December 21, 1989

HYDROTHERMAL PRETREATMENT OF COAL

Quarterly Report No. 1
Covering the Period September 21 to December 15, 1989

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Prepared for:

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Contract DE-AC22-89PC89880
SRI International Project No. 8209

Approved:

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ABSTRACT

We have examined changes in Argonne Premium samples of Wyodak coal following 30 min treatment in liquid water at autogenous pressures at 150°, 250°, and 350°C. In most runs the coal was initially dried at 60°C/1 torr/20 hr. The changes were monitored by pyrolysis field ionization mass spectrometry (py-FIMS) operating at 2.5°C/min from ambient to 500°C. We recorded the volatility patterns of the coal tars evolved over that temperature range, and in all cases the tar yields were 25%-30% of the starting coal on a mass basis.

There was essentially no change after the 150°C treatment. Small increases in volatility were seen following the 250°C treatment, but major effects were seen in the 350° work. The tar quantity remained unchanged; however, the volatility increased so the temperature of half volatility for the as-received coal of 400°C was reduced to 340°C. Control runs with no water showed some thermal effect, but the net effect from the presence of liquid water was clearly evident.

The composition was unchanged after the 150° and 250°C treatments, but the 350° treatment brought about a 30% loss of oxygen. The change corresponded to loss of the elements of water, although loss of "OH" seemed to fit the analytical data somewhat better. The water loss takes place both in the presence and in the absence of added water, but it is noteworthy that the loss in the hydrothermal runs occurs at $p(H_2O) = 160$ atm. We conclude that the process must involve the dehydration solely of chemically bound elements of water; the dehydration of catechol is a specific, likely candidate.

DISCLAIMER

INTRODUCTION AND SUMMARY

We have begun a program of research into the effects of hydrothermal treatment on the reactivity of a series of coals. We started with work on Argonne Premium samples of Wyodak coal, conducted in liquid water at autogenous pressures at 150°, 250° and 350°C. The diagnostic elements of the program will include pyrolysis field ionization mass spectrometry (py-FIMS), elemental analysis, differential thermal analysis, and thermal gravimetric analysis.

The results of work conducted over the first quarter have been compiled into a manuscript to appear in the Preprints of the Fuel Division of the American Chemical Society for the Society's meeting in April 1990. That manuscript, attached as the appendix, describes our work over this period in detail, and we present a summary of the work here.

In introductory work, we showed that the as-received coal, dried initially at 60°C/1 torr/20 hr, evolved only small quantities of volatiles below 300°C. These volatiles were preexisting in the coal matrix and represented only about 10% of the material ultimately volatile. The major fraction emerged at higher temperatures, generated through pyrolytic fragmentation of portions of the coal structure. Next, in work with hydrothermally treated samples of the coal, we found some small effects developed by the 250°C treatment and considerably larger changes for treatment at 350°. The changes were in the form of greater fractions of the volatiles evolving below py-FIMS temperatures of 300°. Since the 350° treatment was in the pyrolytic region, treatments without water were run. Although some thermal effect was seen without water, it was clear that the presence of added water increased the volatilities.

Major products of the py-FIMS studies included phenols and catec..ols, joined in the treated coals by acetone. GC analysis of collected volatiles showed in addition smaller quantities of other simple ketones. This surprising observation suggests there may be cellulosic residues in the coal, and we plan to look further into this finding. Other specific effects of added water include a significantly higher molecular weight for the tars evolved at py-FIMS temperatures above 350°C. This change suggests a lowered degree of thermolytic cracking when hydrothermal conditions are used.

Compositional changes were observed only following the 350°C treatment. About 30% of the oxygen in the starting coal (dried) was lost, and the analytical data were consistent only with loss of elements of water. The O-loss was seen following 350°C

treatment both with and without water; however, the fact that elements of water were lost in the hydrothermal case at 160 atm water showed that the loss of oxygen must involve specific dehydration of chemically bound elements of water in the organic phase of the coal. We suggest that catechol could be involved directly, since under some conditions it condenses readily with loss of water.

FUTURE WORK

During the next period, we plan to complete our work with Wyodak coal, using combinations of thermal gravimetric and differential thermal analyses. We plan to conduct a few experiments with catechol and clays to assess the significance of catechol dehydration in the loss of oxygen. We then plan to examine Argonne Premium samples of Illinois No. 6.

Appendix

THE EFFECTS OF HYDROTHERMAL TREATMENT ON WYODAK COAL

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INTRODUCTION

Recent accounts of the treatment of coal with steam include the work of Beinkowski et al.,[1] Brandes and Graff,[2,3] and Kahn et al.[4] These efforts sought benefits to liquefaction and pyrolytic tar yields and described changes in both the composition and the behavior of the coals. In other work Rozgonyi et al. described ash and sulfur reductions in steam-treated coal,[5] and some of our recent work with Illinois No. 6 coal in hot liquid water is described in a paper elsewhere in these preprints.[6]

The hydrothermal conditions used in these efforts are reminiscent of the hydrous pyrolysis studies conducted in research dealing with the accelerated maturation of oil shale.[7,8] Source rocks are heated in liquid water at 300°-350°C, resulting in the net production of alkanes and other hydrocarbons, in contrast to the case for dry pyrolysis where olefins are produced. The claim that hydrous pyrolysis actually mimics the natural process has been questioned recently,[9,10] but the phenomenology is unquestioned.

