SRI International

DOE/PC/89880--T1

DE91 002604

SRI Report No. 8209-9 - Quarterly Report No. 3 - 14 August 1990

HYDROTHERMAL PRETREATMENT OF COAL

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Covering the Period April 16 to July 15, 1990

Prepared for:

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Received by OSTI

NOV 13 1990

Contract No. DE-AC22-89PC89880

Approved:

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ABSTRACT

We are examining the effects on composition and behavior of Argonne-supplied Wyodak coal under both thermal (no added water/N₂) and hydrothermal (*liquid* water/N₂) conditions at 350°C for periods of 30 min and 5 hr, with emphasis during this period on the longer treatment. We find that thermal treatment at both 30 min and 5 hr reduces the oxygen content of the coal by about 30%. At hydrothermal conditions the O-loss at 30 min is similar to that seen for thermal treatment, but it is reduced by another 15% after the 5 hr treatment. This result demonstrates the action of liquid water, which can hydrolyze ether groups in the coal and free phenolic functionalities which then move to the aqueous phase. In concert with this activity, the aqueous conditions promote the formation of a tar from the coal corresponding to 5-7% of the starting coal, and the shift from 30 min to 5 hr yields a tar that is more volatile and has a slightly increased molecular weight. No tar is seen at thermal conditions.

Field ionization mass spectrometry (FIMS) of the untreated, thermally treated, and hydrothermally treated coals is conducted at conditions where the samples are heated from ambient to 500°C at 2.5°/min. In the 5 hr work the volatilities of the coals are 24%, 16%, and 25% respectively, showing that the thermal treatment promotes regressive reactions, which are in turn inhibited or perhaps eliminated by the addition of the water. Other FIMS data show the thermal treatment significantly to lower the dihydroxybenzenes content of the volatiles significantly, reducing the signals by 40% and 75% in the 30 min and 5 hr runs respectively. The dihydroxybenzenes are primarily catechols, which are known to be reactive under these conditions toward condensations, and in contrast, the levels of phenols, which are far less reactive, remain about the same. At 5 hr hydrothermal conditions, both the phenols and catechols are almost fully eliminated from the FIMS volatiles, a result supporting the suggestion of hydrolysis, and in line with the increased loss of oxygen. All of this activity leads to FIMS volatiles from the hydrothermal treatment that are higher in weight average molecular weight but of comparable volatility to the volatiles from the thermal treatment.

Surprisingly, solvent swelling studies with the recovered coals do not demonstrate the expected lower degree of crosslinking in the hydrothermal case. Both the thermal and hydrothermal treatments yield products with a decreased swelling ratio, but the ratio for the product from the aqueous treatment is slightly lower than that from thermal treatment. At present we cannot reconcile this result with our other data.

INTRODUCTION

We are examining the effects of hydrothermal treatment on the structure and reactivity of Wyodak coal. The studies are conducted in small bomb reactors with Pyrex inserts, under nitrogen, and with sufficient water added to ensure the presence of liquid water at conditions. The coal is "dried" before use by holding it overnight at 1 torr and 60°C. This treatment removes 30% of the coal mass, presumably as water, and all values presented in this report are on the basis of such "dried" samples.

Initial studies at 150° and 250°C over 30 min showed that little change took place. More recent work was conducted at 350°C/30 min, and the work over the past period has focused on exhaustive treatment at 350°C/5 hr. Thermal treatment (no added water) runs are conducted routinely as controls.

The diagnostics include extensive field ionization mass spectrometry (FIMS) analysis. This procedure includes heating small, weighed samples of product at 2.5°C/min from ambient to 500°C and taking spectra of the volatiles at 20°-30° intervals.

PAST RESULTS

In our last quarterly report we discussed our results with following 350°C treatment at 30 min, and included preliminary results from some 5 hr runs (Ross, 1990). We found that both thermal and hydrothermal treatments decreased the oxygen content by around 30%, due primarily to the thermally promoted loss of carbon dioxide and water. A tar was deposited on the insert walls representing 5-7% of the starting coal solely under hydrothermal conditions; at thermal conditions no tar was observed. The recovered coals from hydrothermal runs provided FIMS volatiles, representing around 25% of the coals samples, that were at the same time more volatile and of a higher weight average molecular weight than those from the thermal treatment. They were composed thus of less polar components.

A prominent result involve phenols and catechols, which are conspicuous products in the FIMS volatiles.* We found that 30 min hydrothermal treatment reduced the quantities of both in the FIMS volatiles by 30-40%. Phenols and catechols (along with smaller quantities of resorcinols, hydroquinones, and simple ketones) were identified

* The major components were the areneols, and their respective C₁, C₂, and C₃ derivatives.

qualitatively in the recovered water from the runs, and we presume they are lost by hydrolysis and solubility in the aqueous phase.

