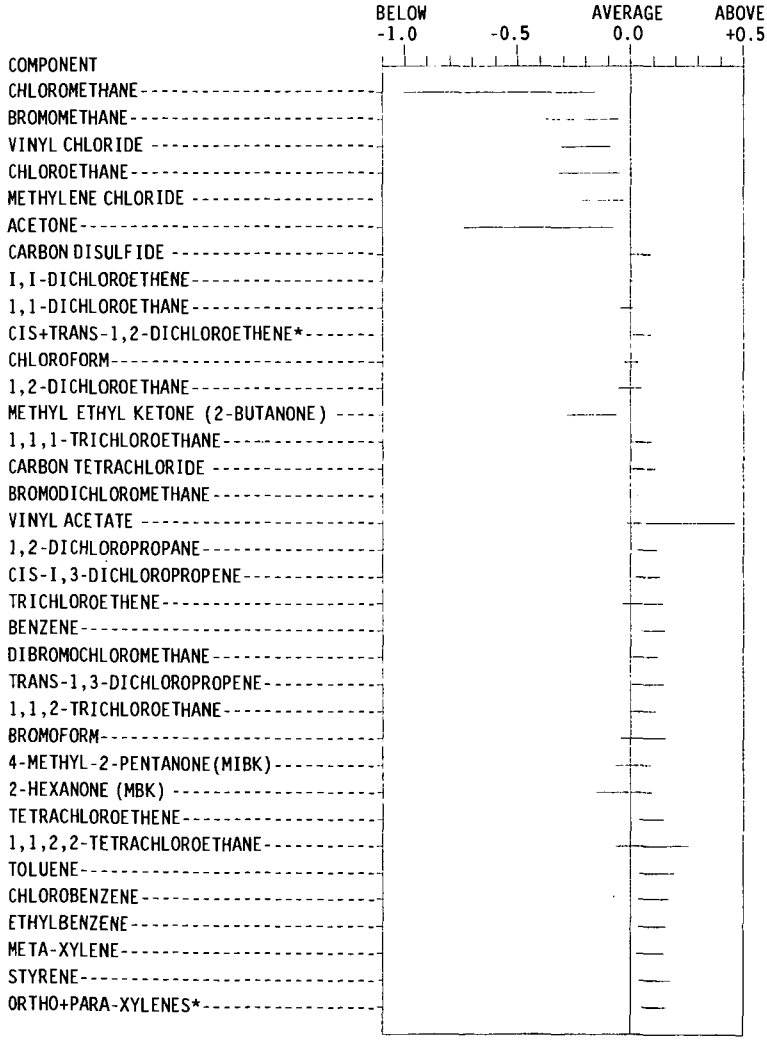


FIGURE II. EFFECTIVENESS OF ACTIVATED COAL CHAR FOR REMOVAL OF VOC FROM WATER
[] Experiment 1. + Experiment 2. ◇ Experiment 3.

FIGURE III. AVERAGE RELATIVE STRENGTH of SORPTION LISTED by COMPONENT



* Coeluting Pair, quantified as single component