

Analytical Characterization of an Industrial Waste Treated by Gasification

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Previous studies by us have shown that an effective general treatment for hazardous wastes is sorption of the waste onto a specially prepared, macroporous coal char followed by gasification of the mixture in reverse mode. In the present study, an industrial waste comprised of styrene manufacturing and petroleum byproducts was gasified, and the waste, coal, virgin char, and char/waste mixture (before and after gasification) were examined by various instrumental methods, infrared, nuclear magnetic resonance, gas chromatography, gas chromatography/mass spectroscopy, scanning electron microscopy, and ultimate and proximate analyses, to determine which methods give useful information. The composition of the waste was found to be 38% water, 27% inorganic, and 35% organic. NMR showed that the organic components are a mixture of aliphatic and olefinic/aromatics. About 8% of the sludge is chromatographable and GC/MS revealed the presence of aromatics and polyaromatic hydrocarbons. Solid-state NMR showed that the sludge components are strongly immobilized on the char up to a 1:1 (wt:wt) ratio. SEM results showed changes in the char macroporous surface as waste is incorporated by the char and as the mixture is subsequently gasified. In addition, a portion of the elemental content of the char surface was revealed by energy dispersive (EDAX) measurements. IR photoacoustic spectroscopy showed that peaks attributable to aqueous and organic fractions of the waste disappear upon gasification.

Introduction

Extensive studies (1–12) by us have shown that a particular mode of gasification, herein referred to as the “reverse mode” (13), that uses a specially prepared char support matrix is both convenient and effective in treating a variety of hazardous substances. Our studies have led to the development of a treatment process, the details of which are given elsewhere (2–12). The process uses char prepared from coal, which is first ground to a granular consistency and then gasified in reverse mode to form macroporous char. Sub-bituminous coal gives excellent results, in which the hard, granular char produced has very large pores that are ideal for sorbing oily sludges. If the char is gasified twice more, it

contains negligible amounts of extractable organics, and this is referred to as “virgin char.” The char is a low grade activated carbon.

For treatment, the waste is first mixed with char by simple stirring. The result is a dry granular material in which the waste is spontaneously sorbed into the porous structure of the char. The char/waste mixture is then gasified in reverse mode using oxygen as the oxidant, the chemically reductive granular char serving as a gas-permeable support matrix. Since less than stoichiometric amounts of oxygen are used in the process, a clean-burning, approximately 300 Btu/scf gas product is formed. The emerging gas flows through a condenser to remove water. The process is operationally simple and tolerates a wide range of waste composition; however, the chemical details are complex and certain aspects of the process are counter-intuitive. The following are important results: (1) Only a small fraction (e.g., 10%) of the original char is consumed. (2) The organic and aqueous portions of the waste are converted to a gas and aqueous condensate, so the char is effectively regenerated and can be recycled in the process. The condensate is also typically recycled in the process, since water is required for efficient gasification. (3) The char product serves to retain the inorganic components, including heavy metals. (4) Inherent char alkalinity retains acid gases such as HCl. (5) NO_x, SO_x, dioxins, and furans are not formed.

Destruction and removal efficiencies (DREs) have been measured for various hazardous components in past studies. For the present study, we are interested in determining the usefulness of various routine analytical instruments in characterizing a typical industrial waste as well as the char, subject to minimal sample preparation procedures such as extractions and separations. The waste, which is a combination of styrene manufacturing wastes and petroleum products, is in the form of an oily sludge; thus, it is a good candidate for treatment by gasification on a char matrix. It is a multicomponent, multiphase inhomogeneous mixture, so it can be only partially characterized at best.

The second focus of the study was the physical and chemical characterization of the char, which is a key factor in the gasification method. We studied it as it exists in the various stages of the process, i.e., virgin char, char mixed with waste, and char after gasification. Char also cannot be fully characterized; however, to the extent that they can be determined, the characteristics of the virgin char can be used as a starting point and a return point for monitoring the waste degradation by gasification. It is important that the distinct characteristics of the char remain after gasification so that the char can be recycled. In addition, the destruction of the organic components of the waste can be inferred under these circumstances.

