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"FUNDAMENTAL STUDIES OF WATER PRETREATMENT OF COAL"

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ABSTRACT

During the past year, a set of water pretreatment experiments was completed on four different coals (Zap, Wyodak, Illinois No. 6, and Pittsburgh No. 8) under two different ranges of conditions (very short and very long pretreatment times). Additional water pretreatment experiments were done with Illinois No. 6 and Pittsburgh seam bituminous coals at selected intermediate points to cover the range of pretreatment behavior. The objective of this work was twofold: 1) to determine how bituminous coals behave during water pretreatment under similar conditions: 2) to verify the effects of water pretreatment on liquefaction yields, which previously have been shown to be different than expectations, i.e, the conditions which give the highest pyrolysis tar yield relative to the raw coal (short pretreatment times) give the lowest liquefaction yields relative to the raw coal and vice versa.

The residues from the steam pretreatment experiments with the four coals were subjected to analysis by TG-FTIR, FT-IR, SEM/x-ray solvent extraction and solvent swelling, along with liquefaction experiments in a donor solvent. The results for pyrolysis tar yields show a sharp maximum for the low rank coals (Zap, Wyodak) at short times (20 minutes) with a gradual decrease at longer times ($\geq$300 minutes) when compared to the raw coal. It was found that, for bituminous coals, the tar yield generally follows a similar trend with increasing pretreatment time, although, on a relative basis the maximum is not as sharp and occurs at longer times. The set of data on pyridine extractables is less complete but indicates that for three of the coals (Zap, Wyodak, Illinois) the yield increases at relatively short pretreatment times (by as much as a factor of two) and gradually declines at longer pretreatment times, thus following the same general trend as the tar yield. In the case of the Illinois coal, pretreatment for 20 minutes resulted in a more than doubling of the % DAF pyridine extractables (81 vs. 36%). The liquefaction results for the two low rank coals indicated significant reductions at short pretreatment times, particularly for the Zap lignite, in the yields of toluene and pyridine sol bles when compared to results for the raw coal. The liquefaction yields for the low rank coa s improved at longer pretreatment times but were generally not as high as for the untreated coal. Conversely, improved or similar yields of oils and toluene solubles are observed for selected pretreatment experiments with Illinois and Pittsburgh coals. However, these results could not be reproduced consistently with Illinois coal. It appeared that the results were sensitive to the "freshness" of the coal. For ampoules which were just opened, the yields of soluble products from the pretreated coals were lower than for samples which had been opened days or weeks earlier and stored in a nitrogen purged glove box.

This hypothesis was tested by doing controlled oxidation experiments on raw and pretreated coals. The results indicate that mild oxidation of a water pretreated Illinois coal gives an increased yield of toluene solubles and oils from liquefaction of the residue and that the values are generally higher than from liquefaction of the raw coal. Similar results are observed for mild oxidation of a water pretreatment residue from Zap lignite. Consequently, these results are consistent with the hypothesis that ortho dihydroxy functionalities created by water pretreatment are responsible for the retrogressive solvent incorporation reactions which artificially reduce the liquefaction yields. This conclusion is based on the fact that the mild oxidation should remove the dihydroxy functionalities.

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SECOND ANNUAL REPORT
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I. INTRODUCTION AND SUMMARY

Introduction

The goals of this project are to gain an understanding of the chemistry of water or steam coal pretreatments and to assess the importance of such pretreatments on subsequent coal liquefaction. For the achievement of these goals, coals, modified coals and model-polymers will be treated with water or steam. This study will include three coals, five modifications (dried, demineralized, ion-exchanged, Ca-loaded, Ba-loaded), three polymers and two polymer modifications (e.g. acid chlorides, amides). Experiments will be performed to investigate both conventional steam pretreatment and the possibility of using the CO/H_2O system of Ross and coworkers as a pretreatment method. The main experimental variables will be sample type and temperature. Detailed characterization of the gas, liquid and solid products from the pretreatment stage will be done. This will include analysis of gases by GC or FT-IR, liquids by capillary GC, FT-IR and FIMS, and residues by solvent swelling, solvent extraction, and elemental analysis. Selected residues will also be evaluated by a standard liquefaction test. Analysis of the raw coals and pretreatment samples will be performed using the above techniques to study changes in the crosslinking, donatable hydrogen, heteroatom composition, evolved gases, functional group composition, extraction yields, molecular weight distributions, etc. Standard tubing bomb liquefaction tests will be used to determine the effect of pretreatment on coal reactivity toward coal liquefaction. A previously developed model for coal liquefaction, the FG-DVC liquefaction model, will be used (after appropriate modifications) to model the physics and chemistry of water pretreatment.

Summary of Work During the Second Year

Task 2 - Pretreatment Experiments - A set of water pretreatment experiments was completed on four different coals (Zap, Wyodak, Illinois No. 6, and Pittsburgh No. 8) under two different ranges of conditions. The first condition was at 350°C, 4000 psig, 20-60 minutes, where maximum tar yields have been observed upon subsequent pyrolysis, but where liquefaction yields were generally lower than for the raw coal. The second condition was at 350°C, 4000 psig, 300-1200 minutes, where pyrolysis tar yields are typically reduced to close to the values for the raw coal, but where liquefaction yields are improved. These two extreme conditions were

established based on work done on the Zap lignite and Wyodak subbituminous coals. Additional water pretreatment experiments were done with Illinois No. 6 and Pittsburgh seam bituminous coals at selected intermediate points to cover the range of pretreatment behavior. The objective of this work was twofold: 1) to determine how bituminous coals behave during water pretreatment under similar conditions: 2) to verify the effects of water pretreatment on liquefaction yields, which previously have been shown to be different than expectations, i.e, the conditions which give the highest pyrolysis tar yield relative to the raw coal give the lowest liquefaction yields relative to the raw coal (short pretreatment times) and vice versa.

Additional experiments were done to investigate the effects of lower pretreatment pressures and variations in the mode of water injection. These variations included early H_2O injection (injection of water prior to heat up of the sample) and continuous injection and removal of H_2O. The latter capability is important in light of recent work by Michael Siskin and coworkers with model compounds which suggest that the initial reaction of water with organics produces compounds (e.g., formaldehyde) which act as reducing agents in subsequent reactions (Siskin and Katritzky, 1991).

Experiments were also done with demineralized coals and coals in which mild oxidation was carried out either before or after water pretreatment. The mild oxidation tests were done to see whether these treatments would remove the dihydroxy functionalities that are believed to be responsible for the retrogressive solvent incorporation reactions which reduce the observed yields from liquefaction of water pretreated coals. In the first case, the dihydroxy compounds which are formed during the water pretreatment process would be removed. In the second case, the phenolic precursors to these compounds would be removed.

Task 3 - Analysis of Products - The residues from the steam pretreatment experiments with the four coals were subjected to analysis by TG-FTIR, solvent extraction and solvent swelling, along with liquefaction experiments in a donor solvent. **The results for pyrolysis tar yields show a sharp maximum for the low rank coals (Zap, Wyodak) at short times (20 minutes) with a gradual decrease at longer times ($\geq$300 minutes) when compared to the raw coal.** It was found that, for bituminous coals, the tar yield generally follows a similar trend with increasing pretreatment time, although, on a relative basis the maximum is not as sharp and occurs at longer times.

The set of data on pyridine extractables is less complete but indicates that for three of the coals (Zap, Wyodak, Illinois) the yield increases at relatively short pretreatment times (by as much as a factor of two) and gradually declines at longer pretreatment times, thus following the same general trend as the tar yield. **In the case of the Illinois coal, pretreatment for 20 minutes resulted in a more than doubling of the % DAF pyridine extractables (81 vs. 36%).**

The liquefaction results for the two low rank coals indicated significant reductions at short pretreatment times, particularly for the Zap lignite, in the yields of toluene and pyridine solubles. The liquefaction yields for the low rank coals improved at longer pretreatment times but were generally not as high as for the untreated coal. **Conversely, improved or similar yields of oils and toluene solubles are observed for selected pretreatment experiments with Illinois and Pittsburgh coals. However, these results could not be reproduced consistently with Illinois coal. It appeared that the results were sensitive to the "freshness" of the coal.** For ampoules which were just opened, the yields of soluble products from the pretreated coals were lower than for samples which had been opened days or weeks earlier and stored in a nitrogen purged glove box. The results are consistent with the fact that the pretreated samples are reacting with the liquefaction solvent, especially the observation of negative oil yields. The very fresh samples appear to be the most reactive toward solvent adduction. This same phenomenon may explain why the liquefaction yields for the pretreated Zap and Wyodak coals go through a minimum at short pretreatment times, and are generally less than for the raw coals.

This hypothesis was tested by doing controlled oxidation experiments on raw and pretreated coals. **The results indicate that mild oxidation of a water pretreated Illinois coal gives an increased yield of toluene solubles and oils from liquefaction of the residue and that the values are generally higher than from liquefaction of the raw coal.** Similar results are observed for mild oxidation of a water pretreatment residue from Zap lignite. Consequently, these results are consistent with the hypothesis that ortho dihydroxy functionalities created by water pretreatment are responsible for the retrogressive solvent incorporation reactions which artificially reduce the liquefaction yields. This conclusion is based on the fact that the mild oxidation should remove the dihydroxy functionalities.

With respect to the effects of pressure, The results to date suggest that the process is not as sensitive to pressure at short pretreatment times, but is at longer pretreatment times where liquefaction is concerned. In the case of experiments with changes in the method of water

injection, one of the more interesting results is that the amount of CO_2 evolved during the water pretreatment step was significantly higher with continuous water injection for the Zap lignite. This suggests that the formation of CO_2 may be limited by equilibrium under these conditions. The fact that continuous H_2O injection gives different results for water pretreatment of Zap and Illinois is supportive of the conclusion Siskin and Katritzky (1991) that a set series of sequential reactions is involved. By injecting water continuously (and removing products continuously), some important intermediates may be lost.

The pyrolysis and liquefaction results for the demineralized residues suggest that demineralization is beneficial prior to water pretreatment of Zap lignite but not for Illinois No. 6 coal. In the latter case, a problem with demineralization is that it is difficult to prevent partial oxidation of the coal during this procedure.

The pyrolysis results for the Zap and Illinois blank experiments do indicate that the presence of added water is important, as the tar yields do not increase significantly without water being present. This was not the case for the Wyodak coal, where the tar yields were comparable. However, the Wyodak does have a high moisture content so the intrinsic moisture content or the pyrolysis water may be providing the water function. Additional blanks will be done with dried coals to address this question.

FT-IR analyses were done of water pretreated residues from all four coals. For all of the coals, except Pittsburgh, pretreatment led to a monotonic decline in the oxygen content. For all four coals, the concentration of phenolic OH declined with pretreatment. The trends for hydrogen functional groups appeared to vary with coal type. For the two low rank coals (Zap, Wyodak), pretreatment increased the fraction of aromatic hydrogen, while for the two high rank coals (Illinois, Pittsburgh), this fraction was decreased. The contrast between the behavior of the Zap and Illinois coals is especially striking in this regard. For the two low rank coals, the amount of aliphatic hydrogen (H_{al}) goes through a maximum with increasing pretreatment time, while for the two high rank coals, H_{al} declines steadily.

Water pretreatment residues for three of the coals (Zap, Wyodak and Illinois) were subjected to an SEM/x-ray microanalysis. For the individual ash components, the most significant trends observed with the Zap are the elimination of Na, increases in Al, Si, and Fe, and a nearly constant value of Ca.

Task 4 - Rates, Mechanisms, and Modeling - The preliminary conclusions can be summarized as follows:

1.   The analysis of pyrolysis and pyridine extractables data from water pretreated Zap lignite and Wyodak subbituminous coal (reduction in CO_2 yield, maximum in tar yield, maximum in extractables, increase in CH_4 yield) shows a strong similarity to an accelerated geological aging process. The results for the Illinois and Pittsburgh bituminous coals were similar though less dramatic, except for the extractables yields.

2.   The geological aging analogy is also consistent with results that were obtained in the literature on steam or water pretreatment, since it explains why the treatment is effective in increasing pyrolysis yields for low rank coals and is ineffective or reduces pyrolysis yields for high rank coals. However, there are certain trends, such as the fact that the CO yield appears to follow the tar yield (goes through a maximum along with the tar) and the extractables yields (which does not have a clear trend in most cases), which do not agree completely with this analogy.

3.   The changes due to water pretreatment are delayed and attenuated as the pretreatment temperature is reduced.

4.   The changes in the mineral composition due to water pretreatment are highly mineral specific.

5.   The FT-IR data indicate a general reduction of oxygen groups during water pretreatment, including hydroxyl groups.

6.   The results from liquefaction experiments on samples produced to date indicate only modest benefits in the best cases. The worst results are obtained at short pretreatment times where solvent incorporation into the coal is apparently reducing the observed yields of soluble products.

7.   The data are consistent with a mechanism in which water pretreatment increases the concentration of ortho dihydroxy species in the coal at short pretreatment times. These functions are believed to be responsible for the solvent incorporation reactions. They can

be removed by increasing the pretreatment time or mild oxidation of the coal after water pretreatment.

II. TASK 1 - PROJECT PLANNING AND SAMPLE SELECTION

This task has been completed.