The work described here is an attempt to bridge the two areas. We are seeking to understand the changes brought about in Wyodak coal by liquid water in the range 150-350°C in terms of its structure. We expect the results of this work to provide some insight into any benefits such treatment provides liquefaction and volatiles production.

EXPERIMENTAL

Our work was conducted with Wyodak samples from the Argonne Premium Coal Bank. In most cases the starting coal was dried in an oven at 60°C/1 torr/20 hr, a pretreatment that resulted in a loss of water representing about 30% of the coal mass. In some runs the as-received coal was used, and we found no difference in behavior following hydrothermal treatment. The as-received coal was also used in a control run

conducted with no added water. In that case the water in the coal may have contributed to the subsequent pyrolytic behavior, as described below.

The hydrothermal treatment was conducted in a 45-mL stainless steel reactor having a tightly fitting Pyrex insert. Sufficient water was used to assure in each case that a liquid phase was present at temperature, and the reactor was charged with 33-50 atm (500-750 psi) nitrogen (cold). The run temperatures (°C) and respective vapor pressures of water (atm) were 150/4.6, 250/38, and 350/160. After treatment the coal/water mixture was centrifuged directly in the insert, most of the water was removed by pipette and saved for later analysis, and the coal was removed in an N_2-purged glove bag. The remaining superficial water was then removed in a stream of dry nitrogen.
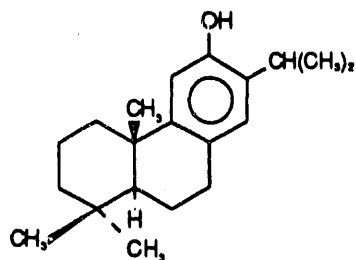
The bulk of the analysis was conducted by pyrolysis field ionization mass spectrometry (py-FIMS). The heating rate used throughout was 2.5°C/min, and spectra were recorded at nominally 30° intervals from ambient to 500°C. In some cases quantities of volatiles from the treated coal were vacuum transferred at 120°C to bulbs for analysis by conventional mass spectrometry. In addition to the parent-peak spectra, py-FIMS output included volatility data and values for the weight average molecular weights ($\bar{M}_w$) of the fractions.

The water fractions were analyzed by first saturating the aqueous phase with NaCl and then extracting with methylene chloride. The extracts were then analyzed by gas chromatography, and identification was confirmed by comparison with authentic samples.
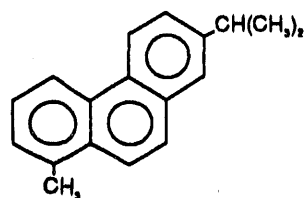
BACKGROUND

Bienkowski et al. reported on the abundance of alkylated phenols and dihydroxybenzenes both in the pyrolysis tars of Wyodak coal and in the water collected following steam treatment.[1] Kahn et al. similarly identified a large collection of phenols in the treatment water.[4] These results are expected based on the lignin residues present in this rank of coal.[11]

A wide range of biomarkers are also reported for the extracts of Wyodak coal in work by Baset et al., who studied benzene/ethanol extracts and pyrolysates evolved directly from the heated coal.[12] The extracts included ferruginol and retene, and they sought but found no pristane.

ferruginol

retene

pristane

The presence of the corresponding olefin pristene in the pyrolysate, however, suggested that the alkane or a precursor was bound to the coal and then released as the olefin when the coal was heated.

The geochemical studies on oil shale could be related to these findings, with the account by Hoering of specific interest.[8] In that work the treatment of preextracted Messel shale in liquid water at 330°C/3 days generated petroleum hydrocarbons including long chain normal alkanes, aromatics, and biomarkers. When D_2O was used, deuterium was heavily incorporated into the hydrocarbons. Hoering's control results and the distributions of isotopic isomers essentially ruled out preexisting, trapped hydrocarbons, and the results suggested that the hydrocarbons were not merely freed, but rather generated in some manner by the water.

RESULTS

We conducted several experiments with hydrothermal treatments at 150° and 250°C and the majority of the work at 350°C. Analyses of the recovered coals included py-FIMS and simple analyses of recovered water and volatiles samples.

Recovered Water, Direct Volatiles Analyses, and Elemental Analysis

As expected, analysis of the recovered water from 350°C treatment runs showed the presence of phenols and dihydroxybenzenes. The most prominent products were catechol (o-$(OH)_2Ph$) and phenol in a ratio of about 2/1. Other products found in smaller quantities

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were resorcinol (m-$(OH)_2Ph$) and hydroquinone (p-$(OH)_2Ph$), with the ratio catechol/(resorcinol + hydroquinone) $\approx$ 6/1.