However under thermal conditions we found the phenols and catechols to behave differently from each other. While the catechols were reduced in content to about the same degree they were in the hydrothermal treatment, the phenolic component of the FIMS volatiles was essentially not effected by the treatment. The catechol loss may reflect the action of acid catalyzed condensation chemistry specific to arenediols as described recently by Stein, et al. (1989). This mode of reaction is significant, since it likely a key element in the crosslinking chemistry prominent in lower rank coals, and is tested for in work described below.

CURRENT RESULTS

FIMS, Phenols and Catechols

If hydrolytic release and condensations of reactive areneols respectively in hydrothermal and thermal treatment were significant, we would expect to find a lower O-content in the former. However as we noted above, the reductions in O-levels were similar for the two treatments. We have surmised that the FIMS results reflect a trend in the O-functionality that could be enhanced at longer reaction periods, and accordingly over this period we focused on the effects of exhaustive (5 hr) aqueous treatment. The oxygen contents of the recovered coals are shown in Figure 1, and the results support this view.

Figure 1. O/C ratios for treated Wyodak coal.

Thermal treatment yields a product with a 30% drop in oxygen, i.e. with no change relative to the 30 min treatment. The hydrothermal treatment, however, yielded a coal product with an additional decrease in total oxygen of about 15%. Over the extended treatment, therefore, water promotes removal of O-components beyond the point where carbon dioxide and water are thermally released. The result is a substantial difference in the behavior of the recovered coals, as shown in other data discussed below.

Some of that difference is reflected in the volatilities of the starting and product coals in FIMS runs. The total volatilities for the untreated, thermally treated, and hydrothermally treated respectively were 24%, 16%, and 25%. The thermal treatment thus substantially reduced the volatility, while the presence of water appears to check the decline. There is more taking place, however, as shown in Figure 2, which presents volatility profiles for the three cases.

The profile for the hydrothermal case increases monotonically throughout the temperature range, behavior anticipated for simple evaporation of volatile material, and little if any thermolytic cracking. The thermally treated coal on the other hand yields a sigmoidal profile, revealing very little volatility up to 350°C, at which point the organic phase in the coal begins to undergo thermolytic decomposition. The profile for the thermal treatment indeed falls below the sigmoid for the untreated coal, the gap reflecting the action of thermally promoted condensation chemistry consuming the sources of the 350°C+ volatiles in the untreated coal.

This behavior is seen again in Figure 3, which presents the weight average molecular weight ($\bar{M}_w$) of the FIMS volatiles from the thermally and hydrothermally treated samples. The thermal case shows a downturn in $\bar{M}_w$ at 350-400°C, representing the emergence of significant thermal fragmentation. However in the hydrothermal case $\bar{M}_w$ continues to climb to temperatures approaching 500°C, again, consistent with simple evaporation, although there appears to be some thermolytic action, beginning at around 480°C. It is also significant that the volatiles from the hydrothermal case are consistently more volatile, while at the same time they are of a comparable molecular weight. (The respective overall $\bar{M}_w$ values for the thermal and hydrothermal cases are 308 and 333 amu.) The hydrothermal volatiles are thus composed of less polar material.

It therefore appears that water assists in the removal of polar functionalities in the coal which otherwise would thermally condense and increase the crosslink density. Likely sites for hydrolysis are the phenol and catechol ethers and perhaps other oxygen functionalities. Such action is demonstrated in Figure 4, which shows the FIMS responses

Figure 2. Volatilities of untreated, thermally treated and hydrothermally treated coal. The data are derived from the FIMS record.

Figure 3. Weight average molecular weights for thermally and hydrothermally treated coal.

Figure 4. FIMS-generated profiles for phenol ($m/e = 94$) and catechol ($m/e = 110$)

vs temperature for phenol (94 amu) and catechol (110 amu) for the untreated coal, and for the products from 30 min and 5 hr runs. The profiles in the figure are representative of those for the respective C₁, C₂, and C₃ derivatives as well.

The untreated coal evolves neither phenol nor catechol below around 300°C, while above that temperature they are generated by thermolytic scission of portions of the organic matrix, and/or thermally desorbed from the mineral phase. Thermal treatment alters the phenol response somewhat, with a small portion of the phenol evolution shifted to temperatures around 150°C. However, there is little change in increasing the treatment period from 30 min to 5 hr. The bulk of the phenol precursors remain after that period, and as for the untreated case, it is released in the thermolytic region above 300°C. For catechol the results are dramatically different. In this case the thermal treatment lowers the response considerably, with the 30 min treatment eliminating about 40% of the catechol signal, while the 5 hr treatment eliminates about 75%. It is notable, however, that even after 5 hr the remaining 25% emerges in the thermolytic region.