Experimental Section

Scanning Electron Microscopy (SEM). Analyses were made using a JEOL 840 scanning electron microscope. Micrographs were obtained in duplicate at magnifications of 25×, 50×, 250×, and 1000×. To determine the elemental composition on the char surface, char particles were individually cemented with silver paint directly onto aluminum SEM mounts. A Balzer model 010 vacuum carbon evaporator was used to overcoat the particles with carbon for electron beam conductivity. The coated particles were examined using a JEOL 840 scanning electron microscope at an accelerating voltage of 10 kV and probe current of 1 nA for both the secondary electron micrographs and X-ray analysis. A Tracor Northern energy dispersive spectrometer (EDS) system

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coupled with the SEM was used to collect X-ray analytical information for elements with atomic number greater than 10.

Elemental Analyses. Elemental analyses and proximate and ultimate analyses were conducted at Galbraith Laboratories (Knoxville, TN).

Infrared Spectroscopy. All spectra were collected at room temperature from 3800 to 700 cm^{-1} using the Nicolet 800 FTIR spectrometer equipped with a germanium-coated KBr beam splitter. A mercury cadmium telluride detector was used to obtain transmission spectra of KBr pellets containing ~1% sample.

Micro attenuated total reflectance (MATR) spectra were also taken. The microscope ATR objective used for MATR spectra has a zinc selenide crystal which has a penetration depth of 2 μm at 1000 cm^{-1} and uses a 45° angle of incidence. This technique is ideal for obtaining information about surface chemistry; however, it is of limited use with hard samples (e.g., char particles) due to poor optical contact between sample and crystal. This problem was partially compensated for by averaging 1000 scans.

Photoacoustic Spectroscopy (PAS). Spectra were recorded at 4 cm^{-1} resolution using a Bruker IFS 88 equipped with an MTEC model 200 photoacoustic accessory. Samples contained in a small sample cell were placed into the photoacoustic accessory and purged for 30 min prior to recording the spectra. A carbon black spectrum was recorded as a background spectrum. Single beam spectra were ratioed against the carbon black spectrum to yield the absorbance spectra, which were then baseline corrected to give final spectra.

Extraction of Solid Coal Samples. Samples were studied before and after gasification. The extraction method is an adaptation of EPA SW-846 Method 3540 (14–16). The procedure used was designed for the extraction of nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes using Soxhlet extraction, which ensures intimate contact of the sample matrix with the extraction solvent. The method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics prior to analysis by a variety of chromatographic procedures. Five-gram portions representative of the total samples were used for the analyses. Surrogate compounds were added to all samples. Aliquots of 0.100 mL of surrogate spiking solution [containing pyrene- d_{10} , chrysene- d_{12} , 2-chlorophenol- d_4 , bis(pentafluorophenyl)phenylphosphine, phenol- d_6 , and 1,2-dichlorobenzene- d_4 at levels of 1000–2000 $\mu\text{g}/\text{mL}$] were added to each sample and blank as markers.

Samples covered by a layer of sodium sulfate were extracted with 200 mL of solvent (methylene chloride or hexane) and transferred to a Kuderna–Danish concentrator, to which a three-ball Snyder column was attached, and the liquid was reduced to less than 10 mL. The extract volume was adjusted to 10.0 mL. The extract was prepared for analysis by a 1:10 dilution, and 0.10 mL of extract was placed into an autosampler vial with 0.10 mL of internal standard (20 ppm anthracene- d_{10}) to give a final concentration for the anthracene of 10 ppm.

Gas Chromatography/Mass Spectrometry (GC/MS). The extract was analyzed by GC/MS using a Hewlett-Packard GC 5890 Series II gas chromatograph with a Hewlett-Packard MS quadrupole engine MS 59827A. The GC was equipped with a 0.32 mm i.d. \times 30 m DB-5 column operated at 50 °C for 4 min and then ramped 8 °C/min to 300 °C. The mass spectrometer scan covered the range from 50 to 800 amu. The Wiley/NBS Registry of MS Spectral Data Library was used for compound identifications.