The same materials were pulled from the coal heated to 120°C in a vacuum line transfer and identified by conventional mass spectrometry. In this case phenol was the most prominent material; however, we were surprised to find acetone as a major volatile product, present in quantities similar to those for phenol.* Smaller quantities of simple ketones including butanone and a pentanone were also identified. These findings are discussed further below.

The elemental analyses from the work at 350°C are presented in Table 1. The %-oxygen values are by direct O-analysis. The final columns in the table show calculated compositions based on specific loss of the elements of CO_2 and H_2O; values for the net loss of OH are shown for comparison. Clearly, CO_2 loss is not significant, and water loss fits rather well. Curiously, loss of OH fits the measured values even better, although the accuracy of the measured values may not warrant our modeling the results to such a degree. The product coals from the 150° and 250°C work showed no O-loss.

Table 1

Analyses of As-Received and 350°C-Treated Wyodak Coal

| | Starting Coal | Treated Coal | | Calculated For Loss Of[a] | | |
		With Water	No Water	CO_2	H_2O	"OH"
%C	66.47 67.60	71.56	72.17	70.45	71.67	71.34
%H	5.10 5.02	4.89	4.99	5.62	4.61	5.04
%N	0.85 0.86	0.95	0.94	0.93	0.91	0.91
%O	20.92 21.63	14.92	15.88	15.48	15.49	15.41
% Ash	8.23 8.58	9.04	9.08	9.08	8.87	8.88

[a]Calculated for loss of elements of CO_2, H_2O, and OH from the starting coal to match a final O-content of 15.4%-15.5%.

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*The possibility of adventitious acetone was considered. However, the presence of acetone solely in runs from the 350°C treatment confirmed its formation in the process.

Thus at 350°C we see about a 30% loss of oxygen, but significantly the loss is independent of the presence of added water. Kahn et al recorded about a 20% O-loss for Wyodak coal with steam at 304-320°C,[4] and we have noted that about half the oxygen in Illinois No. 6 coal is lost in water/N_2 at 400°C.[13] The present results show that, at least for Wyodak coal, the loss is strictly thermally promoted and does not require added water. However, it is notable that the loss of water in the hydrothermal case occurs at a partial pressure of water of 160 atm. The process is thus highly irreversible and obviously does not involve bound or sorbed molecular water. One candidate water source is coal clays, which dehydrate at elevated temperatures.[14] However, that process is reversible and at any rate is very highly suppressed below around 475°C under just a few torr of water vapor.[15]

We conclude that the water loss must involve the dehydration specifically of chemically bound elements of water in the organic phase of the coal. The dehydration may be tied to the fact that catechol is a prominent thermal product, and as we have shown in other work, catechol thermally dehydrates and forms oligomers at 300°-400°C in the presence of kaolinite, one of the clays in coal. We expect to develop a better understanding of this process in further work.

Volatilities

Several different py-FIMS measurements were made of separate samples of the as-received coal on different days to establish the reproducibility of the method and the stability of the instrument. The results of those runs (points) along with those for 150° and 250°C treatments (curves) are presented in Figure 1. The data for the as-received coal fall essentially upon one another, demonstrating a satisfactory precision. The similar alignment of the data from the treated coal shows that little change in the coal takes place at 150°, while some activity is seen at the 250° level. The volatile fractions in these cases and in those below were consistently 25%-30%.

The shape of the curves for the as-received coal demonstrates two regions of activity. Below 300°-320°C the small quantities of preexisting volatile material in the coal are evaporated into the instrument. At higher temperatures, pyrolytic fragmentation of the coal occurs, and products of that process are recorded. Thus for the as-received coal and the 150° sample, no more than about 10% of the ultimately volatile material emerges in the first region. For the 250° treatment, since that temperature was below the point of substantial thermolysis, the increased volatiles for that run must be due specifically to the action of water in the treatment.

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This point is demonstrated more clearly for the 350° work in Figure 2. The figure presents the curves for 30-min runs at 350°C both with added water (2 runs) and without added water, with some data for the as-received coal are shown again for comparison. In this case to assure no confusion from possible thermal effects from oven drying, the as-received coal was used for the run with no water.

The effects tied specifically to the hydrothermal conditions are evident from the profiles. They are emphasized by comparing the %-volatile values at an abscissa value of 350°C, the temperature at which the coal was treated; for the as-received, no water, and hydrothermal samples the volatilities are respectively 22%, 37%, and 52%. The jump from 22% to 37% reflects a thermal effect that can be anticipated since the treatment temperature was in the pyrolysis range, although we cannot rule out some action by the water driven out of the coal. (Work with dried samples is in progress.) The remaining increase to 52%, however, must be due specifically to the presence of water.

Recognizing that the treatment involves holding coal samples at temperature for 30 min and that the py-FIMS heating rate is 2.5°C/min, we can make another useful comparison over the interval 350° to ~425°C (i.e., 350°C to ~[350° + 2.5 x 30]). The pertinent data are presented in Table 2, which shows that the weight average molecular weights $(\overline{M})_w$ for the tars from the hydrothermally treated coal are consistently greater than those for both the as-received and thermally heated samples, a result in turn consistent with the view that added water specifically affects the subsequent pyrolytic properties.