III. TASK 2 - EXPERIMENTS ON THE WATER PRETREATMENT STAGE

Experiments with a Range of Coals - A set of water pretreatment experiments was completed on four different coals (Zap, Wyodak, Illinois No. 6, and Pittsburgh No. 8) under two different ranges of conditions. The first condition was at 350°C, 4000 psig, 20-60 minutes, where maximum tar yields have been observed upon subsequent pyrolysis, but where liquefaction yields were generally lower than for the raw coal. The second condition was at 350°C, 4000 psig, 300-1200 minutes, where pyrolysis tar yields are typically reduced to close to the values for the raw coal, but where liquefaction yields are improved. These two extreme conditions were established based on work done on the Zap lignite and Wyodak subbituminous coals. Additional water pretreatment experiments were done with Illinois No. 6 and Pittsburgh seam bituminous coals at selected intermediate points to cover the range of pretreatment behavior. The objective of this work was twofold: 1) to determine how bituminous coals behave during water pretreatment under similar conditions: 2) to verify the effects of water pretreatment on liquefaction yields, which previously have been shown to be different than expectations, i.e, the conditions which give the highest pyrolysis tar yield relative to the raw coal give the lowest liquefaction yields relative to the raw coal (short pretreatment times) and vice versa.

Low Pressure Experiments - A set of water pretreatment experiments was done at 350°C, for 20 minutes or 180 minutes and 1,000 - 2,000 psig instead of 4,000 psig with the Wyodak subbituminous coal. This was done to study the effects of water pretreatment under lower pressure conditions which were more common in previous studies (Graff and Brandes, 1986, 1987; Khan, et al., 1989). Additional low pressure (1000 psig) water pretreatment experiments were done with the Illinois coal at 350°C, 180 minutes. These were done in order to study the effects of water pretreatment under lower pressure conditions which were more common in previous studies (Graff and Brandes, 1986, 1987; Khan et al., 1989).

Early H_2O Injection - In the standard pretreatment experiments, ~1 ml of water is added at the beginning and then the sample is immersed in the fluidized sand bath for rapid heating to the final pretreatment temperature, during which water is pumped continuously until a volume corresponding to the desired final pressure has been injected (Case 1). For example, to achieve 4000 psig at 350°C, ~15 ml of water is pumped into the system. A concern was raised that the samples may be heated through the active crosslinking period (200-350°C) without the full water

pressure being exerted. Consequently, the experiment was modified so that the full 15 ml is injected at the very beginning prior to the heatup period (Case 2). Experiments were done for both Zap and Illinois coals using this modified procedure.

Continuous H₂O Injection - The water pretreatment system was modified to allow the water to be injected (and removed) continuously during the pretreatment process (Case 3). This capability is important in light of recent work by Michael Siskin and coworkers with model compounds which suggest that the initial reaction of water with organics produces compounds (e.g., formaldehyde) which act as reducing agents in subsequent reactions (Siskin and Katritzky, 1991). A second motivation was that reactivity tests were being done on the residues from water pretreatment to test the hypothesis of geological aging (more mature coals are less reactive). It was thought that the water soluble material may deposit on the surface of the residue and obscure these results. The continuous water extraction experiments were done with Zap, Illinois and Pittsburgh coals at conditions of 350°C, 4000 psig, 60-180 minutes pretreatment time.

Demineralized Coals - Water pretreatment experiments were done with demineralized Zap, Wyodak and Illinois coals. The demineralized coals were prepared using the procedure of Bishop and Ward (1958), which involves treatment with HCl and HF. The pretreatment experiments were done at the following conditions: 350°C; 4000 psig; 20, 60 or 120 minutes.

Blank Experiments - A set of blank experiments was done with all four coals in helium at the following conditions: 350°C; 4000 psig; 20 minutes. An additional experiment was done with the Zap lignite at atmospheric pressure. Helium was used instead of nitrogen since it can be obtained in highly pure grades. The purpose of the blank experiments is to determine how much of the water pretreatment process is a thermal and/or pressure effort. Of course, since the coals contain moisture, it is difficult to rule out the effect of H₂O on the basis of these blank experiments. A second series of experiments will be done where the coal is dried "in-situ" prior to the helium pretreatments. However, even this is not definitive for low rank coals since water is formed from pyrolysis reactions under the standard pretreatment temperatures (~350°C).

Mild Oxidation Experiments - A series of experiments was done on fresh samples of Illinois No. 6 coal and Zap lignite in which water pretreated residues were subjected to mild oxidation with 0.003-1M solutions of hydrogen peroxide (H₂O₂). A second series of tests was done with Illinois No. 6 coals where only the mild oxidation was carried out, or else it was done prior to

water pretreatment. The mild oxidation tests were done to see whether these treatments would remove the dihydroxy functionalities that are believed to be responsible for the retrogressive solvent incorporation reactions which reduce the observed yields from liquefaction of water pretreated coals. In the first case, the dihydroxy compounds which are formed during the water pretreatment process would be removed. In the second case, the phenolic precursors to these compounds would be removed.

In the case of the Illinois No. 6 coal, it was thought that the mild oxidation may have a deleterious effect on the catalytic activity of the pyrite. Consequently, a third type of experiment was done where a sample was subjected to mild oxidation and then liquefied in the presence of H_2S to maintain the pyrite activity.

IV. TASK 3 - ANALYSIS OF PRODUCTS

Experiments with a Range of Coals - The residues from the steam pretreatment experiments with the four coals were subjected to analysis by TG-FTIR, solvent extraction and solvent swelling, along with liquefaction experiments in a donor solvent. Selected results are summarized in Table IV-1. **The results for pyrolysis tar yields show a sharp maximum for the low rank coals (Zap, Wyodak) at short times (20 minutes) with a gradual decrease at longer times ($\geq$ 300 minutes) when compared to the raw coal.** It was found that, for bituminous coals, the tar yield generally follows a similar trend with increasing pretreatment time, although, on a relative basis the maximum is not as sharp and occurs at longer times.

Some results from TG-FTIR analysis of water pretreated Wyodak subbituminous coal are shown in Figure IV-1. This figure includes results for the balance curve, tar evolution and CO_2 evolution from raw, water pretreated (350°C), 4000 psig, 20 min.) and demineralized Wyodak coal, respectively. Both the water pretreated coal and the demineralized coal show a significant increase in tar and a reduction in CO_2 evolution where compared to the raw coal.

In a separate study (Contract No. DE-FG05-90ER80887) samples of the three Wyodak coals pyrolyzed at low heating rates in the TG-FTIR (results shown in Fig. IV-1) were also pyrolyzed at high heating rates ($\sim$ 5000 °C/sec) in an entrained flow reactor. The results for t' e yields of tar plus light hydrocarbon gases are plotted in Figs. IV-2 along with the TG-FTIR results. It can be seen that the differences in tar yields due to water pretreatment or demineralization are even more pronounced at high heating rates.

The set of data on pyridine extractables is less complete but indicates that for three of the coals (Zap, Wyodak, Illinois) the yield increases at relatively short pretreatment times (by as much as a factor of two) and gradually declines at longer pretreatment times, thus following the same general trend as the tar yield. This conclusion is based on some additional data for Zap and Wyodak which are not shown in Table IV-1. The expanded set of data for the Illinois coal is quite clear with regard to this trend. **In the case of the Illinois coal, pretreatment for 20 minutes resulted in a more than doubling of the % DAF pyridine extractables (81 vs. 36%).** The results were lower when an ampoule of Illinois coal was used which was not freshly opened (75 vs. 81%). The results to date indicate that of the four coals examined (Zap, Wyodak, Illinois,

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TABLE IV-1

COMPARISON OF PYROLYSIS TAR, EXTRACTABLES, AND LIQUEFACTION YIELDS
FOR FOUR COALS WHICH HAVE UNDERGONE WATER PRETREATMENT

Coal	Run Number	Experimental Conditions			Pyrolysis Results (norm. wt%)			Pyridine Extractables		Liquefaction Yields (DAF wt.%)		
		Temp (°C)	Press (psig)	Time (min.)	Tar	CO$_2$	CH$_4$	Norm. wt.%	Dry DAF %	Oils	Toluene Solubles	Pyridine Solubles
Zap	1001	—	—	—	6	4.8	1.1	9	5	14	36	44
	6	350	4000	20	12	3.3	1.5	8		12	18	21
	26	350	4000	600	10	2.1	1.6	3		7	35	50
Wyodak	1003	—	—	—	9	6.1	1.5	11	11	15	41	65
	23	350	4000	20	13	3.9	1.9			18	35	53
	25	350	4000	600	8	1.8	2.1	8		10	30	54
Illinois	1005*	—	—	—	29	0.9	2.2	33	36	17	47	98
	36	350	4000	20	31	0.7	2.1		75	1	47	86
	66*	350	4000	20	34	0.7	2.4		81	-13	11	58
	37	350	4000	60	27	1.1	2.4		79	39	59	93
	60*	350	4000	60	20	0.5	1.8		76	-27	40	90
	48	350	4000	300	22	0.5	1.3		45	17	41	86
	68*	350	4000	300	23	1.2	2.9		40	14	35	50
	45	350	4000	1080	17	0.7	2.2		32	11	29	40
Pittsburgh	39	—	—	—	23	2.6	3.7	23	28	4	24	90
	38	350	4000	20	21	0.7	3.0		44	3	31	82
	42	350	4000	180	26	0.7	2.8		44	10	26	85
	56	350	4000	1200	24	2.1	4.3		63	14	37	58
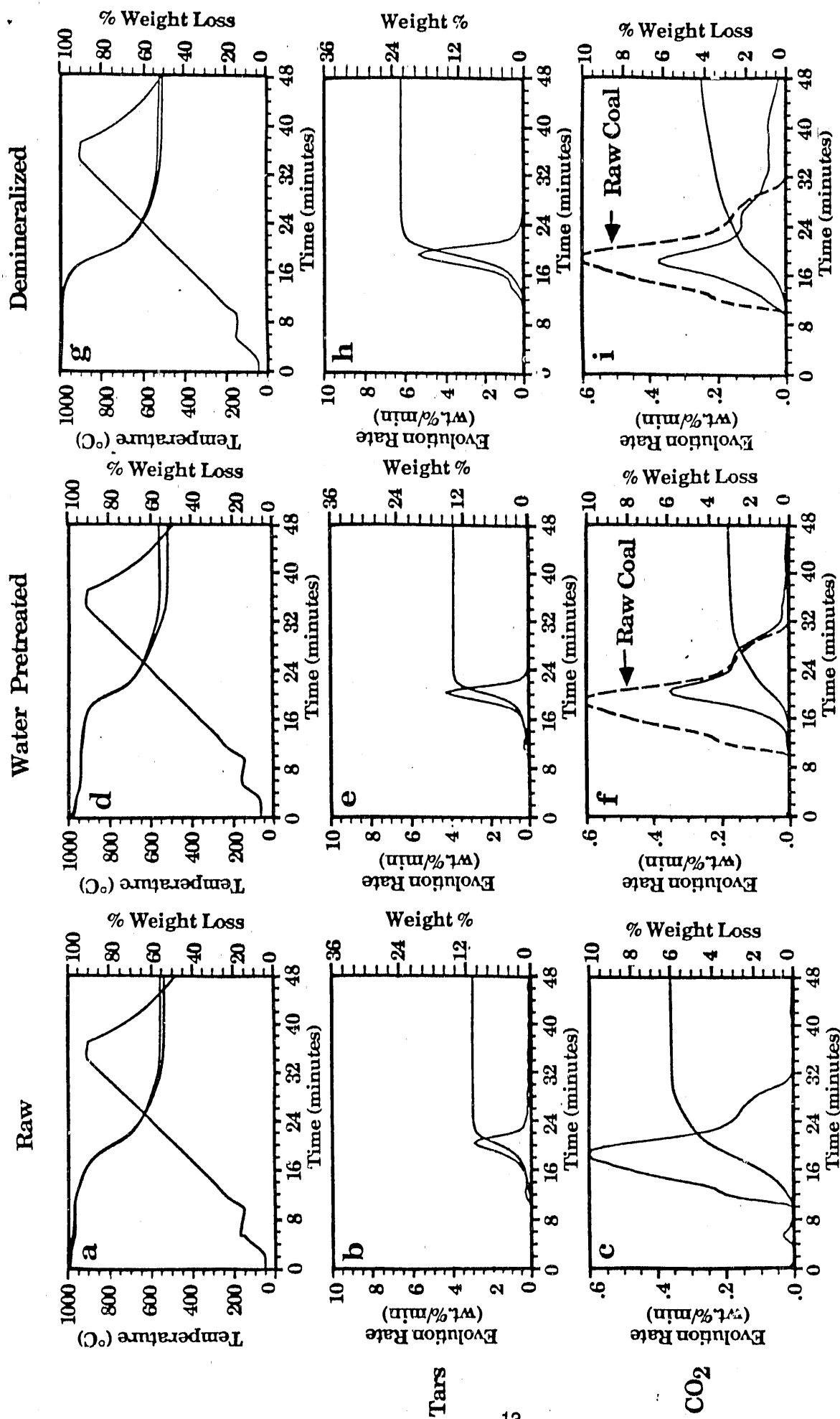
Figure IV-1. Product Evolution Curves for Raw, Water Pretreated and Demineralized Wyodak Subbituminous Coal. a, d, g) Weight Loss and Temperature Profile; b, e, h) Tars Evolution and Weight Loss; c, f, i) CO_2 Evolution and Weight Loss. Raw Coal Evolution Curve is Indicated in (f) and (i) as a Dashed Line for Comparison.
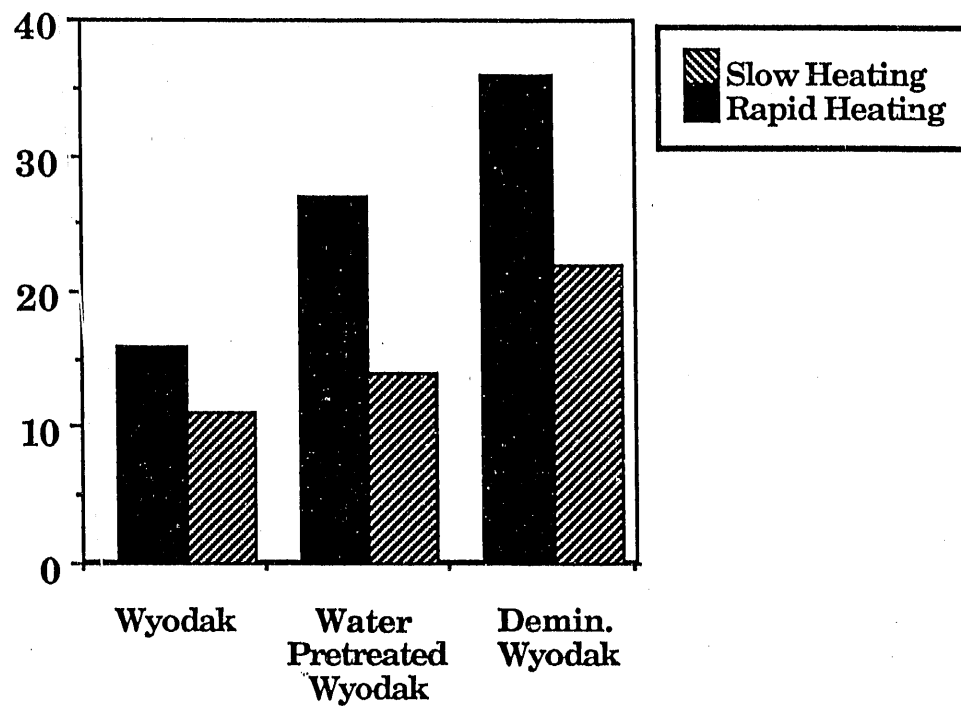
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Figure IV-2. Yields of Liquids Plus High BTU Fuel Gas from Low Heating Rate (TG-FTIR) and High Heating Rate (HTR) Pyrolysis of Coal.

