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**THE DUAL ROLE OF OXYGEN FUNCTIONS IN COAL PRETREATMENT AND
LIQUEFACTION: CROSSLINKING AND CLEAVAGE REACTIONS**

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**THE DUAL ROLE OF OXYGEN FUNCTIONS IN COAL PRETREATMENT AND
LIQUEFACTION: CROSSLINKING AND CLEAVAGE REACTIONS**

SIXTH QUARTERLY REPORT - CONTRACT NO. DE-AC22-91-PC91026

TABLE OF CONTENTS

Disclaimer	i
Abstract	ii
I. INTRODUCTION	1
II. TASK 1 - WORK PLAN	1
III. TASK 2 - STUDIES WITH COALS AND MODIFIED COALS	1
IV. TASK 3 - STUDIES WITH POLYMERIC MODEL SYSTEMS	12
V. TASK 4 - DATA INTEGRATION AND REPORTING	22
VI. PLANS FOR SEVENTH QUARTER	22
References	22

DE-AC22-91-PC91026
SIXTH QUARTERLY
REPORT

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ABSTRACT

Water Addition to Liquefaction Systems - It is known from our results and the literature that the moisture is associated with cations in raw low rank coals. Consequently, an investigation was made to determine if the deleterious effects of cations could be mitigated by adding water to the donor solvent liquefaction system. Experiments were done with raw and demineralized Zap at three different temperature levels. At temperatures near or below the critical temperature of water (374° C), it appears that there is a profound beneficial effect of added water for the raw coal. Conversely, there is a significant deleterious effect of added water for the demineralized coals. The ability of water to interact with cations and affect the course of the thermal decomposition behavior is consistent with results that have been observed in hydrothermal treatment of coal, which mimics the geological aging process in many respects.

Analysis of MBI Samples - Upon the recommendation of Malvina Farcasiu, a sample of demineralized (DMN) Argonne Wyodak coal was prepared for the Michigan Biotechnology Institute (MBI). This was subjected to biological pretreatment for removal of carboxyl groups and sent back to us along with samples of biopretreated raw coal and a control sample. The control sample was a raw Wyodak sample which had been added to the growth medium but which was not inoculated with bacteria. At AFR, the five samples were subjected to FT-IR pellet analysis, TG-FTIR analysis, SEM/x-ray analysis, and liquefaction experiments in a donor solvent. In summary, the results from the various analyses indicate a modest benefit to the MBI biotreatment process for the raw coal and a negative result for the demineralized coal. In all cases, the best sample from a liquefaction standpoint was the normal demineralized coal. This is consistent with our other data from coal and model compound studies which suggest that carboxyl groups are not bad actors as far as retrogressive reactions are concerned but rather the cations which are exchanged on these groups. Consequently, efforts on biological pretreatment should be redirected toward removal of cations rather than carboxyl groups.

Synthesis of $-(C_6H_4-O-CH_2CH_2)_n-$ Polymers - In the current work, we have successfully developed a new route to these C-C-O polymers, and we believe they re-emerge as the better vehicle for addressing, in a polymeric context, the question of the effect of decarboxylation and other factors on crosslinking in low-rank coals. We felt last quarter, in fact, that we had come to a satisfactory optimization of this new synthetic route with a single-reaction vessel preparation which would go all the way from the starting 4-hydroxyphenethyl alcohol to the 4-hydroxyphenethyl iodide by using three equivalents of trimethylsilyl iodide. However, this conclusion was premature: we found out in this quarter that the final step - polymerization of the iodide - proceeds with poor yield because base-catalyzed elimination of HI is the major pathway. In the current quarter we have made what we believe is the last change in this synthesis, switching to the use of trimethylsilyl bromide.