An effect is apparent as well from inspection of the Pyrex inserts after the runs. For the hydrothermal treatment, they showed considerable quantities of tar deposited on the walls. For the thermal treatment case, however, the walls were clean, except for droplets of water driven from the coal during the treatment. Some insight into the these effects can be developed from inspection of the various FIMS spectra, with attention to the effects of treatment on individual compound classes.

FIMS Spectra and Coal Tars

Treatment at 350°C. FIMS spectra are presented in Figure 3 for the as-received coal and for the 350° treatment both with and without water. Each spectrum is the accumulated signal for each sample up to a py-FIMS temperature of 300°C, and the differences in volatilities shown in Figure 2 are evident here.

Table 2

Weight Average Molecular Weights of Tars from As Received, Thermally Treated, and Hydrothermally Treated Wyodak Coal
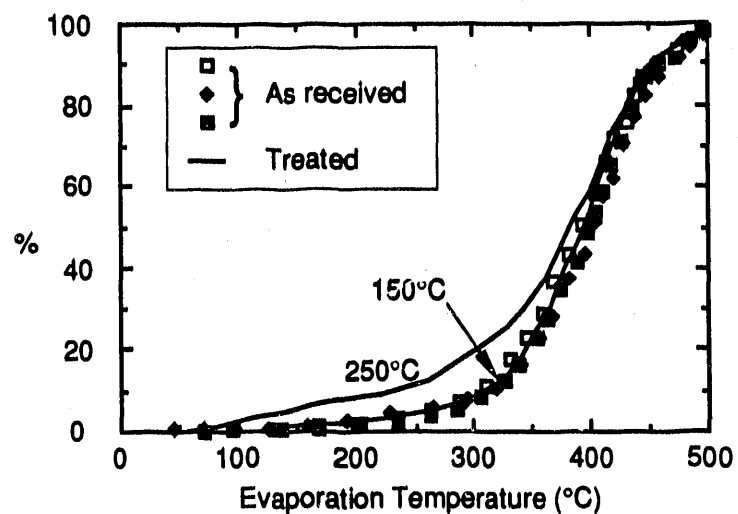
py-FIMS Temperature Interval (°C)	Sample[a]	$\overline{M}_W$
332-359	As received	458
	Thermal	434
	Hydrothermal	518 /
362-389	As received	455 ✓
	Thermal	449
	Hydrothermal	516
392-419	As received	431 ⸱
	Thermal	427
	Hydrothermal	507
422-449	As received	366
	Thermal	356
	Hydrothermal	403

[a]Thermal and hydrothermal samples heated at 350°C/30 min.

Specific effects of the addition of water can be gathered from the difference spectrum shown in Figure 4. The figure represents [hydrothermally treated] *minus* [thermally treated] and is derived from the respective spectra for the full volatiles fractions evolved to 500°C. The data from the two runs have been normalized so that the differences reflect changes in the compositions. Thus the addition of water shifts the thermolytic behavior of the coal so that the volatiles are richer in dihydroxybenzenes and a broad range of coal tar material at m/z values 200-500 amu, and depleted in phenols.
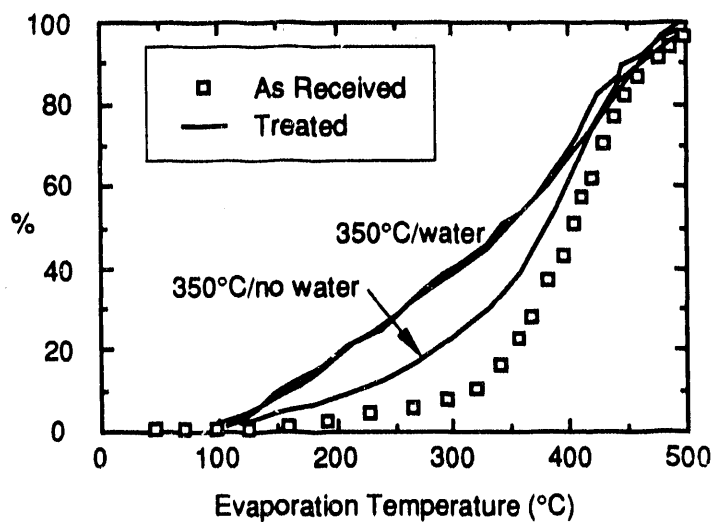
Also very prominent in both spectra is m/z = 58, identified as acetone by vacuum line isolation and analysis. The difference spectrum shows that its levels are elevated relatively in the pyrolysate from the thermally treated coal, probably due to its solubility in water. Other simple ketones in smaller quantities were also identified as noted above. We are not aware of accounts of acetone or other simple ketones as products of coal thermolysis, although such compounds are identified in wood tars and are derived from cellulose.[16] This finding could reflect the presence cellulose residues in Wyodak coal, and we expect to look further into this matter in future studies.