High-Resolution Nuclear Magnetic Resonance (NMR). NMR spectra were obtained with either a 300 or a 400 MHz

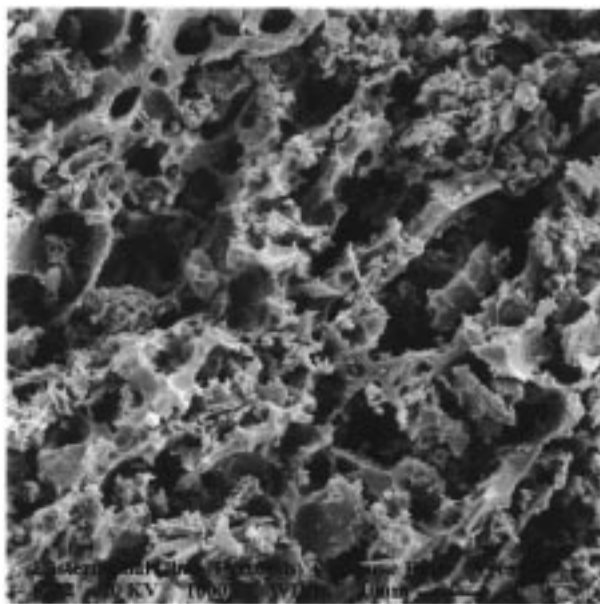


FIGURE 1. Scanning electron micrograph of gasification char, showing the macroporous surface at 1500 \times magnification.

Varian NMR spectrometer containing a four-nucleus NMR probe (5 mm) for observing ^1H , ^{19}F , ^{13}C , and ^{31}P . The entire mix of sludge components except insoluble inorganics was studied by dissolving in acetone- d_6 , centrifuging, and passing through a 0.2 μm filter. Water was eliminated from the component mixture by dissolving the sludge in deuterated chloroform.

Solid-State Nuclear Magnetic Resonance. Several fractions of the sludge mixture as well as char samples containing sorbed sludge were examined by solid-state NMR. A home-built spin–echo type NMR spectrometer operating at 17 MHz was used to observe Bloch decays following a 90° pulse. These decays are Fourier transforms of the NMR line shapes, and they reflect the degree of molecular motion present in the sample.

Results

Characterization of the Virgin Char. Analytical techniques, involving SEM, elemental analysis, FTIR, PAS, and GC/MS, were used to examine the char. These techniques are typically used to characterize coal, so they should also be applicable to char.

SEM Micrographs. The SEM micrograph of gasified char is shown in Figure 1. It is evident that the char has a spongelike surface with unusually large pores, many greater than 10 μm in size. These pores are larger than what are normally called macropores, so they could be called “supermacropores.” Surface area measurements made previously by us on chars of this type were in the range of 150–250 m^2/g . However, the spongelike surface enhances the sorbing capacity of the char for liquids and semisolids beyond that of activated carbon.

For comparison, Figure 2 shows the micrograph of a char prepared by a pyrolysis process in which coal was heated in the absence of air to drive off volatiles and moisture. The spongelike surface is clearly missing. The pyrolysis char was subsequently gasified, and the micrograph shows that the surface of this char is also spongelike following gasification. It should be noted that both pyrolysis and gasification chars have low densities. SEM data indicate that the low density of pyrolysis char arises from the very large holes in the structure (17), whereas the low density of gasification char arises from the macropores.

Elemental Analyses. The results of the analyses are compiled in Table 1. The char, as expected, is mostly

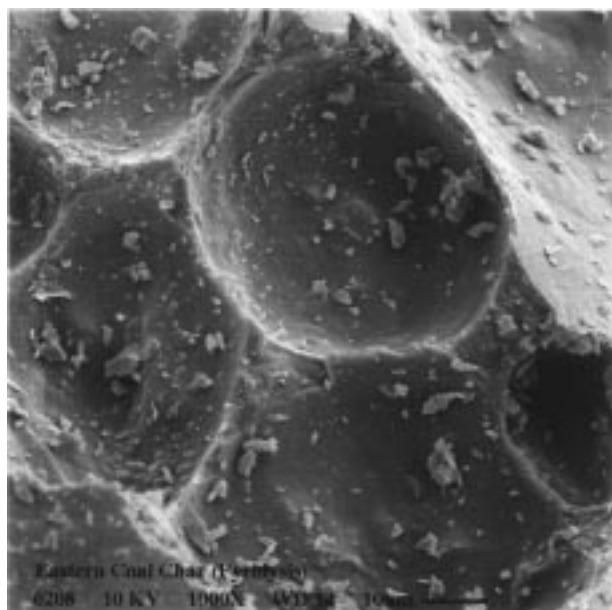


FIGURE 2. Scanning electron micrograph of pyrolysis char, showing the smooth surface at 1000 \times magnification.