Larger Scale Preparation of the $-(C_6H_4-O-CH_2CH_2)_n-$ Polymers - The first attempted larger scale synthesis of the basic β -ether- bridged polymer involved the use of trimethylsilyl iodide, as indicated above. Starting with 5 grams of the 4-hydroxyphenethyl alcohol, we obtained the $-(C_6H_4-O-CH_2CH_2)_n-$ polymer in good purity (by solution-phase ^{13}C - and proton- NMR), but in a yield of only ~16%. This gave us only about 700 mg of purified material, not enough even to perform one liquefaction experiment at the 1-gram scale now used at AFR. Since increasing the scale even to 10 grams would not give enough for more than 1 liquefaction experiment, and increasing the scale further can introduce other problems that would then have to be worked out, we decided to try another variation of the same basic approach.

Because the polymerization of an earlier step-wise preparation of 4-hydroxy-phenethylbromide had been quite efficient (though the bromide itself had been rather difficult to obtain), we tried a final variation in which the trimethylsilyl iodide was replaced by trimethylsilyl bromide. Starting with 5.0 grams of the 4-hydroxyphenethyl alcohol, we obtained 3.1 grams of the solid polymer (90% yield). The yield was not only very good, but this preparation appears to be substantially higher in molecular weight than our previous preparations. It is completely insoluble in methylene chloride, THF, DMSO, and DMF. The structure and purity of this and the earlier soluble preparations of this polymer was examined based on GPC, NMR, and FIMS analyses. In brief, this higher molecular

weight, insoluble polymer preparation has passed all the structure and purity tests to which it has been subjected. At this point, the only remaining test for this latest product is elemental analysis.

Preparation of the $-\text{[C}_6\text{H}_3(\text{o-Me})\text{-O-CH}_2\text{CH}_2\text{]}_n\text{-}$ Polymer- The $-\text{O-C-C-}$ linked polymer with a methoxy located ortho- to the bridge oxygen contains what is probably the most common lignin linkage type. Furthermore, it is undoubtedly a more reactive structure (presumably both with respect to cleavage and to crosslinking) than is $-(\text{C}_6\text{H}_4\text{-O-CH}_2\text{CH}_2)_n\text{-}$ itself. Therefore, we consider the methoxy-substituted polymer to be the model system that will reveal the most about the chemistry of low-rank coals. We chose to synthesize $-(\text{C}_6\text{H}_4\text{-O-CH}_2\text{CH}_2)_n\text{-}$ first, anticipating both that the chemical behavior of the more complex polymer will be less informative if it is observed in isolation, and that we would learn useful lessons in the synthesis of the simpler polymer. The synthesis of the methoxy-substituted polymer has thus far shown the second expectation to be correct. We have now performed four of the five steps necessary to obtain the polymer, leaving only the polymerization step itself.

The Decarboxylation and Coupling of Aromatic and Aliphatic Acids - During this quarter, we completed our survey of the decarboxylation and coupling of some prototypical monomeric carboxylic acids under "liquefaction" conditions. The bulk of these results were discussed in the previous quarterly report and in the American Chemical Society Fuel Division preprint. The experiments performed this quarter involved testing the effect of iron sulfide as another iron salt of potential importance in crosslinking during the heating of coals. We also tested the effect of water on the behavior of phenylacetic acid. Finally, we have prepared, purified, and tested the behavior of the calcium salts of benzoic acid and anisic acid $[\text{Ca}^+\text{C}_6\text{H}_4(\text{o-OCH}_3)\text{CO}_2^-]$. In brief, the results are that the decomposition of the calcium salts does *not* substantially increase the tendency for crosslinking to occur in association with decarboxylation. This is surprising in light of the evidence for cation influence on retrogressive reactions in coals and modified coals. This result suggests that an important experiment would be to study carboxyl polymers with/without calcium salts. However, it is unlikely that this can be done under the current program since these polymers are not readily available.