The profiles for the generation of acetone, phenol, and dihydroxybenzene as a function of temperature are shown in Figure 5. For the as-received coal the activity is
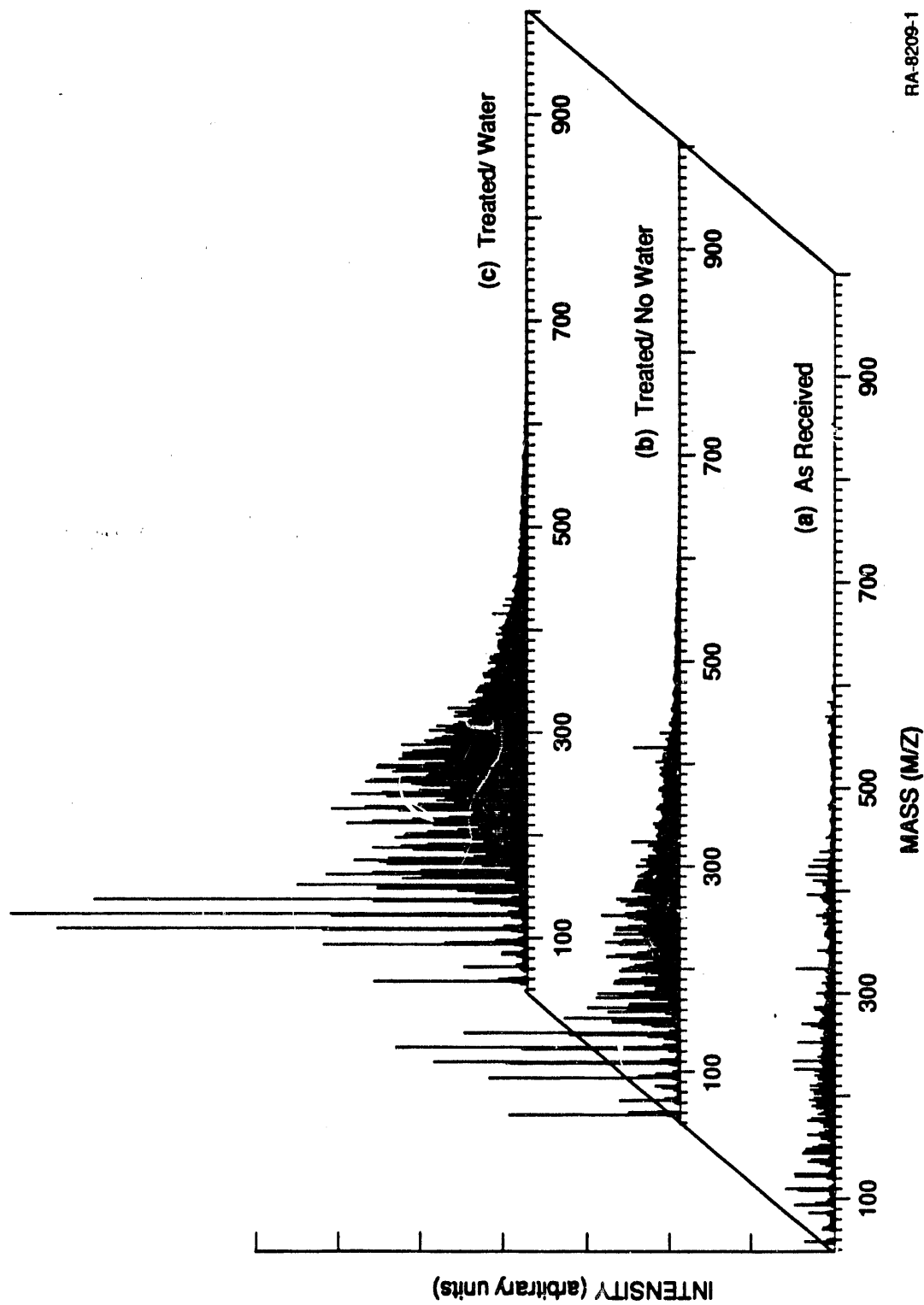
RA-M-8209-2

Figure 1. Evaporation curves for the as-received coal and the 150° and 250°C coal products.

RA-M-8209-3

Figure 2. Evaporation curves for the as-received coal and products from 350°C runs both with (2 runs) and without water.