Pittsburgh), the Illinois coal is the most sensitive to coal freshness. For the Pittsburgh coal, the pyridine extractables increase slowly with increasing pretreatment time.

The liquefaction results for the two low rank coals indicated significant reductions at short pretreatment times, particularly for the Zap lignite, in the yields of toluene and pyridine solubles (see Table IV-1). The liquefaction yields for the low rank coals improved at longer pretreatment times but were generally not as high as for the untreated coal. **Conversely, improved or similar yields of oils and toluene solubles are observed for selected pretreatment experiments with Illinois coal. However, these results could not be reproduced consistently with Illinois coal. It appeared that the results were sensitive to the "freshness" of the coal.** For ampoules which were just opened, the yields of soluble products from the pretreated coals were lower than for samples which had been opened days or weeks earlier and stored in a nitrogen purged glove box. The results are consistent with the fact that the pretreated samples are reacting with the liquefaction solvent, especially the observation of negative oil yields. The very fresh samples appear to be the most reactive toward solvent adduction. This same phenomenon may explain why the liquefaction yields for the pretreated Zap and Wyodak coals go through a minimum at short pretreatment times, and are generally less than for the raw coals. This hypothesis was tested by doing controlled oxidation experiments on raw and pretreated coals, as discussed below. **The liquefaction results for the Illinois and Pittsburgh coals are significant since these are the first indications from our own work that water pretreatment can be beneficial to yields in direct liquefaction.**

Low Pressure Experiments - The residues from the steam pretreatment experiments with Wyodak coal at lower pressures (1000-2000 psig) were subjected to analysis by TG-FTIR and liquefaction in a donor solvent. For the experiments at 20 minutes, the results from these analyses were similar to the results from the residues produced at 4,000 psig, except for a significant reduction in the amount of CO_2 released during pyrolysis. For the longer pretreatment time (180 minutes), the liquefaction yields were significantly lower. **The results to date suggest that the process is not as sensitive to pressure at short pretreatment times, but is at longer pretreatment times where liquefaction is concerned.** The reactor system was redesigned so that better control of pressure can be achieved in the low pressure experiments.

The residues from the low pressure (1000 psig) experiments with Illinois No. 6 coal were also subjected to TG-FTIR analysis (programmed pyrolysis) and donor solvent liquefaction. When

compared to results at 4000 psig, there was a slight reduction in the pyrolysis tar yield, a slight improvement in the yield of extractables, and slight improvement in yields of oils, toluene solubles and pyridine solubles from liquefaction. There was a significant reduction in the yield of toluene solubles and pyridine solubles from the lower pressure pretreatment experiment when compared to the raw coal. However, these results will have to be considered in light of the difficulty in reproducing the liquefaction results for water pretreated Illinois coals, as discussed above, and will require repetition to confirm the trends.

Early H_2O Injection - The residues from the water pretreatment experiments with Illinois and Zap coals using early H_2O injection were subjected to analysis by TG-FTIR and donor solvent liquefaction. For the Zap coal, the tar yields from pyrolysis were not much different than for the standard water pretreatment experiments under the same final temperature (350°C), pressure (4000 psig) and time (20 min., 60 min.) conditions. However, the yield of CO_2 from pyrolysis was much lower. There was a significant increase in the yields of pyridine extractables (~ factor of two) from the Zap coal pretreated with early H_2O injection. There was also a significant improvement in the yields of toluene solubles and pyridine solubles from liquefaction of the Zap coal compared to the standard pretreatment condition. However, the liquefaction results were still lower than for the raw coal.

In the case of the Illinois coal, pretreated with early H_2O injection, the pyrolysis results were similar to the standard pretreatment case except for lower CO_2 evolution, while the yields of oils and toluene solubles from liquefaction were significantly lower than for the standard pretreatment. However, the latter results must be considered in light of the difficulty in obtaining reproducible liquefaction yields for water pretreated Illinois coal.

Continuous H_2O Injection - The residues from the continuous water injection experiments with Zap, Illinois and Pittsburgh coals were subjected to analysis by TG-FTIR, solvent extraction, solvent swelling, oxygen reactivity index and donor solvent liquefaction. **One of the more interesting results is that the amount of CO_2 evolved during the water pretreatment step was significantly higher with continuous water injection for the Zap lignite.** This suggests that the formation of CO_2 may be limited by equilibrium under these conditions. In the case of Zap lignite, the amount of CO_2 produced by pyrolysis of the water pretreated residue was significantly lower than for Case 1. However, not much change was observed for Illinois or Pittsburgh.

It was also found that the oxygen reactivities of the residues produced with continuous water injection were higher. Consequently, it appears that the film of water soluble material which normally deposits on the water pretreated residues must mask the true reactivity.

With regard to pyridine extractables yields, there did not appear to be much difference for Zap, while the amounts were lower for Illinois and higher for Pittsburgh. In the case of liquefaction yields, the amounts were generally lower for Zap and Illinois and somewhat better for Pittsburgh. **The fact that continuous H_2O injection gives worse results for water pretreatment of Zap and Illinois is supportive of the conclusion Siskin and Katritzky (1991) that a set series of sequential reactions is involved.** By injecting water continuously (and removing products continuously), some important intermediates may be lost.

Demineralized Coals and Blank Experiments - The residues from the water pretreatment experiments with demineralized Zap, Wyodak and Illinois coals and the blank experiments in helium with Zap, Wyodak, Illinois and Pittsburgh coals were subjected to analysis by TG-FTIR, solvent extraction, solvent swelling, oxygen reactivity index and donor solvent liquefaction.

For demineralized Zap, the major changes were lower yields of pyrolysis CO_2, higher yields of extractables and higher yields of pyridine solubles from liquefaction at short pretreatment times (20 minutes). At long pretreatment times (1200 minutes), there is not yet a corresponding experiment with the raw coal. However, a striking result was the very high yield of pyridine solubles from liquefaction (99 wt.% DAF), more than double the value for either the raw coal (44 wt.% DAF) or the highest value observed for water pretreated raw Zap lignite (50 wt.% DAF for 600 minutes).

In the case of demineralized Wyodak coal, a single pretreatment experiment was done at a 60 minute pretreatment time (350°C, 4000 psig). There was a significant reduction in the amount of pyrolytic CO_2 and CO evolved from the residue when compared to water pretreatment of the raw coal under the same conditions. Conversely, the amount of CO_2 evolved during the pretreatment step was significantly higher. The amount of pyridine extractables was higher but the liquefaction yields were lower.

In the case of Illinois coal, a single pretreatment experiment was done at 60 minutes (350°C, 4000 psig) and the results for tar yields, liquefaction yields and extractables yields were all lower.

The pyrolysis and liquefaction results for the demineralized residues suggest that demineralization is beneficial prior to water pretreatment of Zap lignite but not for Illinois No. 6 coal. In the latter case, a problem with demineralization is that it is difficult to prevent partial oxidation of the coal during this procedure. As discussed above, it has been found that the Illinois coal from the Argonne premium sample bank is particularly sensitive to exposure to oxygen.

The pyrolysis results for the Zap and Illinois blank experiments do indicate that the presence of added water is important, as the tar yields do not increase significantly without water being present. This was not the case for the Wyodak coal, where the tar yields were comparable. However, the Wyodak does have a high moisture content so the intrinsic moisture content or the pyrolysis water may be providing the water function. Additional blanks will be done with dried coals to address this question.

The data on pyridine extractables yield were only available for the Illinois coal. In this case, the amounts were comparable to the reference water pretreatment experiment.

In the case of the liquefaction results, the blank experiments were very coal specific. For the Wyodak coal, which did not show much effect of added water on pyrolysis tar or extractables yields, the liquefaction yields are uniformly lower than for a reference water pretreatment experiment. In the case of the Zap lignite, the results for oils and toluene solubles were comparable, while the results for pyridine solubles were comparable. In the case of the Illinois coal, the liquefaction results for the blank pretreated coal are in the middle of the range of results for water pretreated coal under the same conditions.

Mild Oxidation Experiments - The samples generated in the controlled oxidation studies under Task 2 were subjected to characterization by TG-FTIR, solvent extraction, solvent swelling and liquefaction in donor solvent. Selected samples were analyzed by FT-IR to see if the increase in dihydroxy compounds could be measured.

The samples were subjected to a standard donor solvent liquefaction experiment (30 min., 400°C in dihydrophenanthrene). The results for toluene solubles and oils for most of the mild oxidation experiments are summarized in Table IV-2. **Experiment #80 indicates that mild oxidation of a water pretreated Illinois coal gives an increased yield of toluene solubles and oils from**

TABLE IV-2 - SUMMARY OF LIQUEFACTION EXPERIMENTS ON ILLINOIS AND ZAP COALS

Coal Type	Run No.	Treatment	Liquefaction Yields DAF %			Pyrolitic NH_3
			Toluene Solubles	Oils		DAF %
Ill. #6		—	42 to 48	14 to 17		0.75
		pretr.	11 to 40	(-12) to 40		1.10
	80	pretr. + H_2O_2[b]	64	19		0.52
	84	H_2O_2[a] + pretr.	48	7		0.53
	88	H_2O_2[b] + pretr.	62	19		0.60
	91	Fe^{e+}[c]				
	85	H_2O_2[b]				
		H_2O_2[b] + H_2S)				
Zap		—	26 to 36	12 to 14		1.10
		pretr.	18 to 21	12 to 15		0.70
	82	pret. + H_2O_2[b]	30	14		0.50

TABLE IV-3 - FT-IR ANALYSES OF STEAM PRETREATED RESIDUES FROM FOUR COALS

(WEIGHT PERCENT dmmf)