TABLE 1. Proximate and Ultimate Analyses for Coal and Char

component	coal	char
Proximate Analysis (%)		
moisture	7.65	0.89
volatile matter	37.42	10.16
ash	2.64	6.49
fixed carbon (by difference)	52.29	82.46
Ultimate Analysis (%)		
moisture	7.65	0.89
carbon	66.75	67.25
hydrogen	5.49	0.63
nitrogen	1.45	1.5
sulfur	0.3	0.61
chlorine	0	0
ash	2.64	6.49
oxygen (by difference)	15.72	22.63

composed of carbon and has less volatile matter, less moisture, and more ash than does coal. The ultimate analysis shows that it also has more oxygen, less hydrogen, and about the same amount of carbon as does coal. It should be noted that fixed carbon includes everything not volatilized by heating less the ash.

IR Spectra. The MATR spectrum of char, which is not presented here, showed two broad, featureless absorption bands, one at about 3300 cm^{-1} , which is associated with water, and the other at 1200 cm^{-1} , which is indicative of SiO_2 . A smaller band at 1630 cm^{-1} is attributed to carbonyls, and a second smaller band at approximately 1400 cm^{-1} is attributed to CH deformations. The MATR technique is of limited use in the present study.

The KBr spectrum of char, which is not presented here, showed no evidence of the Si–O stretch in the 1200 cm^{-1} region. Weak bands were observed at 3400 cm^{-1} (NH or OH stretching), 1740 cm^{-1} (carbonyl; five-membered cyclic imide), 1540 cm^{-1} (aromatic ring mode), and 1453 cm^{-1} (aliphatic CH deformation). The dilution of the char with KBr caused a large reduction in signal intensity and the resulting spectra provided little information.

PAS Spectra. The PAS spectrum of coal, shown in Figure 3, compares well with published spectra (18). The broad band at 3400 cm^{-1} is attributed to OH, and atmospheric carbon

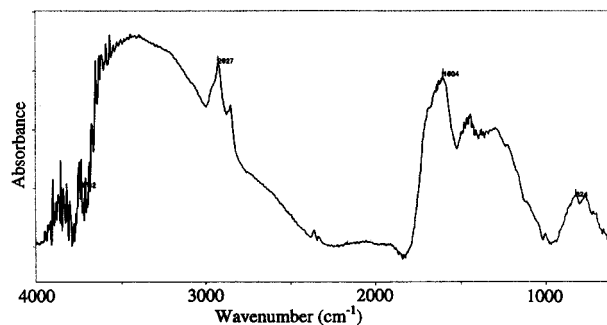


FIGURE 3. Photoacoustic spectrum of coal.

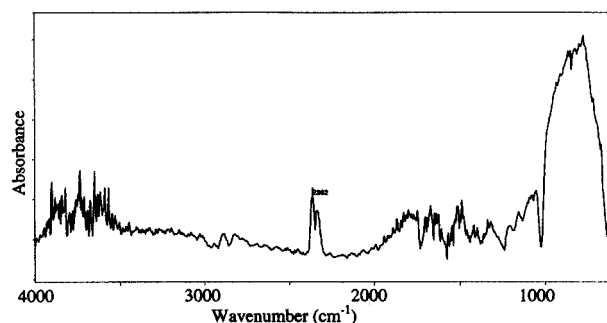


FIGURE 4. Photoacoustic spectrum of gasification char.

dioxide bands are present at 2362 cm^{-1} . The band at 2927 cm^{-1} is assigned to aliphatic CH stretch. The strong band at 1604 cm^{-1} is attributed to aromatic and carboxylic acid salt modes. The band at 1445 cm^{-1} is attributed to CH deformations, and bands below 1000 cm^{-1} are probably attributable to an aromatic substitution pattern.

The spectrum of char is shown in Figure 4. The most striking feature is that the large bands for OH at 3400 cm^{-1} , CH at 1445 cm^{-1} , and aromatics at 1604 cm^{-1} for coal are all essentially eliminated. The broad band at about 830 cm^{-1} remains.