Next, for hydrothermal treatment, the figure shows that treatment for 30 min seems to do little that is different from the thermal treatment. However the results for the 5 hr exposures are striking. The treatment appears to eliminate virtually all of the thermal sources of phenol and catechol (and their alkyl derivatives), apparently "stripping" the coal the coal of these materials.

But there is an important distinction to be made between the thermal and hydrothermal results for catechol. In the thermal case the 5 hr treatment eliminates the major fraction of the catechol signal; however the O-content of the coal remains virtually unchanged. We interpret the reduction in the signal to be due to thermally promoted condensation of the catechols or their sources, rather than material loss to the aqueous medium. On the other hand the pointed reduction in phenol and catechol response after the 5 hr hydrothermal treatment coincides with an additional loss of oxygen. Thus we conclude that in the latter case we are observing hydrolysis of the ether precursors to the areneols, and their subsequent removal in the aqueous medium.

The "stripping" of the coal in the 5 hr treatment is striking appears to go beyond the areneols. Figure 5A shows profiles derived from FIMS data from the 5 hr samples for m/z 58; the mass corresponds to acetone at the lower temperatures, and most likely butane at the higher. For the untreated and thermally treated coal, butane emerges in the 350+°C range as a product of thermal degradation, while added water virtually fully eliminates its source.

Figure 5. A. Profiles for $m/e = 58$. The peak corresponds to acetone at lower temperatures, and most likely to butane above 250°C.

B. Profiles for the sum of the responses for $m/e = 56, 70, \text{ and } 84$, corresponding to propylene, butene, and pentene.

Acetone is a significant product from the hydrothermally treated coal; its origin remains to be identified, although lignin pyrolysis is known to produce acetone.

Similar results are shown in 5B for the C₄, C₅, and C₆ olefins at m/e values 56, 70, and 86. They are prominent as thermolytic products for both the untreated and thermally treated coal. But the pretreatment with water eliminates the source almost completely. This result is notably similar to that in several accounts on oil shale pyrolysis, where olefin levels are substantially reduced by the addition of water (Lewan, et al., 1981; Hoering, 1984). We presume this action is due to the removal by water of the carboxylic acids in the coal.

Extractions and Solvent Swelling

With these results in hand we conducted extraction and solvent swelling experiments. We anticipated that the swelling results would support the view that hydrothermal treatment lowered the degree of thermally promoted crosslinking. As shown here, however, that expectation was not realized. The extraction solvents were pyridine and toluene, and the solvent swelling was done with pyridine.

Our data are presented in Figure 6. The extractions in the hydrothermal cases were performed on the recovered coal, *not* including the tar that we have reported to be deposited on the reactor walls. The tar represented 5-7% of the starting coal, and about 30% of it was toluene soluble. For the pyridine extractions in 6A the figure shows that both thermal and hydrothermal treatment modestly increase the extractability after 30 min of treatment. A similar increase is seen for the 5 hr hydrothermal treatment product; the data for the thermal control run are forthcoming. For the 30 min case the presence of added water provided a small, apparent increase in extraction yield, and if the tar were included in the tabulation the difference would be moderately greater.

The results for the toluene extractions in 6B are somewhat more revealing, although it must be acknowledged that the values themselves are small. There is clearly an increase in the extraction yield following both 30 min thermal and hydrothermal treatment, and like for the pyridine case the presence of added water increased the yield even more. For the 5 hr runs there is a decrease in yield for both the dry and water-added pretreatment, consistent with unfavorable, thermally promoted condensations. However the decrease in the thermal pretreatment case brings the extraction yield to below that for the starting coal. The result for the hydrothermal pretreatment in contrast is still greater than the starting

Figure 6. Data from solvent extraction and swelling determinations.

A. Pyridine extraction of coal and coal products.

B. Toluene extraction of coal and coal products.

C. Solvent swelling (pyridine) of coal and coal products.

value. As stated above, the absolute values here are small; nonetheless the data at present are consistent with the curbing of undesirable thermal reactions by added water.

That picture becomes clouded, however, with attention to our solvent swelling results in 6C. Here we seen that the thermal treatment decreased the swelling ratio in a response similar to that seen by Deshpande et al.(1988), and since the 30 min and 5 hr treatments gave similar values, it appears that the reactions responsible for the reduced swelling are rapid and completed within the shorter heating period. However the results for the hydrothermal treatment were a surprise. That treatment reduced the ratio even further, as shown in the figure. This result suggests that the presence of added water increases the crosslinking rate during the treatment, a conclusion at odds with the extraction results, and moreover quite inconsistent with our picture of coal and coal reactivity developed with the data collected in this program thus far.

At present we have no satisfying explanation for these findings. We anticipate running conversion runs during the next period, and expect that those data will help clarify the situation.

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