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Figure 3. FIMS spectra for the as-received coal and for the coals treated at 350°C both thermally and hydrothermally.
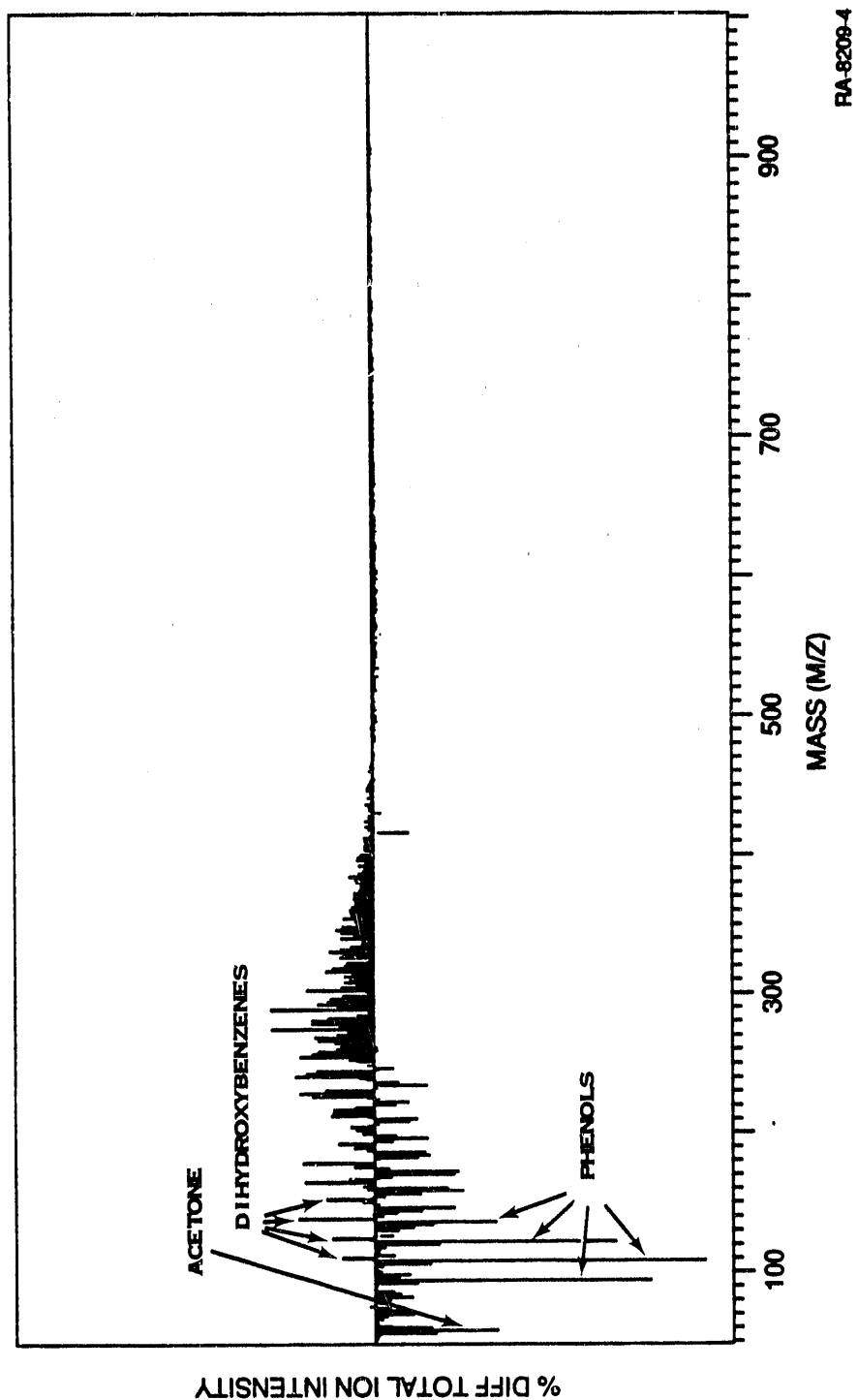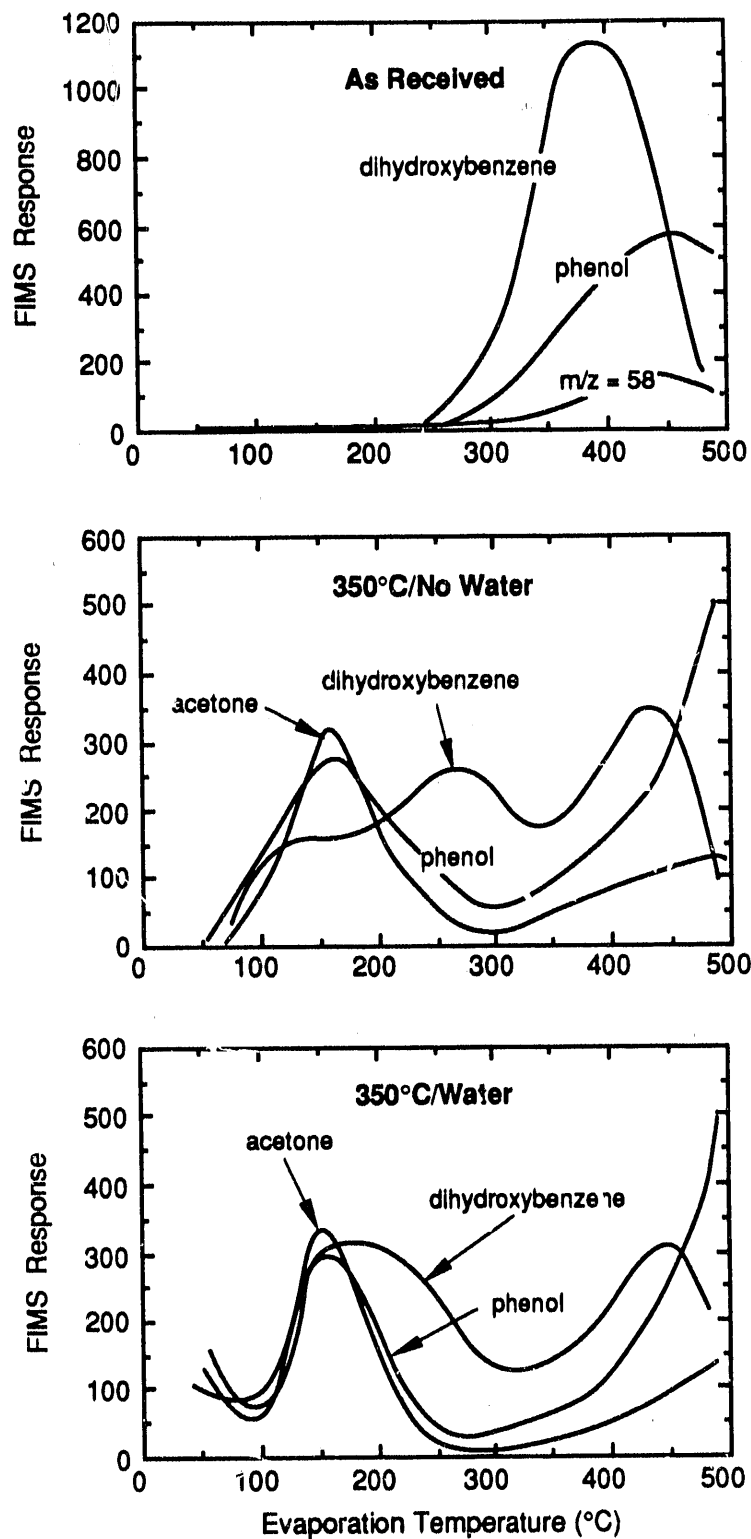
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Figure 4. FIMS difference spectrum representing [hydrothermally treated] *minus* [thermally treated] for the volatiles evolved from ambient to 500°C.