The PAS spectrum of pyrolysis char (not shown) gave strong evidence of aromaticity, with intense bands below 1000 cm^{-1} . Also, with significant absorption between 1000 and 2000 cm^{-1} , with a strong band at 1606 cm^{-1} . The broad band at 3400 cm^{-1} attributable to OH is essentially missing. No significant changes in the PAS spectrum of pyrolysis char were observed after gasification.

Extraction of Coal and Char. Soxhlet extractions of the char and coal were made with methylene chloride and with hexane. GC/MS total ion chromatograms were run for the extracts, and blanks were run for the solvents. Similar profiles of extractable organics were obtained from coal with both solvents and also from char with both solvents. The identified extractable organics in char were phenols, straight and branched aliphatic hydrocarbons, and aromatic hydrocarbons, as shown in Table 2.

The concentrations are calculated relative to the internal standard (10 $\mu\text{g/mL}$ anthracene- d_{10}). The RT values are the components' average retention times. Qual is the percentage quality of the computer's spectra match, with 100% being a perfect match. Matches less than 60% are not shown.

Characterization of the Waste Sludge. The sludge is a heterogeneous mixture of styrene manufacturing wastes and petroleum products. It is stringy, sticky, and difficult to manipulate. It has the appearance of a tar and exhibits a slight vapor pressure from incorporated petroleum products. A total identification of the sludge components is not possible or practical; however, identification of some components is possible with the analytical techniques used in the previous section in addition to NMR.

TABLE 2. Compounds Found in Both Methylene Chloride and Hexane Extracts of Char

extractable organic	concn ($\mu\text{g/L}$)	RT	qual	total ppm ^a
phenol	4.5	6.374	91	0.18
4-methylphenol	6.4	8.702	94	0.26
2,6,10,14-tetramethylhexadecane	2.6	16.126	86	0.10
2,3,6-trimethyl-naphthalene	2.9	17.655	62	0.12
1,4,5-trimethyl-naphthalene	4.8	18.042	78	0.19
1,6-dimethyl-4-(1-methylethyl)naphthalene	11.0	19.427	96	0.46
2,6,10,14-tetramethylhexadecane	1.6	19.752	72	0.06
2,6,10,15,19,23-hexamethyltetracosane	3.8	19.849	68	0.15
dioctadecyl ester phosphonic acid	3.7	21.049	90	0.15
1-tetracosanol	3.2	21.049	64	0.13
9-eicosene	4.1	21.05	87	0.16
1-hexadecanol	4.5	21.051	90	0.18
octadecane	6.2	21.148	98	0.25
nonadecane	2.5	22.473	96	0.10
hexacosane	1.7	22.478	72	0.07
eicosane	10.0	23.741	95	0.42
2,6,10,15-tetramethylheptadecane	5.5	24.952	96	0.22
heneicosane	7.4	24.958	93	0.30
2,6,10,15-tetramethylheptadecane	4.9	24.96	93	0.20
4,4'-(1-methylethylidene)bisphenol	1.1	25.929	72	0.04
3,4,5,6-tetramethylphenanthrene	6.4	26.332	93	0.26
1-methyl-7-(1-methylethyl)phenanthrene	1.1	26.341	72	0.04
tricosane	3.4	27.237	93	0.14
total	103.3			4.16

^a Total ppm extracted from char.

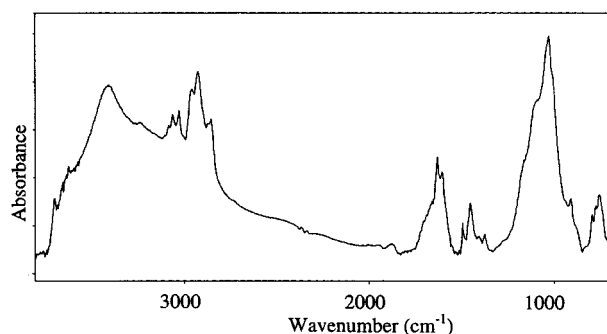


FIGURE 5. FTIR spectrum of sludge.