| Coal	Pretreat Time (min.)	HYDROGEN					AROMATIC HYDROGEN			CARBON	CARBONYL	OXYGEN		
		H_{al}	H_{oh}	H_{ar}	H_{total}	H_{ar}/H_{total}	1 Adj	2 Adj	3 or more	C_{al}	Units (Abs. x cm^{-1})	O_{oh}	O_{ether}	O_{sum}
ZAP	--	2.02	0.34	1.58	3.94	0.40	0.46	0.74	0.37	13.47	24.67	5.5	5.0	10.5
	20	2.81	0.39	1.67	4.87	0.34	0.51	0.89	0.28	18.70	16.22	5.0	4.7	9.7
	180	2.06	0.22	2.10	4.37	0.48	0.54	0.96	0.60	13.70	6.49	3.5	4.7	8.2
	1080	2.06	0.20	2.27	4.52	0.50	0.53	0.98	0.77	13.70	4.27	3.2	3.5	6.7
WYODAK	--	3.03	0.33	1.73	5.09	0.34	0.52	0.78	0.43	20.20	23.86	5.2	5.0	10.2
	20	3.61	0.28	1.48	5.36	0.28	0.50	0.72	0.26	24.19	14.41	4.5	4.3	8.8
	180	2.80	0.21	1.95	4.99	0.39	0.57	0.87	0.52	18.84	8.30	3.4	4.6	8.0
	1080	2.12	0.19	1.62	4.01	0.41	0.36	0.70	0.57	14.77	4.05	3.0	4.0	7.0
ILL #6	--	3.41	0.23	2.07	5.71	0.36	0.69	0.78	0.60	22.73	4.48	3.7	2.3	6.0
	20	2.76	0.18	1.49	4.44	0.34	0.50	0.61	0.39	18.47	6.15	2.8	2.6	5.4
	300	2.85	0.18	1.22	4.25	0.29	0.38	0.46	0.39	19.0	2.01	2.9	2.2	5.1
	1080	2.25	0.17	0.96	3.38	0.28	0.31	0.35	0.30	15.0	1.54	2.8	1.7	4.5
PITT	--	3.60	0.16	2.07	5.83	0.36	0.67	0.80	0.60	24.00	0.86	2.5	1.9	4.4
	20	3.63	0.12	2.12	5.86	0.36	0.72	0.84	0.56	24.17	15.14	1.9	4.4	6.3
	180	3.31	0.17	1.79	5.26	0.35	0.58	0.74	0.48	22.80	10.47	2.7	2.3	5.0
	1200	2.81	0.15	1.77	4.72	0.37	0.59	0.66	0.52	18.74	1.28	2.4	1.7	4.1
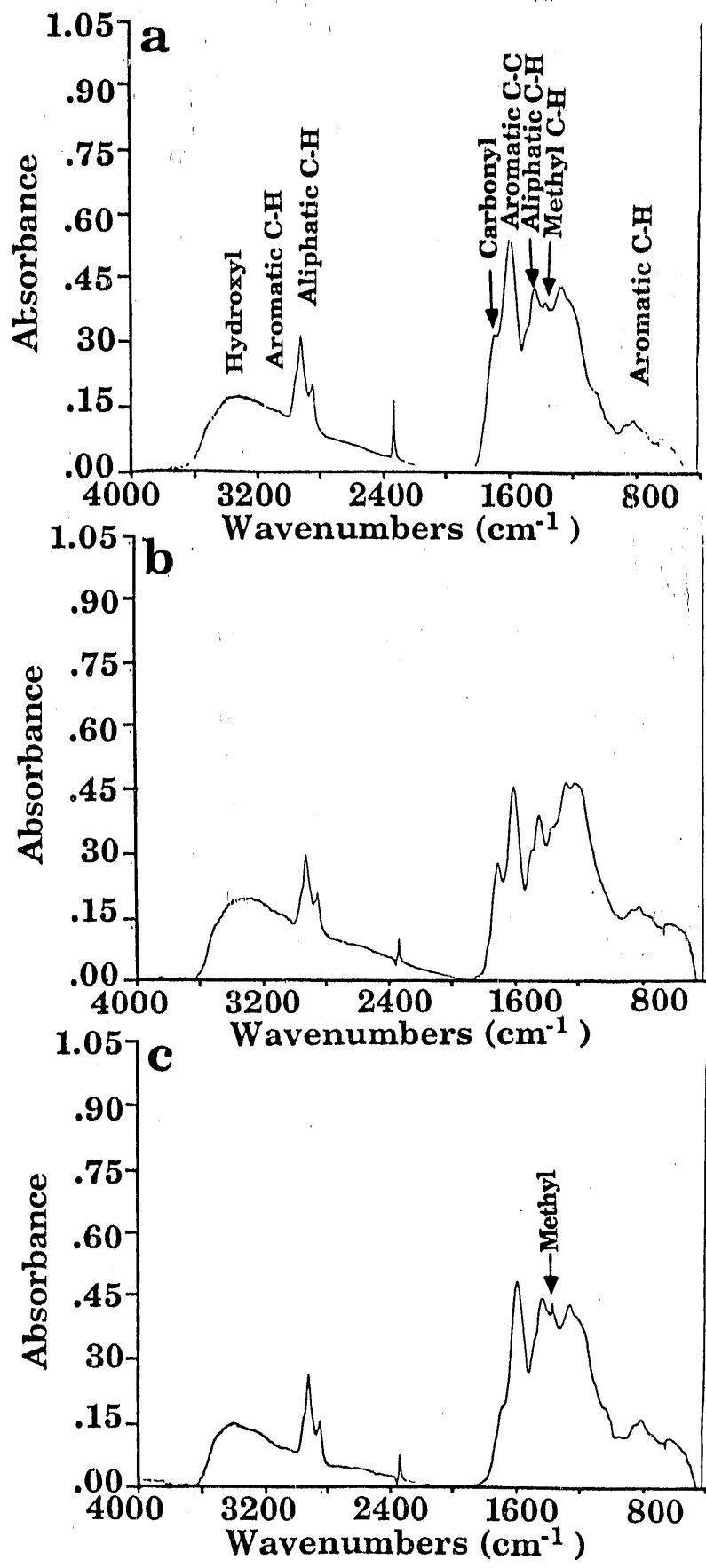
Figure IV-3. Quantitative FT-IR Spectra of Wyodak Coals. a) Raw Coal, b) Demineralized Coal and c) Water Pretreated Coal.

liquefaction of the residue and that the values are generally higher than from liquefaction of the raw coal. Similar results are observed for mild oxidation of a water pretreatment residue from Zap lignite (see experiment #82 in Table IV-2). **Consequently, these results are consistent with the hypothesis that ortho dihydroxy functionalities created by water pretreatment are responsible for the retrogressive solvent incorporation reactions which artificially reduce the liquefaction yields.** This conclusion is based on the fact that the mild oxidation should remove the dihydroxy functionalities. Additional experiments were done with Illinois coal (#84, #88) where the coal was oxidized prior to water pretreatment. This would serve to remove dihydroxy functionalities which are already present in the coal and the phenolic groups that are precursors to the dihydroxy functionalities that are formed during water pretreatment. In this case, the toluene solubles and oil yields are also higher than for the coal that was only subjected to water pretreatment.

Also shown in Table IV-2 are the yields of NH_3 from TG-FTIR analysis of the water pretreated residues. It appears that NH_3 is a sensitive indicator of the modifications in the coal structure, although the underlying chemistry for this has not been established. The addition of a molecule of H_2O to an aromatic ring, thus creating a phenolic group, would release two hydrogen atoms which could add to other parts of the coal structure. This hydrogen addition could explain the significant increase in pyrolysis NH_3 after steam pretreatment of Illinois coal. The oxidation of phenolic groups would remove hydrogen from the coal and reduce the yield of NH_3. However, this picture is not consistent with the changes in the NH_3 yield with the Zap coal.

FT-IR Analyses of Water Pretreated Coals - Residues from water pretreatment of all four coals were subjected to analysis by quantitative FT-IR functional group analysis. The samples were chosen from a range of pretreatment times (20, 180, 300, 1080, 1200 minutes) at 350°C, 4000 psig. An example of an FT-IR spectrum from a water pretreated (350°C, 4000 psig, 20 min.) Wyodak coal is shown in Figure IV-3 along with a spectrum from a raw coal and demineralized raw coal. The water pretreated coal has a higher concentration of aliphatic and methyl hydrogens and a lower carbonyl and hydroxyl concentration compared to the raw or demineralized coal. The reduced carbonyl concentration for the water pretreated coal is consistent with a reduction in CO_2 yield in pyrolysis (See Fig. IV-1), assuming that carboxyl groups are the source of CO_2 evolution.

The quantitative results for all four coals are given in Table IV-3. The general trends were as

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follows. **For all of the coals, except Pittsburgh, pretreatment led to a monotonic decline in the oxygen content.** This is consistent with previous work on water pretreatment (Brandes et al., 1989; Ross et al., 1987 a,b, 1990; Khan et al., 1989) and with the idea that the process is similar to an accelerated aging of the coal.

A lot of attention has been paid to the effect of water or steam pretreatment on hydroxyl groups. **For all four coals, the concentration of phenolic OH declined with pretreatment. This is in agreement with the results of Khan et al. (1989) but not with Brandes et al. (1989).** Brandes et al. (1989) concluded that steam pretreatment significantly increased the number of hydroxyl groups. This conclusion was primarily based on the fact that mild O-alkylation of steam pretreated coal with labeled methyl iodide introduced twice the enrichment of ^{13}C when compared to the raw coal. Some IR data was also used to support this conclusion, although the interpretation of the changes of the IR spectrum in this region is not straightforward. It is possible that the loosening of the structure resulting from steam pretreatment makes the coal more reactive toward the O-Alkylation procedure, and that the actual number of hydroxyl groups does not increase significantly. It is also possible that the concentration of OH groups increases on the surface of the water pretreated coals but not in the bulk. Of course, any comparison with previous work must consider the fact that the results in Table IV-3 are for samples produced in subcritical water and over a wide range of pretreatment times. Most of the previous studies (Brandes et al., 1989; Khan et al., 1989) were done in subcritical steam at lower pressures (~1000 psig).

The trends for hydrogen functional groups appeared to vary with coal type. For the two low rank coals (Zap, Wyodak), pretreatment increased the fraction of aromatic hydrogen, while for the two high rank coals (Illinois, Pittsburgh), this fraction was decreased. The contrast between the behavior of the Zap and Illinois coals is especially striking in this regard. For the two low rank coals, the amount of aliphatic hydrogen (H_{al}) goes through a maximum with increasing pretreatment time, while for the two high rank coals, H_{al} declines steadily.

Most of the data in this table are the result of averages of four determinations (duplicate samples of residues produced in 2 separate experiments). However, the raw data will require further study to verify some of the numbers, such as the significant increase in carbonyl content for the Pittsburgh seam coal at relatively short pretreatment times. One problem is that coal modifications can shift the locations of certain peaks, while the quantitative routine usually

assumes these locations are fixed. As part of a separate study, we are developing more advanced routines for the quantitative measurement of oxygen functional groups by FT-IR.

SEM/X-ray Analysis of Pretreatment Residues - The data on SEM/x-ray analysis of steam pretreated residues is summarized in Table IV-4. This table includes new data on the Wyodak and Illinois coals, along with previously reported data on the Zap lignite. The data on the Zap lignite suggest that the ash content goes through a minimum after about one hour. There is not enough data on the other coals to verify this trend. **For the individual ash components, the most significant trends observed with the Zap are the elimination of Na, increases in Al, Si, and Fe, and a nearly constant value for Ca.** The increases in Al and Fe may be due to partial dissolution of the reactor system, as discussed previously (Serio, et al., 1991). This will be checked by doing water pretreatment experiments in the presence of a glass insert. The trends for the other two coals are generally consistent with these observations.

In the case of sulfur, it appears that the mineral sulfur is reduced at short pretreatment times for Zap lignite while the organic sulfur is largely unchanged. The opposite trend was observed for the Wyodak. The mineral sulfur appears to increase for the Illinois coal without much change in the organic sulfur. However, the values of both mineral and organic sulfur are highly variable for repeat measurements for Illinois coal, so this may be a problem with the sample homogeneity.

An increase in sulfur content of Illinois coal following steam pretreatment was also observed by Brandes et al. (1989). A real increase could occur if the loss of material during the pretreatment process contains relatively little sulfur. Mapstone (1991) observed little change in the total sulfur from steam pretreatment of Illinois and Wyodak coals at 350°C and a slight reduction in the case of Pittsburgh coal. The total ash content was also largely unchanged in each case. However, he only examined a relatively short pretreatment time (15 min.) at this temperature. Rozgonyi et al. (1988) have reported reductions in ash and sulfur from steam pretreatment.

FIMS and FT-IR Analyses of Tars - Under a separate DOE program (Contract No. DE-FG05-90ER80877, samples of water pretreated Wyodak coal generated under the current program (350°C, 4000 psig, 20 min.) were pyrolyzed in an entrained flow reactor and samples of the tar were collected and subjected to analysis by FT-IR and FIMS. These results were compared to analyses of tars produced from pyrolysis of raw and demineralized Wyodak coal in the same or

TABLE IV-4 - COMPARISON OF X-RAY ANALYSES FOR RAW AND WATER PRETREATED
(350°C, 4000 psig) ZAP, WYODAK AND ILLINOIS COALS

Coal	Sample	Pretreatment Time	Na	Mg	Al	Si	K	Ca	Ti	S(O)	S(M)	Fe	Ash
Zap	Raw	—	0.31	0.35	0.33	0.38	0.02	1.09	0.03	0.30	0.39	0.17	6.9
	W9	10 min.	0.00	0.31	0.45	0.76	0.02	1.30	0.04	0.31	0.21	0.26	6.7
	W33,34	20 min.	0.00	0.26	0.43	0.48	0.03	1.41	0.04	0.25	0.16	0.26	5.8
	W6	60 min.	0.02	0.29	0.40	0.51	0.02	0.99	0.04	0.23	0.34	0.19	5.8
	W2	180 min.	0.02	0.40	0.55	1.05	0.02	1.38	0.035	0.21	0.19	0.34	7.6
	W4	240 min.	0.00	0.37	1.09	1.18	0.01	1.26	0.04	0.25	0.36	0.43	9.7
Wyodak	Raw	—	0.04	0.20	0.41	0.32	0.02	1.10	0.06	0.48	0.11	0.20	5.3
	W31,32	20 min.	0.00	0.10	0.53	0.61	0.03	1.21	0.06	0.27	0.11	0.49	5.8
Illinois	Raw	—	0.02	0.00	0.81	2.28	0.14	0.50	0.08	1.16	1.42	0.58	10.9
	W36	20 min.	0.00	0.00	1.06	2.56	0.15	0.41	0.07	0.96	2.15	0.36	12.0
	W37	60 min.	0.00	0.00	0.90	2.12	0.13	0.70	0.07	1.14	1.46	0.69	11.4