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Figure 5. FIMS-derived profiles for acetone, phenol, and dihydroxybenzene for runs at 350°C. The dihydroxybenzene is primarily catechol.

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almost solely in the pyrolysis region, and dihydroxybenzene (most likely, catechol) is the most prominent product, with its production peaking at around 400°C. Both the thermal and hydrothermal treatments shift the production of all three materials to lower temperatures, but the presence of added water does not appear to affect the phenol and acetone release. The addition of water clearly affects dihydroxybenzene evolution, however, moving it to lower temperatures.

The assignments in the figure are probably satisfactory to py-FIMS temperatures up to 300°C and for m/z = 90 and 110 perhaps all the way to 500°C. However m/z = 58 above 300°C probably represents butane rather than acetone, although as the figure shows it is not significant in that region. It is prominent, however, at lower temperatures for the thermally and hydrothermally treated coal, its peaking coinciding closely to that for phenol. Given that all three compounds are volatile, it is surprising that the maximum in their lower temperature evolution falls at around 140°C. For the hydrothermally treated coal, there is some immediate evolution, which then declines, and we assign this behavior to some material fully released by the water and thus simply "sitting" on coal and readily pumped into the FIMS instrument. However, the delayed, common peaking temperature for much of the phenol, dihydroxybenzene, and acetone suggests that they are present together in a nonvolatile, complexed form generated in initial thermal or hydrothermal treatment. We expect to continue work in this system to develop a better understanding of the sources of these materials.

Treatment at 250°C. Just as for the 350° work, treatment at 250°C promoted the production of coal tar, albeit at a lower level. The fact that tar was produced with treatment at a temperature below the pyrolysis region is another reflection of the specific action of water in the treatment. However, there were significant differences between the 350° and 250° results. First, as shown in Figure 6, the phenols and benzenediols for the treated coal emerge fully in the pyrolysis region, and no acetone is seen. In this regard the treated coal acts like the as-received coal, and the result is not surprising since from the 350° work we learned that the phenols and acetone were pyrolytically produced. (in la Fire ?)