IR Spectra. Because the sludge is heterogeneous, spectra of several different parts of the sample were taken using the microscope attachment. All contained the same peaks, but the intensities varied. A typical spectrum is shown in Figure 5. An intense absorption band at about 1000 cm^{-1} can be assigned to the Si–O stretch. This band is indicative of minerals and clays or what may be considered the inorganic component of the sludge. The large broad band at 3400 cm^{-1} is due primarily to water. The other bands found in the spectrum are attributable to the organic component. The absorption bands between 2800 and 3000 cm^{-1} arise from aliphatic and aromatic methyl C–H. The bands between 3000 and 3100 cm^{-1} are attributable to methylene C–H. Also, the bands between 1400 and 1500 cm^{-1} are due to H–C–H bending. The band at 1630 cm^{-1} is associated with aromatic ring distortion.

NMR Spectra. The NMR spectrum of the acetone extract (not shown) has a large peak at about 4 ppm due to water. Peak integration shows that the predominant proton signal of water is about 3 times as intense as the total of all signals from the organic components. Downfield peaks, between 6.2 and 8.2 ppm, are attributable to aromatic and/or olefinic groups, and upfield peaks, between 0 and 3 ppm, to aliphatic groups. In the spectrum of the chloroform extract, shown in Figure 6, the water peak is absent, and the organic protons can be clearly seen. The results of this analysis do not identify specific compounds within the sludge, but they do give the

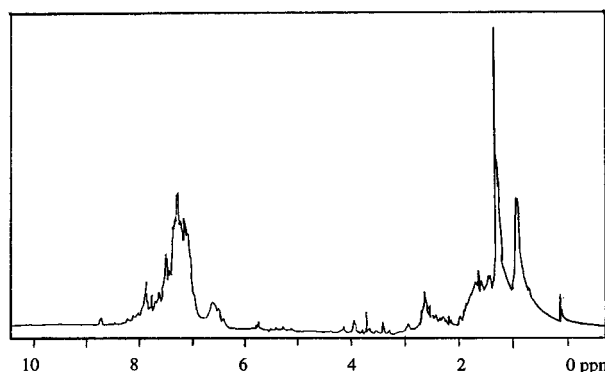


FIGURE 6. NMR spectrum of chloroform extract of sludge.

relative amounts of protons of the two gross types of compounds found in the sludge.

NMR spectra were also run on extracts that had been previously centrifuged and for which the aqueous layer had been removed. NMR analysis showed that there was very little organic content in the aqueous layer, so we will consider it to be solely water. By use of internal standards (benzene and hexadecane), we estimate that water constitutes about 32% of the sludge weight, which is consistent with the 38% moisture reported in the elemental analysis.

GC/MS Analysis. The sludge was extracted with two solvents, acetone and chloroform. Various procedures were used in which the sludge was centrifuged or heated prior to extraction. The extracts were analyzed by GC/MS, and a very large number of compounds was detected in each case, although the relative fraction of the sludge that could be identified by GC/MS was small, varying between about 1% and 8%. A typical result is shown in Table 3, which was obtained with an acetone extract. The results also showed that very little of the sludge (about 2%) is volatilized by simple heating.

The organic compounds detected were primarily aromatic and polyaromatic hydrocarbons. The table contains the identified components, which were found at levels between 1300 and 17 000 ppm level. The total amount of organic

TABLE 3. GC/MS Analysis of Acetone Extract of Sludge

identified compounds	area	concn (ppm)	qual
styrene	16 394 577	3700	94
1-methylethenylbenzene	7 023 557	1600	97
1-chloroethylbenzene	711 410	160	91
(1-nitroethyl)benzene	26 054 609	5800	72
azulene	1 033 393	230	76
3,7,7-trimethylcyclohepta-1,3,5-triene	1 283 935	290	87
2,3,5-trimethylphenol	3 171 879	710	64
4-methoxybenzaldehyde	737 555	170	58
1-methylnaphthalene	1 915 226	430	95
1-methylnaphthalene	2 469 461	550	94
1,1'-biphenyl	19 484 436	4400	93
2-ethylnaphthalene	1 126 358	250	93
1,5-dimethylnaphthalene	1 425 987	320	97
1,2-dihydroacenaphthylene	1 132 976	250	93
2,3-dimethylnaphthalene	3 867 475	870	97
2,6-dimethylnaphthalene	1 847 267	410	96
2-methyl-1,1'-biphenyl	6 018 045	1300	92
acenaphthylene	6 490 595	1600	90
1,2-dihydroacenaphthylene	6 279 312	1400	94
1,1'-ethylidenebisbenzene	3 1431 548	7100	86
4-methyl-1,1'-biphenyl	7 063 026	1600	96
1,1'-(1,2-ethanediyl)bisbenzene	10 432 221	2300	81
1,1'-(1-methyl-1,2-ethanediyl)bisbenzene	14 402 720	3200	70
2-ethyl-1,1'-biphenyl	26 911 109	6000	98
1,3-diphenylbutane	28 922 264	6500	93
heptadecane	28 492 046	6400	92
1,1'-(1,4-butanediyl)bisbenzene	34 413 251	7700	70
1,1-dicyano-2-methyl-4-(p-cyanophenyl)propane	15 948 676	3600	74
anthracene- <i>d</i> ₁₀	835 552	10	