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similar reactors. The results of the FIMS analyses are shown in Figure IV-4. The peak of the tar molecular weight distribution (MWD) is lowest for the tar from the water pretreated coal (~ 275 daltons) when compared to the raw coal (~ 325 daltons). This is consistent with the FIMS results of Ross et al. (1991). The tars from the demineralized coal had the highest peak molecular weight (~ 350 daltons). Conversely, the tar from the raw coal had the highest volatility in the FIMS apparatus (83%), compared to 69% for the water pretreated Wyodak tar and 67% for the demineralized Wyodak tar. This is likely due to a greater concentration of hydroxyl groups for the latter two tars, which would reduce the intrinsic volatility and increase the opportunity for retrogressive reactions. For example, the results of the FT-IR analysis of the tar from the water pretreated Wyodak coal showed twice the concentration of hydroxyl compounds when compared to the tar from the raw coal. This is consistent with our hypothesis that steam pretreatment for short times creates dihydroxy groups in the coal. However, when the FIMS analysis data was examined for phenol and catechol and the C_1, C_2 and C_3 derivatives, the concentrations were found to be higher in the tar produced from the raw coal. We will try to resolve this apparent discrepancy between the FT-IR and FIMS data during the next quarter.
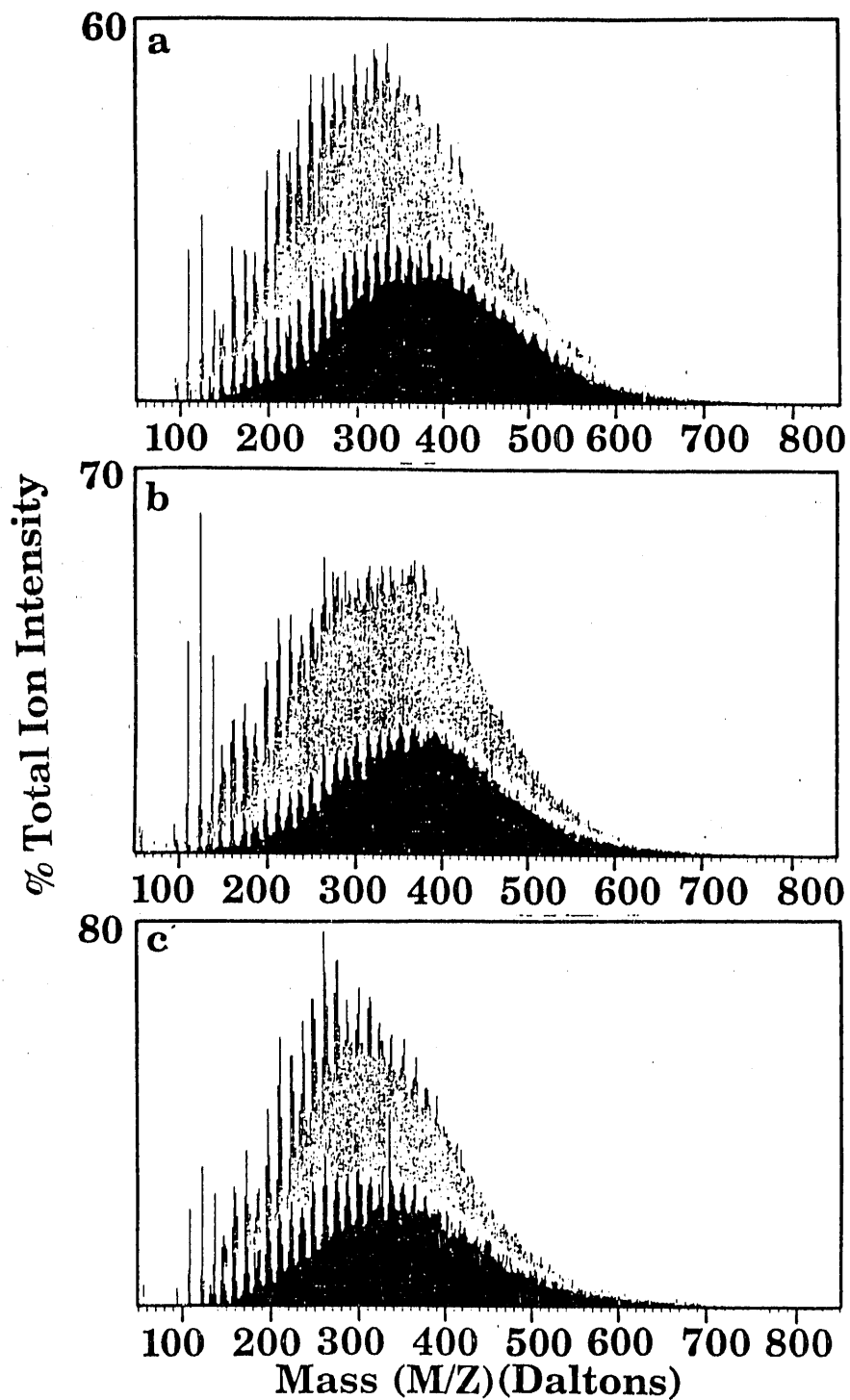
Figure IV-4. Field Ionization Mass Spectrometer (FIMS) Analysis of Wyodak Mild Gasification Liquids. a) Raw Wyodak, b) Demineralized Wyodak and c) Water Pretreated Wyodak.

V. TASK 4 - RATES, MECHANISMS AND MODELING

Introduction - Our previous work on retrogressive reactions in coal liquefaction indicated a close correlation of pyrolysis liquid (tar) yields and the yields of toluene and pyridine solubles in direct liquefaction (Serio et al., 1989, 1990). Our current data suggests that this correlation may not necessarily hold for water pretreated coals. The reasons for this are still being investigated, but a plausible explanation was developed based on a review of literature results in the context of our own data. The literature work is being evaluated in light of the hypothesis that water pretreatment is similar to an accelerated geological aging of the coal. This hypothesis is generally consistent with the observed effects of rank and temperature on the effectiveness of water pretreatment in increasing tar and extractables yields from pyrolysis of low rank coals.

Most of the previous work has been done at lower pressures (~1000 psig) than in the current work (~4000 psig) where the coal is heated in the presence of steam rather than subcritical water. Our preliminary results on the effect of pressure (discussed in Section IV) indicate that it does make a difference, which must be considered when comparing our results to literature data.

A visit was made to AFR by Dr. Michael Siskin who has been working for several years on the reactions of water with model compounds in the temperature range of 200-350°C (Siskin and Katritzky, 1991). His work concludes that 1) it is the ionic chemistry of water that is important under the pretreatment conditions; 2) that reactions in water systems are often "autocatalyzed" by water soluble organic reaction products; 3) aqueous chemistry provides cleavage pathways for major oxygen crosslinks which are too stable to cleave thermally; 4) reactions of water with organics can be catalyzed by clays. His work has demonstrated that there are plausible pathways for water to remove or reduce oxygen functional groups (e.g., conversion of alcohols to methyl groups) which is observed in water pretreatment of coal. Because of the direct relevance of the work of Siskin and coworkers to the conditions and functionalities present during water pretreatment of coal, it will receive careful attention in completing the mechanistic framework.

Background - Recent investigations on aqueous pretreatment of coal have shown increased yields from pyrolysis (Graff and Brandes, 1986, 1987; Khan et al., 1989) and extraction (Brandes

et al., 1989; Blenkowski, et al., 1987 a,b) and enrichment in lower molecular weight material at the expense of higher weight tars (Ross and Hirschon, 1990). In spite of this improvement in lower molecular weight fragments and loosening up of the coal structure, no significant improvement was observed in the toluene soluble fraction after liquefying hydrothermally pretreated Illinois No. 6 coal (Ross and Hirschon, 1990).

Our work has focused on hydrothermal treatment and subsequent liquefaction of different rank coals to find correlations between pyrolysis, extraction and liquefaction yields as a dependence of pretreatment time. Based on our experimental observations, we were seeking to find chemical reactions that might occur in coal contacting water at elevated temperatures. As discussed below, the hypothesis of a reaction between phenoxy radicals and water provided a satisfactory explanation for most of the experimental results.

Results and Discussion - A summary of our data on water pretreatment of our coals is shown in Table V-1. The increase in pyridine extractables and tar yields is consistent with literature observations (Graff and Brandes, 1987; Brandes et al., 1989; Khan et al., 1989). The decrease in density indicates a loosening up of the coal structure as was suggested earlier (Brandes et al., 1989). The tar yields and pyridine solubles yields show a maximum with increasing pretreatment time (except for the Pittsburgh coal) which indicates the onset of retrograde reactions as pretreatment proceeds. Conversely, the yields of toluene solubles (TS) from liquefaction are at a minimum where pyrolysis tar yields are at maximum, which is contrary to previous studies on liquefacation (Serio, et al., 1989, 1990) and expectations. The Pittsburgh coal is an exception here, also. However, the individual experimental data around the minimum toluene solubles values were very dispersed, especially for the Illinois No. 6 coal. Figure V-1 shows a graphical comparison of selected results for the Zap and Illinois coals which illustrates these trends. The dashed line in each plot is the result for the raw (untreated) coal.

Table V-2 shows the liquefaction results of individual experiments with Illinois No. 6 coal in somewhat more detail. Since the oil fraction is measured by weight difference, the only explanation for negative values is that there was solvent incorporation into the toluene insoluble part of the coal matrix and that this depends on how fresh the coal was. The results for the samples which were freshly opened show the negative oil yields for samples that were subjected to water pretreatment (see runs 60 and 66 in Table V-2). The results of a standard liquefaction experiment without prior water pretreatment do not appear to be as sensitive to the length of

TABLE V-1 - Summary of Extractables, Pyrolysis and Liquefation Results for Four Coals Which Have Undergone Water Pretreatment[a]

Coal	Pretr. Time Min.	Pyridine Sol. DAF %	Gross Density g/ml	Pyrolysis Tar DAF %	Toluene Solubles* DAF %	Pretreat CO DAF%	Pyrolysis CO DAF %
ZAP	no	5	0.76	10	36	---	13.7
	20	9	0.67	16	19	1.0	14.1
	120	11	---	---	---	0	11.3
	300	---	---	11	40	0	9.6
WYODAK	no	11	0.78	14	41	---	11.1
	20	15	0.66	20	32	0.05	14.7
	120	---	---	23	35	0.06	11.3
	600	---	---	14	30	0	8.4
ILL #6	no	36	0.78	34	44	---	4.0
	20	78	0.67	43	29[b]	0	4.7
	60	72	0.69	33	46[b]	0	4.4
	120	66	0.73	37	36	0	4.7
	300	43	0.70	38	38	0.	4.5
PITT	no	28	0.78	26	24	---	3.1
	20	44	0.68	24	31	0	3.2
	180	44	0.67	30	26	0	3.4

NOTES:

*	Toluene solubles after liquefaction
(a)	All experiments done at 350°C, 4000 psig pretreatment conditions
(b)	Large variation in results

TABLE V-2 - Results of Individual Liquefaction Experiments with Water Pretreated Illinois No. 6 Coal

Exp. #	Pretr. Time (min.)	Hexane Solubles (oils) DAF %	Toluene Solubles DAF %	Pyridine Solubles DAF %
1005*	0	17	47	98
40	0	13	42	99
36	20	1	47	86
66*	20	-13	11	59
31	60	39	59	93
46	60	7	38	73
60*	60	-27	40	90

*   freshly opened sample vial
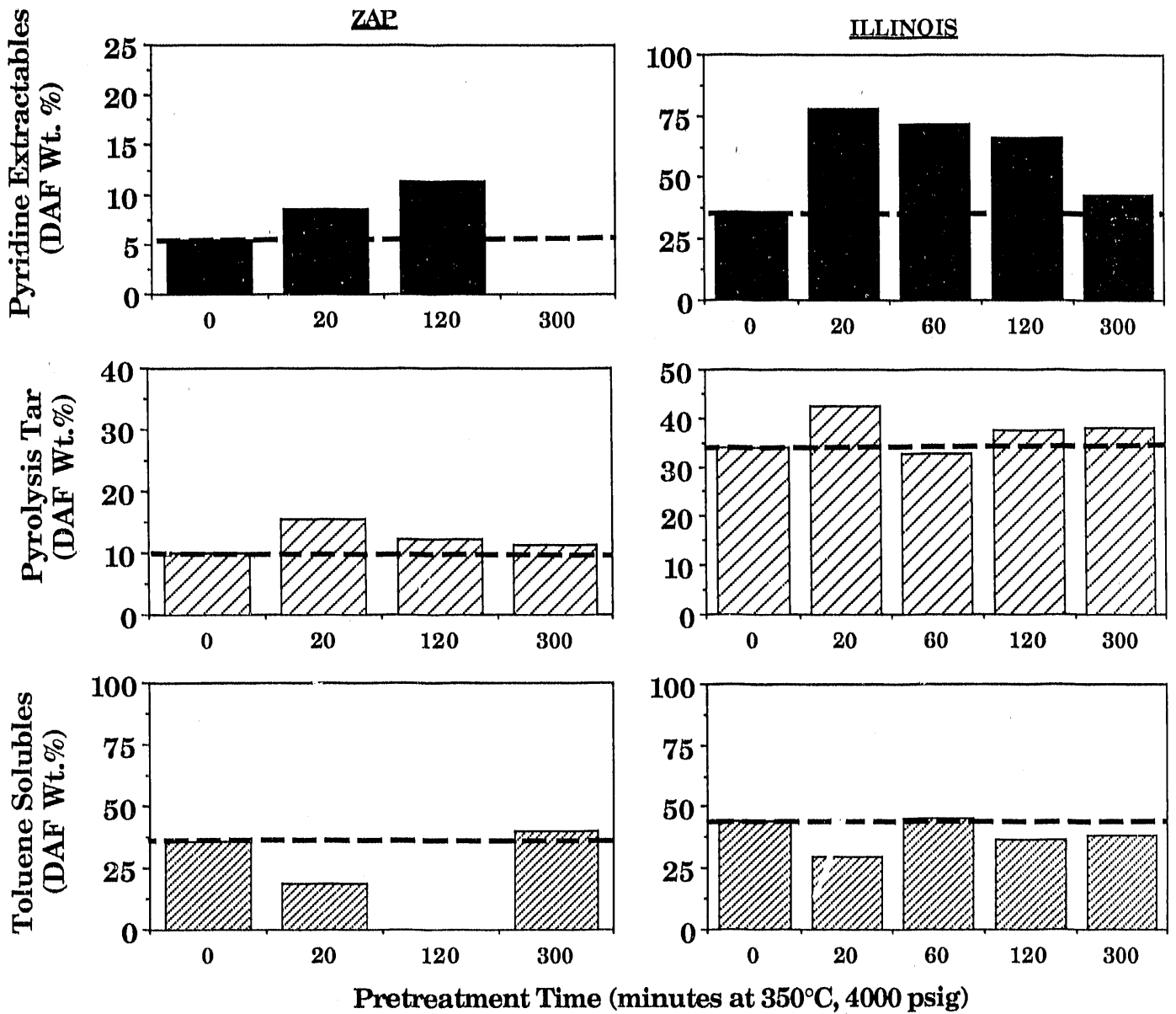
Figure V-1. Comparison of Yields of Pyridine Extractables, Pyrolysis Tar and Toluene Solubles from Liquefaction for Zap and Illinois Coals.