Second, several prominent peaks appear in the FIMS of the tars of the treated coal, but are present in neither the as-received nor the 350°-treated coal. These compounds emerge at py-FIMS temperatures around 100°C, with m/z values corresponding to the parent masses of some biomarkers. They include peaks at 234, 268, and 270 amu, which correspond respectively to retene, pristane, and ferruginol. A prominent peak also appears a m/z = 252, and we are aware of no corresponding biomarker.
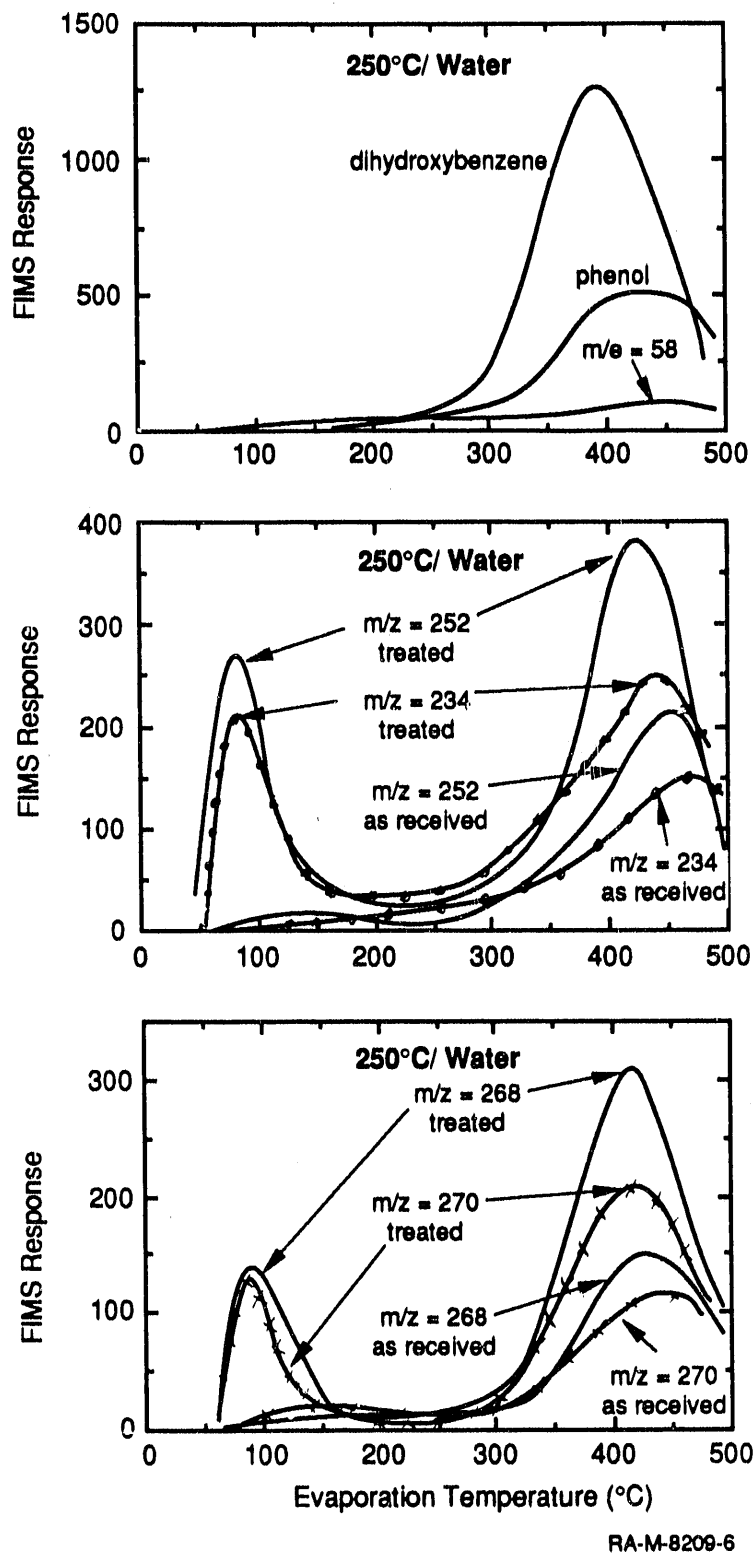
Figure 6. FIMS-derived profiles for several products from runs at 250°C. The m/z values at 234, 268, and 270 correspond to the parent masses for retene, pristane, and ferruginol, respectively.

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We emphasize that, although these parent masses correspond to the biomarkers, at present we have no additional information on the structures. However, it appears that there is some hydrolytic release of biomarkers. The mechanism of that action is of interest, particularly in the case of hydrocarbons such as retene and pristane, which have no "handles" for the action of water. The question of the role of mineral matter in these processes must be raised, including aspects of coal structure that might provide substantial and widely ranging interaction between the organic and mineral components in coal.

DISCUSSION

Our accumulated evidence thus far shows that there are both water-independent and water-promoted modes of release of tars and specific compounds. Phenols and acetone are evolved thermally at temperatures above 300°C, while hydrothermal conditions affect the dihydroxybenzene evolution. The question remains as to what features in the structure are responsible for this behavior. The production of acetone and other simple ketones may reflect the presence of some cellulose-related residue in the coal.

The water-promoted evolution of tars and biomarkers seems similar to the observations from the hydrous pyrolysis studies of oil shale. For oil shale such chemistry probably involves interfacial chemistry at the boundary joining the organic and mineral surfaces. In the case of coal, Allen and VanderSande have estimated that ultrafine mineral matter in the organic phase may represent up to 15% of the total quantity of mineral material in coal,[17] and the distribution of such a fine mineral material throughout the organic phase would lead to a significant interfacial volume. Our results may thus mirror the existence of such a volume and specific interfacial chemistry generating and/or liberating volatile materials.

Finally, a possible parallel between oil shale and coal structure leads to an interesting surmise regarding the distribution of heteroatom components in coal. The heteroatom-containing fractions of oil shale are concentrated at the mineral surfaces,[18] presumably migrating over geologic time to acid/base sites in the clays. Were such a condition to exist in coal, we would then expect a nonrandom distribution of heteroatom components, localized at the mineral inclusions within the organic phase. Such a picture of coal is considerably different from the structures commonly considered and could be significant to the processing of coal.

ACKNOWLEDGMENT

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