compounds identified was 210 000 ppm. Assuming that the extract is 37% of the sludge and that the organic compounds identified by GC/MS are 21% of the extract, we conclude that the identified compounds represent about 8% of the total sludge.

FTIR Spectra. The inorganic component, when separated from the other components by extraction, appeared to be gray "dirt." This was analyzed by FTIR using a microscope attachment to focus on separate regions of the material and also using a KBr pellet. Both spectra had an intense absorption band at about 1000 cm^{-1} that can be assigned to Si—O stretching. These bands are indicative of minerals and clays or what may be considered the inorganic component of the sludge. A broad band at 3400 cm^{-1} is attributable to NH or OH stretching and is probably due to the water.

Sludge Composition. From the elemental analysis, the sludge was found to be 38% water, 27% inorganic, and 35% organic. From gravimetric and NMR analyses, the component percentages were found to be 32% water, 32% inorganic, and 36% organic residue. We also found that nearly half of the water can be separated from the sludge by centrifugation, and NMR analysis showed that the remaining half of the water in the sludge was solubilized with the extractable organic component. These results are surprisingly consistent given the heterogeneous nature of the sludge. The organic components are a mixture of aliphatic and olefinic/aromatic organic compounds that should be readily degraded by gasification.

Char:Sludge Interactions and Gasification

NMR Analyses. Proton NMR Bloch decays were observed for the raw sludge and for two fractions separated by centrifugation. The light fraction (which is water rich) exhibits exponential behavior with a relaxation time of about 7 ms. The heavy fraction exhibits nonexponential behavior, with a long tail observable after about 10 ms. The raw sludge also exhibits nonexponential behavior, which arises as a combined effect from both fractions. A detailed interpretation of these

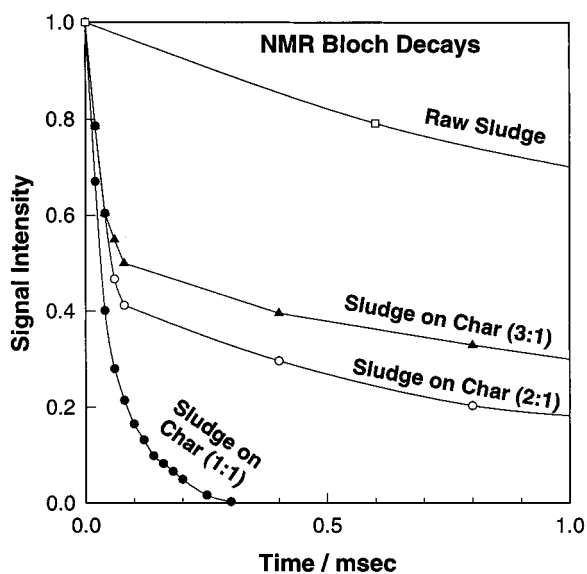


FIGURE 7. NMR bloch decays for sludge and sludge/char mixtures.

data would be difficult; however, the important point is that the time-scale of the relaxation is on the order of 10 ms.