time after opening of the ampoule (compare runs 1005 and 40 in Table V-2). In the case of the Illinois coal, an exposure of this particular coal to even very low oxygen concentrations prior to pretreatment apparently causes a very significant change in the pretreatment behavior. There are reports in the literature of the sensitivity of Illinois No. 6 coal to oxidation at ambient temperatures (Gethner, 1987; Kelemen and Freund, 1989). The problem of measuring the incorporated solvent calls for a proper separation of the solvent and solvent derivatives which is very difficult to do on a quantitative basis given the complex nature of the coal liquid. An example of how this could occur is shown in Fig. V-2. The organic part of the coal is designated as "A". For the purposes of this calculation, the formation of gas is assumed to be negligible. After a liquefaction experiment, the coal is initially extracted with toluene and the residue is the toluene insoluble (T_i) portion. Consequently, the toluene soluble (T_s) portion is determined by the difference of these two quantities:

$$T_s = A - T_i \tag{1}$$

Next, the toluene solubles are extracted with hexane to remove the oils plus the solvent. The remainder is the asphaltenes, which are measured directly. The oils are calculated by difference.

$$Oils = T_s - Asph. \tag{2}$$

There are two possible anomalies as far as the solvent is concerned. One is that the solvent is incorporated into the toluene insoluble fraction $(T_i + T_i^+)$. This is what is believed to happen during liquefaction of the short time (< 60 min) water pretreated residues. The second possibility is that the solvent is incorporated into the asphaltene fraction $(Asph + T_s^+)$. If either or both of these occur, the calculated oil yield will be lower as indicated by the calculation in Figure V-1.

A second approach, which we have taken, is to hypothesize a reaction scheme for that particular behavior which is in harmony with the experimental data and then to test it. Our hypothesis is that it is the phenoxy radical which reacts with water to form dihydroxy products, as illustrated in Fig. V-3, and that the recombination of the dihydroxy and solvent radicals leads to solvent incorporation into the coal matrix, as illustrated in Fig. V-4. However, dihydroxy compounds are not stable at such high temperatures and must therefore appear only as intermediate products leading to the "recovery" of the toluene solubles (TS) yields after prolonged pretreatment. An example of two decomposition routes for ortho dihydroxy benzenes is shown in Fig. V-5.
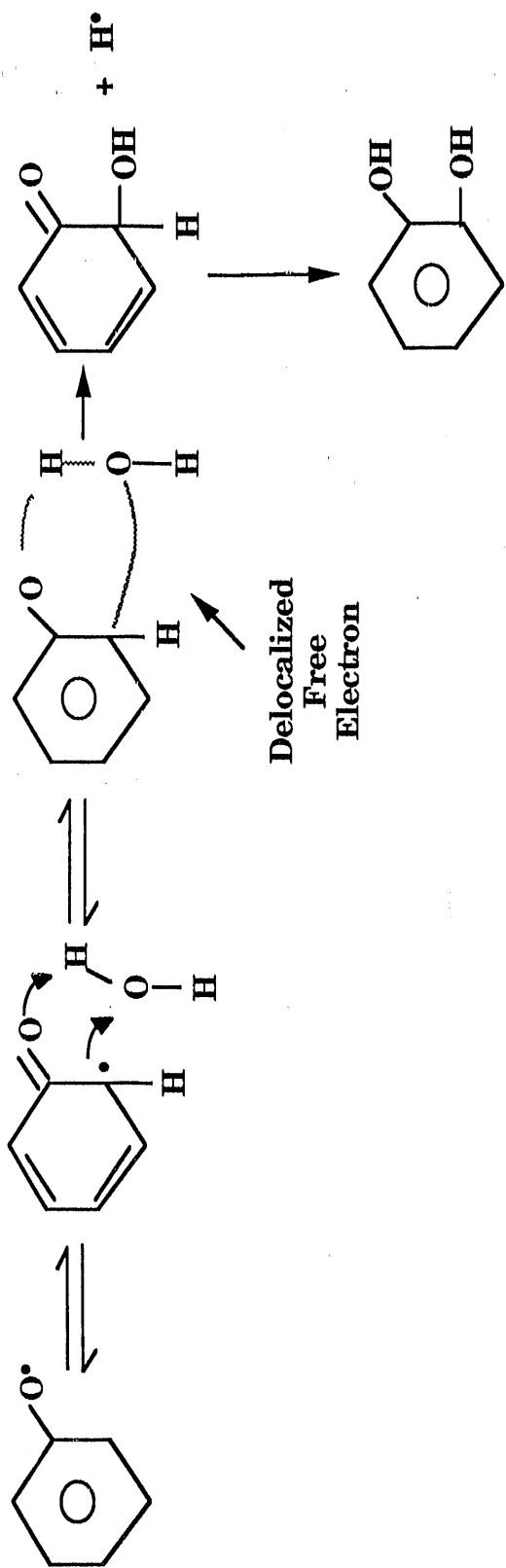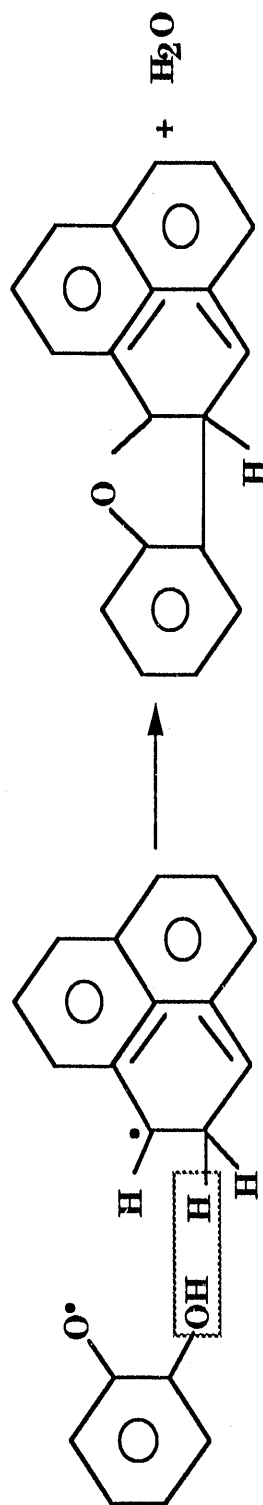
Figure V-3. Reaction of Phenoxy Radicals with Water.

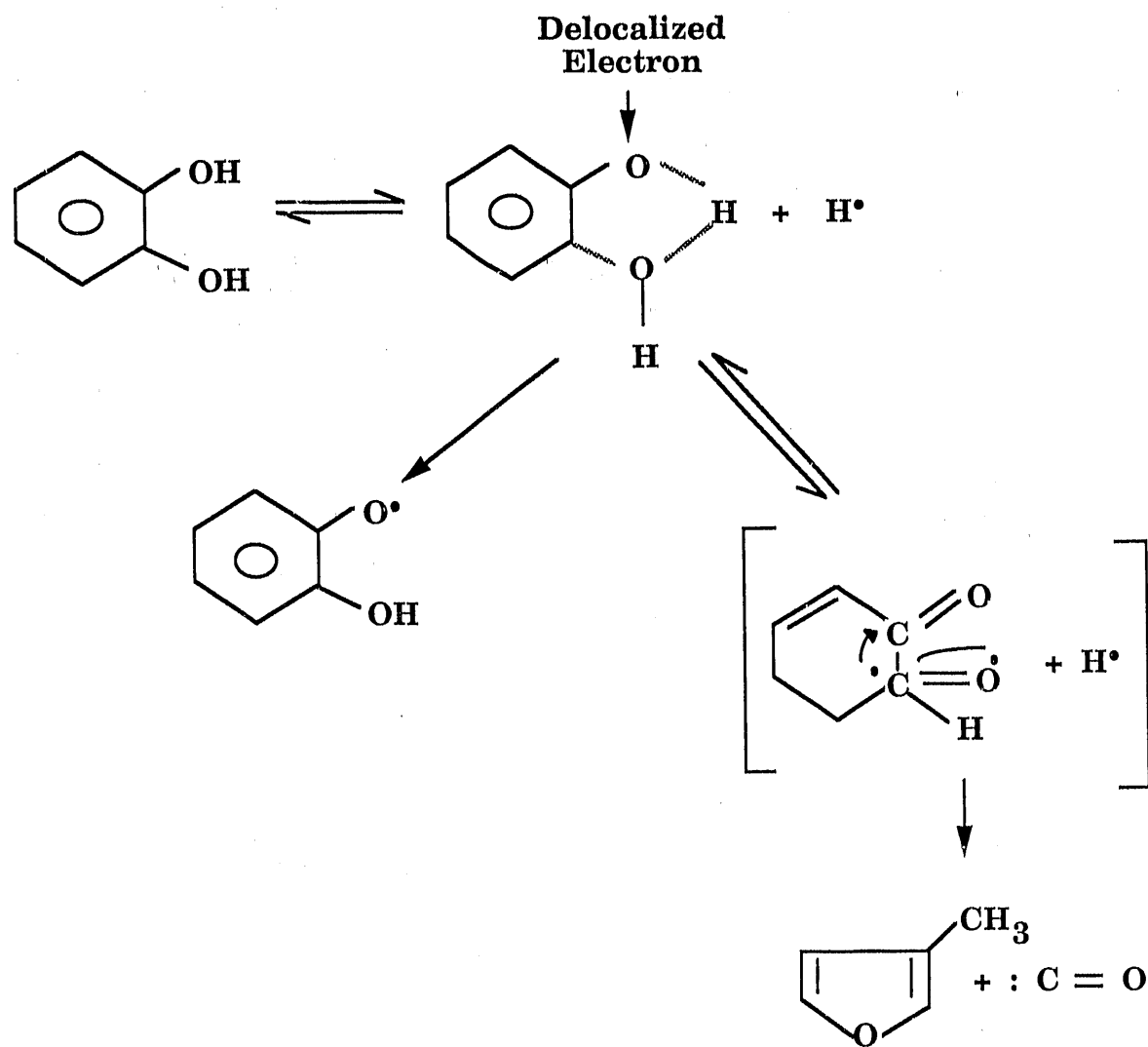**Figure V-4.** Recombination-Condensation Reaction with The Solvent Radical.

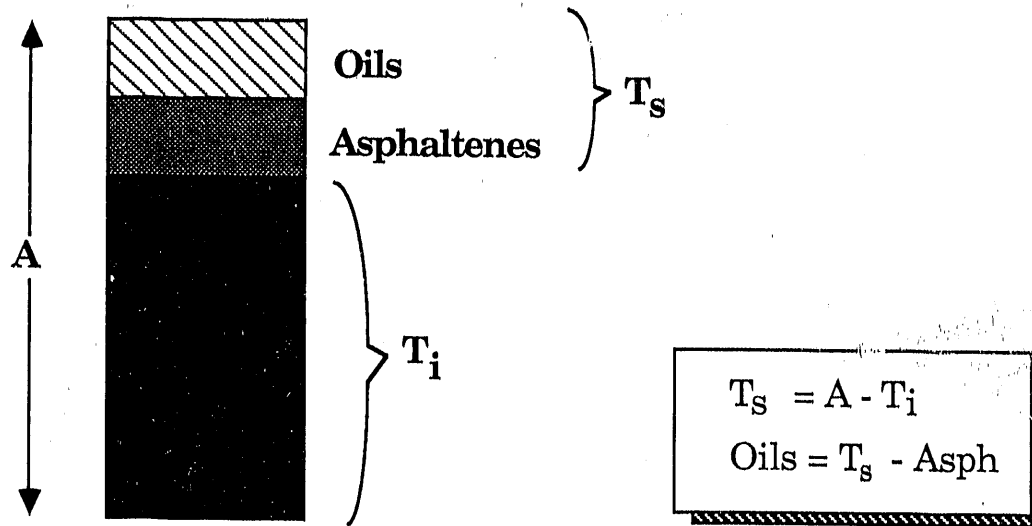**Figure V-5.** Decomposition of Dihydroxy Aromatics.

$$T_S = A - T_i$$
$$Oils = T_s - Asph$$

$$T_s' = A - (T_i + T_i^+) < T_S$$
$$Oils' = A - (T_i + T_i^+) - (Asph + T_s^+) < Oils$$

Figure V-2. Scheme for Analysis of Liquefaction Products from Water Pretreatment Residues.

Phenols are the most widespread components of coals and literature data show a decrease of total phenolic OH in the coal as well as increase of low molecular weight dihydroxy benzenes during water pretreatments (Ross et al., 1990). Since phenoxy radicals are relatively stable due to resonance stabilization, they represent a high steady state concentration at elevated temperatures. As the number of condensed aromatic rings adjacent to the phenoxy radical increases, the stability increases and the reactivity decreases. This might be an explanation as to why the Pittsburgh coal behaves differently during water pretreatment than the lower rank coals.