Dramatic effects are observable in the decays for the sludge on char as contrasted with those from the sludge per se. Figure 7 shows that the time scale of the decay for 1:1 loading is on the order of 100 μs , so the signal is no longer observable after about 0.4 ms. This is indicative of very slow motion, of the type observed in solids in which there is only very limited molecular motion. Bloch decays for completely rigid organic molecules in general persist for times less than 50 μs . The char itself exhibits a very small, fast decaying signal, about 1% of the total signal, which is due to protons in the char matrix. Thus, the NMR signal indicates that the sludge is immobilized on the char. At higher loading, the initial rapid decay is followed by a slower decay (long tail), and the tail

TABLE 4. Ultimate and Proximate Analyses of Various Samples

components	1:1 char sludge			char
	no RB	1×RB	2×RB	
Ultimate Analysis (%)				
moisture	13.88	1.68	1.02	0.89
carbon	68.15	49.31	58.39	67.25
hydrogen	3.36	0.74	0.94	0.63
nitrogen	1.23	1.24	1.40	1.5
sulfur	1.08	0.87	0.81	0.61
chlorine	0.63	0.44	0.43	0
ash	19.50	19.91	30.29	6.49
oxygen	6.05	27.49	7.74	23.52
(by difference)				
Proximate Analysis (%)				
moisture	13.88	1.68	1.02	0.89
volatile matter	18.37	7.95	7.26	10.16
ash	19.50	19.91	30.29	6.49
fixed carbon	48.25	70.46	61.93	82.46
(by difference)				

becomes more intense as the loading increases. This long tail is indicative of increased motion or less immobilization. Thus the Bloch decay indicates that a portion of the sludge is immobilized while the remaining portion is not. We conclude that the char has the capacity to capture and immobilize roughly an equal weight of sludge.

Elemental Analyses. The results of the analyses are compiled in Table 4. The sludge/char mixture has more moisture and volatile matter than does the char per se. Gasification of the mixture returns the percentages of the various components to near their original levels. A second gasification does not significantly further alter these percentages.

These analyses show that chlorine, which is associated primarily with the sludge, is retained on the char after gasification. The mechanism for the removal of chlorine from the sludge presumably involves formation of HCl and subsequent neutralization by the alkaline char (5) so that the char matrix retains chloride ions. In addition, as in the gasification of coal, the volatile matter is reduced without significant increase in ash content.

The ultimate analyses show a substantial drop in carbon and increase in oxygen after the first gasification. The carbon level is partly restored and the oxygen level drops to near its original value after the second gasification. The small value for carbon and the large value for oxygen after the first gasification are difficult to interpret. At face value, it would suggest that there is a substantial amount of oxygen functionality on the char which disappears after the second gasification. This suggests that the first gasification, which uses most of the sludge as fuel, results in partial oxidation of the surface of the char. The subsequent gasification uses the oxidized surface as fuel and reduces the surface of the char.

SEM Micrographs. Micrographs (not shown) were taken of virgin char and char coated with sludge, before and after gasification. The sludge components could be clearly seen on the char surface. The elements detected by use of the EDS technique are listed below in Table 5. The heterogeneous nature of the sludge gave rise to different levels of detection at different positions on the surface. The elements detected with the exception of chlorine can be found in coal and coal chars (19). The chlorine is associated with the sludge, as confirmed by elemental analysis of the coal and char prior to mixing with the sludge.

PAS Spectra. The spectrum of char and sludge in 1:1 weight ratio (not shown) exhibits the features of both the char (Figure 4) and the sludge (Figure 5), with aliphatic and aromatic CH stretches at 2924 and 3031 cm^{-1} , respectively,

TABLE 5. Elements Detected by Energy Dispersive Spectrometry

sample	elements
char	aluminum, silicon, sulfur, calcium, iron, magnesium
waste/char mixture prior to gasification	aluminum, silicon, sulfur, calcium, iron, magnesium, chlorine, potassium, titanium, sodium
after gasification	aluminum, silicon, sulfur, calcium, iron, magnesium, potassium, titanium, sodium

bands at 1452 and 1375 cm^{-1} attributable to CH deformations, and an aromatic band at 1603 cm^{-1} . A broad band at 1044 cm^{-1} is due to Si—O, and another broad band around 3300 cm^{-1} indicates the presence of an OH and/or NH group. The major difference is that the band at 1000 cm^{-1} is broader than that in the sludge and contains more features around 800 cm^{-1} (as expected for a mixed sample).

In the spectrum of sludge/char 1:1 after gasification (not shown), the absorptions above 2500 cm^{-1} are removed and the appearance is similar to that of virgin char. This indicates that the organics have been destroyed.

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