Dihydroxy benzenes are prone to retrograde reactions (McMillen et al., 1985 a,b) or decomposition. One type of decomposition may lead to CO evolution as shown in Fig. V-5. **Our experimental data show an increase in the pyrolytic CO evolution with a maximum in time corresponding to a minimum in the TS yield (see Table V-1).** This is in sharp contrast to a general decline in pyrolytic CO_2 and H_2O with increased pretreatment time and a corresponding reduction in organic oxygen content for the water pretreatment residues, as indicated in Tables IV-1 and IV-3 (Section IV). There is a small amount of CO formation during pretreatment, but it is an intermediate product only (see Table V-1). It is known that the CO can react with the coal under hydrothermal conditions via base catalyzed reaction pathways (Ross, et al., 1987 a,b). Our data (Table V-2) indicate that a very mild weathering of Illinois No. 6 coal resulted in very high oil yield (39%) in one particular case, after water pretreatment and subsequent liquefaction. If this condition can be reproduced, it would suggest significant benefits for water pretreatment of Illinois coal.

Literature reports indicate that mild weathering of this particular coal results in oxidized sulfur forms (Kelemen and Freund, 1989), and changes in the oxygen functional groups (Gethner, 1987). It is possible that the benefit of mild weathering of the Illinois coal is the result of the oxidation of an electron-transfer complex between phenols and FeS and that the improvement is the result of reduced phenol concentration of the parent coal, with a corresponding reduction in the phenoxy radical concentration. A possible reaction scheme is shown in Fig. V-6. This suggests that a controlled mild preoxidation of the Illinois coal prior to the steam pretreatment would help eliminate the solvent adduction problem. The preliminary results of such experiments (discussed in Section IV)) are consistent with this hypothesis.
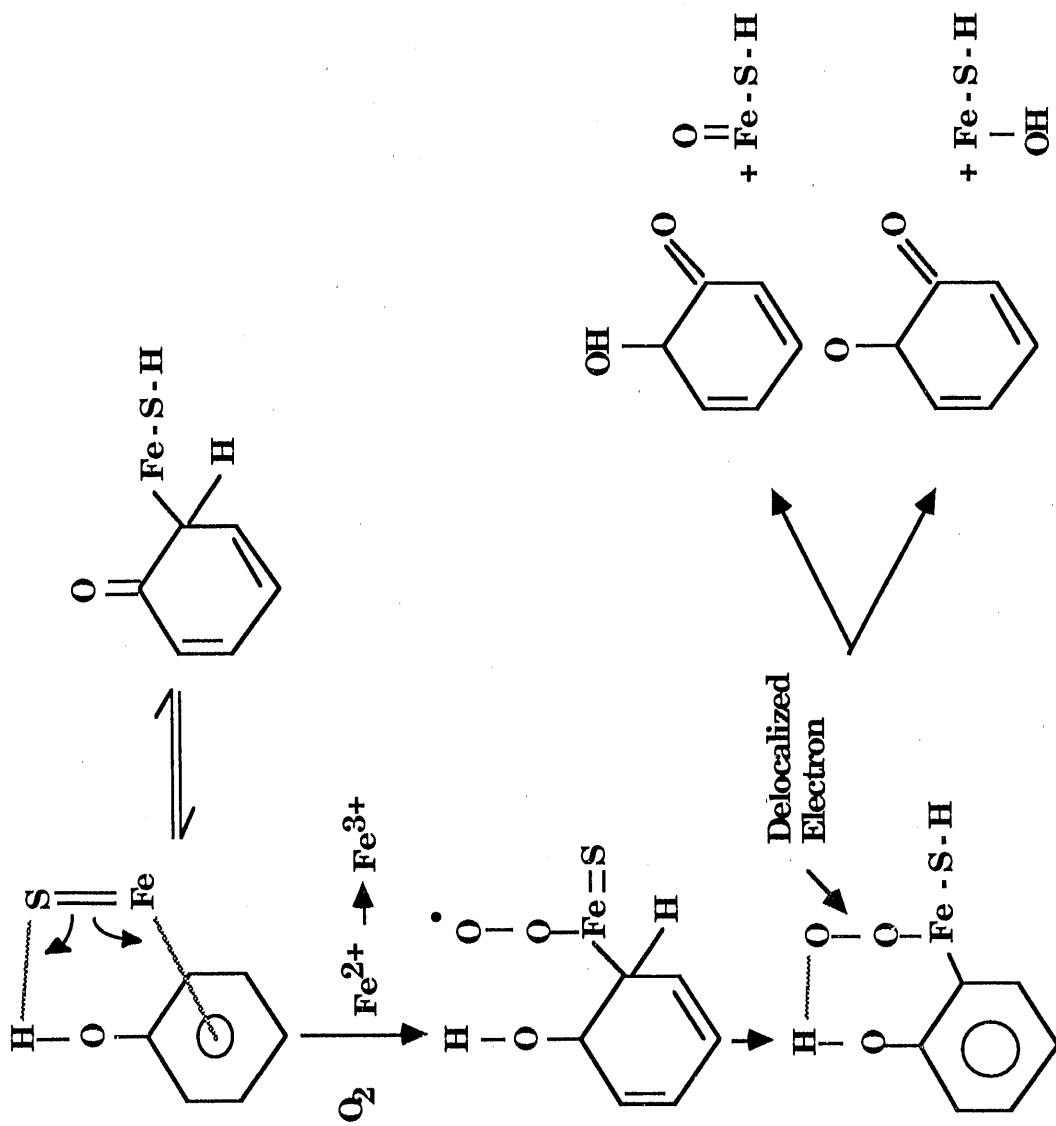
Figure V-6. Interaction of Phenols and FeS.

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Hydrothermal Pretreatment Reaction Pathway Considerations - *Ortho-* and *para-* dihydroxy compounds can always be found among the coal tar components and are probably present in the original coal. *Para*-dihydroxies are more unstable and easily form adducts or polymers (Bredenberg and Ceylan, 1983). *Meta*-dihydroxies are particularly abundant in coal hydrogenation products (Donath, 1954). Ross et al. (1991) conclude, based upon FIMS analyses of hydrothermally treated coal, that the treatment released a portion of the phenols and catechols (*ortho*-dihydroxy phenol) fr∵m the strongly bonded coal environment which are then redeposited and weakly bound to the coal network upon cooling.

The work of Ross et al. (1991) can be summarized as follows:

1. The amount of phenol and catechol loosely bound to the coal structure was increased significantly by hydrothermal or thermal treatment at 350°C, 30 min.

2. However, in the case of catechol, the relative amount of loosely bound material was significantly higher for the hydrothermal case.

The second observation led Ross et al. (1991) to conclude that water is involved in the release of the major portion of the catechols produced at lower temperatures.

After 5 hours of pretreatment at 350°C, the differences between the thermal and hydrothermal case were even more pronounced. The residues produced by hydrothermal treatment produced almost no phenol or catechol above 300°C. The work of Ross et al. supports the conclusion that phenols and catechols are key functionalities in understanding the chemistry of hydrothermal treatment and that catechols are more reactive than phenols under these conditions. It is also consistent with the suggestion that the catechols are formed by reaction of the phenols with water and that these species are decomposed at long pretreatment times.

Brandes et al. (1989) found that the OH concentration increased in the coal as a result of hydrothermal treatment whereas the total oxygen content decreased. They postulated the loss of organic oxygen as a result of dehydration of alcohols formed by cleavage of aliphatic ethers. These authors used DRIS (diffuse reflectance infrared spectroscopy) which measures functional groups on the surface of the coal particles. Consequently, an increase of the hydroxyl group concentration on the surface of the particles could be accompanied by a decrease in the bulk.

This picture would coincide with that of Ross and coworkers who found loosely bound phenols and catechols, as discussed above. Brandes et al. (1989) also found a shift in the OH band towards higher energies (less hydrogen bonded) at the expense of low energy species, which was consistent with swelling data showing a decrease in hydrogen bonding. However, comparing the IR spectra of mono and dihydroxy aromatic compounds clearly shows that exactly the same shift could be arrived at by replacing part of the monophenols with ortho diphenols. This would agree with Ross et al. (1991) who found catechol (ortho-$(OH)_2$Ph) and phenol in a ratio of about 2/1. Other products were resorcinol (meta-$(OH)_2$Ph) and hydroquinone (para-$(OH)_2$Ph), with the ratio catechol/(resorcinol + hydroquinone) = 6/1 in the aqueous phase.

McMillen and coworkers (1985a,b) found that, under liquefaction conditions, dihydroxy compounds readily couple with themselves or with the solvent (in their case, tetrahydroquinoline) and also form high molecular weight products, the amount of which increases in the presence of coal. The self coupling produces a diaryl cyclic ether molecule. This explains our FT-IR data, (see Table IV-3) which show the ether group concentration reaching a maximum or declining slowly after relatively short hydrothermal treatment times, while the concentration of hydroxyl decreases steadily.

Our suggestion is that one of the principal reactions to cause solvent incorporation into the coal matrix under liquefaction conditions is the reaction of surface ortho dihydroxy functionalities with the solvent. A short hydrothermal treatment will enhance solvent incorporation due to the increased surface concentration of dihydroxies. Prolonged pretreatment will destroy these functionalities (as shown by Ross et al., 1991) thus reducing solvent additions but introducing strong crosslinks and resulting in a decrease in liquefaction yields. A parallel process of depolymerization of the coal during hydrothermal treatment is compensating for this new crosslink formation, the final result being a slight increase or no increase of liquefaction yields relative to the untreated coal at long pretreatment times. The proposed mechanism is summarized in Fig. V-7.

Stein et al. (1987) have shown that the ortho-hydroxy substituents decrease the energy requirement for homolysis by about 7 Kcal/mol. This increases the radical concentration on the coal surface under liquefaction conditions and thus the probability of recombination reactions with solvent molecules. This route produces the same cyclic ether type bonds as with the self
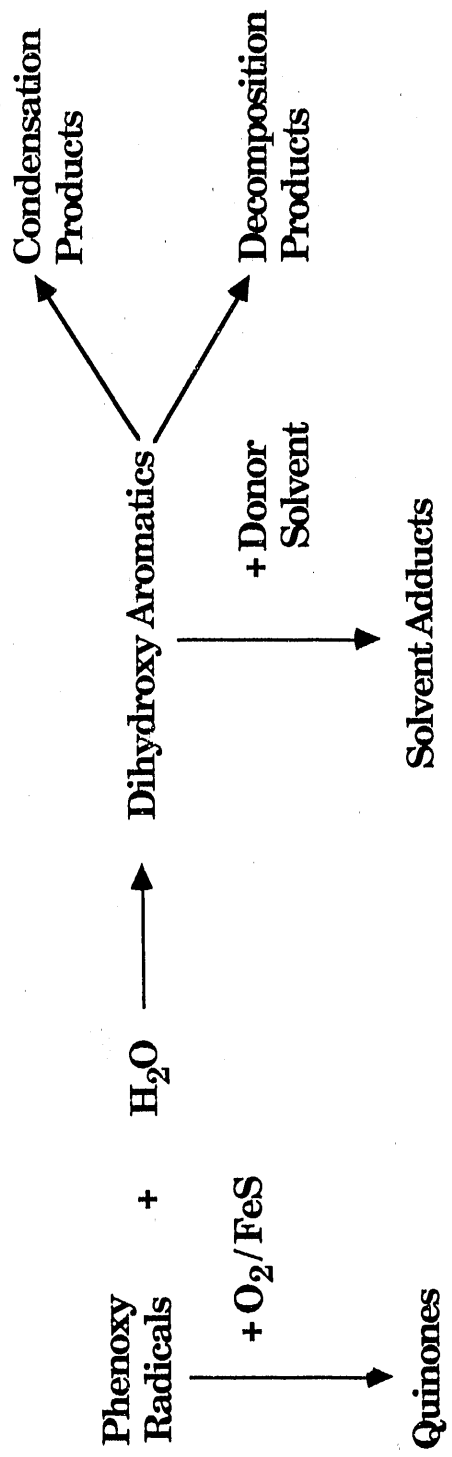
Figure V-7. Proposed Mechanism for Water Pretreatment as it Impacts Liquefaction Yields.

coupling of dihydroxyls. Since the adjacent solvent ring is unsaturated there is a probability for a successive condensation reaction to take place which would essentially irreversibly incorporate the solvent into the coal structure.

Since higher yields of toluene solubles and oils were obtained from samples of Illinois coal that were not freshly opened, our suggestion is that a mild oxidation substantially decreased solvent incorporation. This result suggests a possible way to avoid the detrimental effect of solvent incorporation and thus significantly increase liquefaction yields from water pretreated coals. Future work will involve designing experiments and a search for additional literature work to test the hypothesis.

Summary - The preliminary conclusions can be summarized as follows:

1. The analysis of pyrolysis and pyridine extractables data from water pretreated Zap lignite and Wyodak subbituminous coal (reduction in CO_2 yield, maximum in tar yield, maximum in extractables, increase in CH_4 yield) shows a strong similarity to an accelerated geological aging process. The results for the Illinois and Pittsburgh bituminous coals were similar though less dramatic, except for the extractables yields.

2. The geological aging analogy is also consistent with results that were obtained in the literature on steam or water pretreatment, since it explains why the treatment is effective in increasing pyrolysis yields for low rank coals and is ineffective or reduces pyrolysis yields for high rank coals. However, there are certain trends, such as the fact that the CO yield appears to follow the tar yield (goes through a maximum along with the tar) and the extractables yields (which does not have a clear trend in most cases), which do not agree completely with this analogy.

3. The changes due to water pretreatment are delayed and attenuated as the pretreatment temperature is reduced.

4. The changes in the mineral composition due to water pretreatment are highly mineral specific.

5. The FT-IR data indicate a general reduction of oxygen groups during water pretreatment,

Including hydroxyl groups.

6.   The results from liquefaction experiments on samples produced to date indicate only modest benefits in the best cases. The worst results are obtained at short pretreatment times where solvent incorporation into the coal is apparently reducing the observed yields of soluble products.

7.   The data are consistent with a mechanism in which water pretreatment increases the concentration of ortho dihydroxy species in the coal at short pretreatment times. These functions are believed to be responsible for the solvent incorporation reactions. They can be removed by increasing the pretreatment time or mild oxidation of the coal after water pretreatment.

Quantitative Modeling - Work was begun on using the AFR FG-DVC pyrolysis/liquefaction model to model the results of the steam pretreatment experiments with Zap lignite. It was decided to use the Zap data from pretreatment at 350°C since this is the most complete data set and has the most number of repeats. We also restricted ourselves to the data from short pretreatment times, since it appears that the behavior at long pretreatment times is more complex. The pyrolysis version of the FG-DVC model was successful at predicting the increase in pyrolysis tar yield based on the lower amounts of CO_2 and the higher amounts of extractables and CH_4, which are inputs into the model. A comparison of the measured (*-*) and predicted (---) pyrolysis yields is given in Fig. V-8 for the raw and water pretreated coals. The simulation of the liquefaction results for these same conditions indicated about a 25% increase in the pyridine solubles, a 10% increase in toluene solubles, and a 5% increase in hexane solubles. A comparison of the measured (symbols) and predicted (lines) liquefaction yields is given in Fig. V-9 for the raw and water pretreated coals. The FG-DVC liquefaction model provides good predictions of data for raw coals, as shown in Fig. V-9a and modified coals (Serio, et al., 1989). However, the model is not in good agreement with the liquefaction data for the water pretreated coal (discussed in Section IV), which show a significant decline in these values, at short pretreatment times.

In Fig. V-10, a plot is shown of a van Krevelen diagram for the Argonne coals. The simulation of the standard FG-DVC model for maturation conditions is shown as a solid line. The simulation of a modified FG-DVC model for maturation in which CO and CO_2 are removed with a higher rate
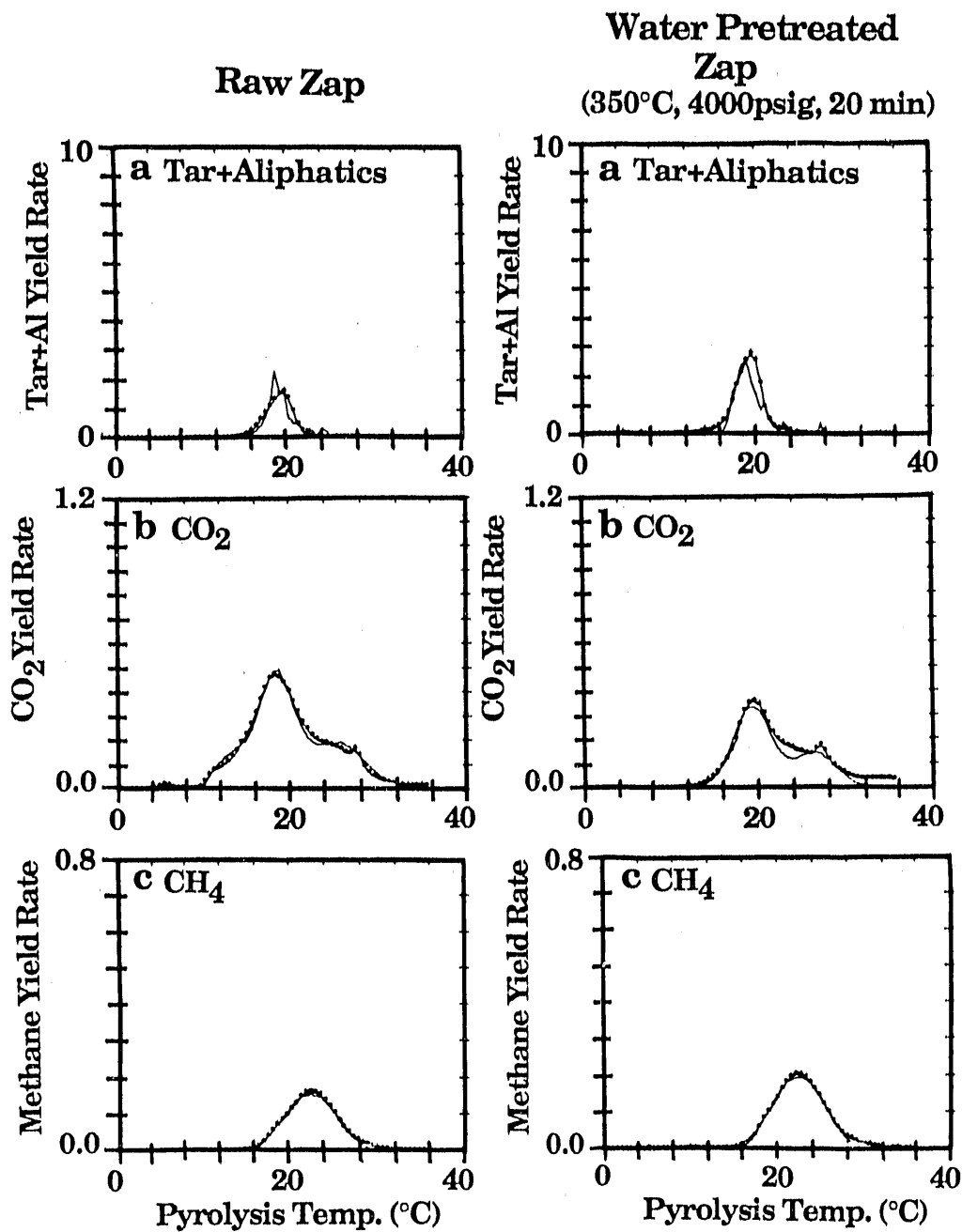
Raw Zap

Water Pretreated
Zap
(350°C, 4000psig, 20 min)

a Tar+Aliphatics

a Tar+Aliphatics

b CO_2

b CO_2

c CH_4

c CH_4

Pyrolysis Temp. (°C)

Pyrolysis Temp. (°C)

Figure V-8. Comparison of Measured and Predicted Yields from Pyrolysis of Raw Zap and Water Pretreated Zap Lignites.
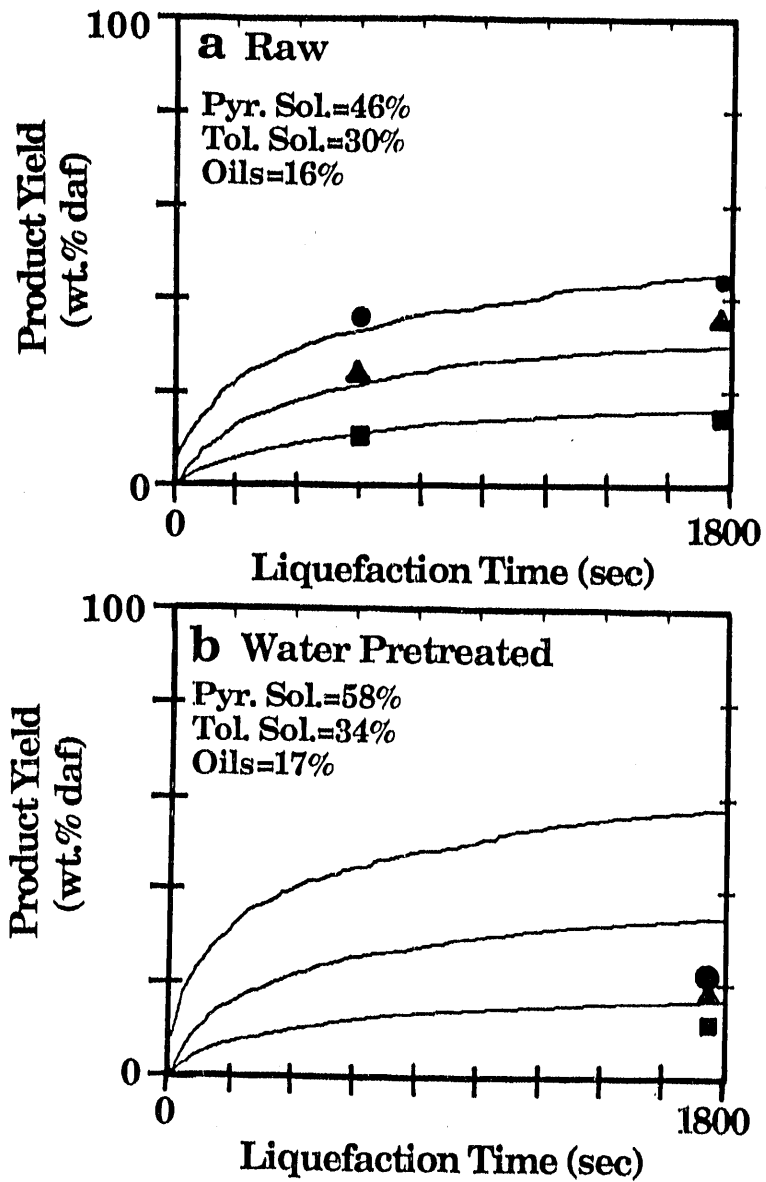
Figure V-9. Comparison of Measured and Predicted Yields From Liquefaction of Raw Zap and Water Pretreated Zap Lignites.
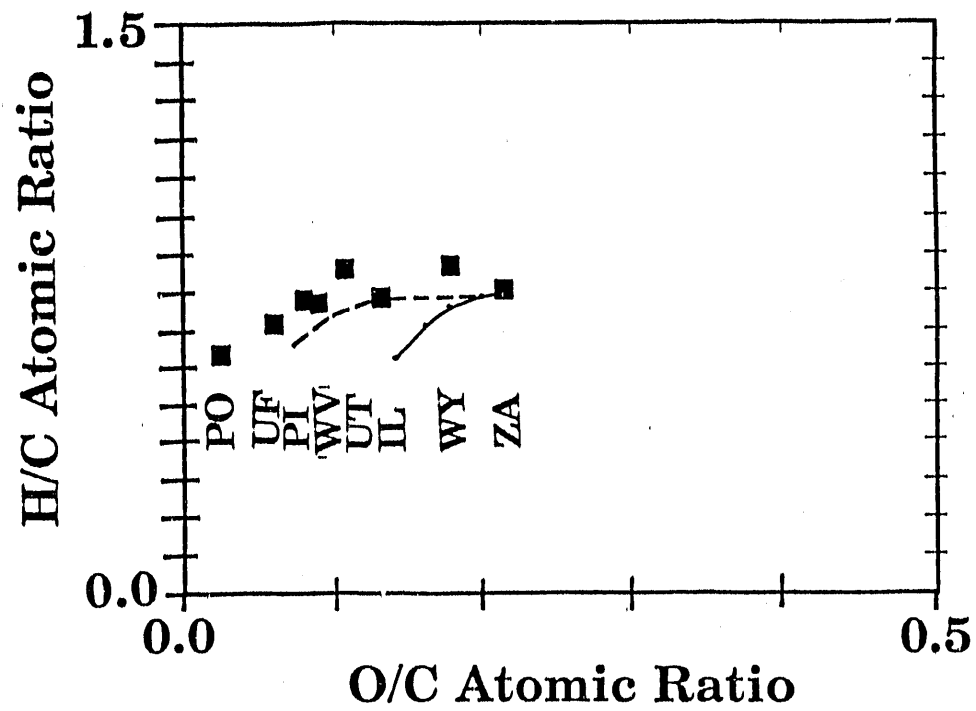
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Figure V-10. Maturation of Coal.

process is shown as a dashed line. This work is discussed in more detail in Solomon et al (1990). The results for the gas yields and FT-IR analysis of the water pretreated residues indicates that the process more closely follows the dashed line than the solid line. However, this will need to be confirmed by doing elemental analysis of the residues and additional FT-IR analyses.

Data Analysis - Work was completed on a paper which summarized our work on water pretreatment of coal. It was presented at the Symposium on "Fuel Pretreatment for Conversion" at the Atlanta (April 14-19, 1991) ACS meeting. It is included as Appendix A of the Sixty Quarterly Report.

The data from the experiments done on water pretreatment were entered into a spreadsheet in order to facilitate comparison with the changes in experimental conditions and coal types. The spreadsheet program also interfaces with a plotting program which simplifies the generation and updating of plots. A macro was developed to automatically generate plots from this database. The database includes more than 90 experiments and each experiment has more than 50 columns of data on conditions, pretreatment yields, residue analyses, etc., since the data are often calculated on more than one basis (dry, DAF, normalized, etc.). Consequently, the use of the spreadsheet became necessary. While it took some time to set this up, it is easy to maintain and will also make it easy to share data with others in the water pretreatment research area.

VI. PLANS FOR THE NINTH QUARTER

- Do water pretreatment experiments on demineralized and other modified coals.

- Do additional blank pretreatment experiments to assess the effects of temperature, pressure and moisture.

- Do additional pretreatment experiments on Illinois No. 6 coal, including mild oxidation before and after pretreatment.

- Do additional experiments to vary the type (continuous or batch) and mode (early or late) of water injection.

- Do additional characterizations (FT-IR, FIMS, elemental) of steam pretreated residues.

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