I. INTRODUCTION

The overall objective of this project is to elucidate and model the dual role of oxygen functions in thermal pretreatment and liquefaction of low rank coals through the application of analytical techniques and theoretical models. The project will be an integrated study of model polymers representative of coal structures, raw coals of primarily low rank, and selectively modified coals in order to provide specific information relevant to the reactions of real coals. The investigations will include liquefaction experiments in microautoclave reactors along with extensive analysis of intermediate solid, liquid and gaseous products. Attempts will be made to incorporate the results of experiments on the different systems into a liquefaction model.

II. TASK I - WORK PLAN

This task is complete.

III. TASK 2 - STUDIES WITH COALS AND MODIFIED COALS

Moisturized Coal Samples - Remoisturization of vacuum dried Zap and Wyodak was done in the attempt to understand if moisture uptake for low rank coals is a reversible process and to see if moisture influences the role of the cations. The remoisturized samples were analyzed by programmed pyrolysis with TG-FTIR. Preliminary results show that the moisture content can be restored to values which are close to those of the raw coals, especially for Zap.

The detailed results for the pyrolysis and liquefaction experiments are given in Tables III-1 and III-2 and were discussed in the Fifth Quarterly Report. In general, pyrolysis tar yields and the toluene solubles yields from liquefaction for the remoisturized samples were similar to those for the vacuum dried samples. It appeared that the liquefaction results were more sensitive to the presence of moisture, although the increases in asphaltene yields were generally balanced by decreases in oil yields. A possible explanation for the difference is that most of the moisture is depleted early in the pyrolysis process, whereas the moisture is retained in the reactor during liquefaction and can exist in a liquid phase under the right conditions.

It is also known from our results (1) and the literature (2) that the moisture is associated with cations in raw coals. Consequently, an investigation was made to determine if the deleterious effects of cations could be mitigated by adding water to the donor solvent liquefaction system. Results from experiments with raw and demineralized Zap at three different temperature levels are given in Table III-3. At temperatures near or below the critical temperature of water (374° C), it appears that there is a profound beneficial effect of added water for the raw coal (note the significant reduction in CO₂ evolution). Conversely, there is a significant deleterious effect of

TABLE III-1 - Liquefaction Results of Vac Dry Modified Coal Samples

TABLE III-1 - Liquefaction Results of Vac Dry Modified Coal Samples											
	Toluene Solubles			Toluene Insolubles	Gas						
Coal (Type/Preparation)	Total	Oils	Asphaltene		Total	H ₂	CO ₂	CO	CH ₄	C ₂ H ₆	C ₂ H ₄
Zap Vac Dry											
demin.	52	26	26	46	2.2	0.02	1.1	0.43	0.27	0.29	0.05
demin. + K ⁺ (pH8)	30	11	19	62	8.4	—	7.7	0.27	0.17	0.20	0.02
demin. + Ca ⁺⁺ (pH8)	25	13	12	72	3.4	—	2.7	0.30	0.22	0.14	—
demin. + Ba ⁺⁺ (pH8)	37	25	12	55	8.2	0.02	7.3	0.40	0.20	0.24	—
demin. + K ⁺ (pH12.5)	17	5	12	77	5.8	0.05	5.0	0.24	0.27	0.28	—
demin. + Ca ⁺⁺ (pH12.5)	(—)	(—)	3		0.9	—	0.7	0.04	0.08	0.07	—
demin. + Ba ⁺⁺ (pH12.5)	15	15	0.5	84	1.0	—	0.3	0.27	0.02	0.41	—
Wyodak Vac Dry											
demin.	54	22	32	43	2.9	0.01	2.2	0.31	0.11	0.24	0.04
demin. + K ⁺ (pH8)	46	26	20	46	8.5	0.04	7.6	0.34	0.21	0.27	0.01
demin. + Ca ⁺⁺ (pH8)	14	4	10	82	4.1	—	3.8	0.19	0.04	0.06	—
demin. + Ba ⁺⁺ (pH8)	37	25	12	62	0.7	0.02	—	0.43	0.08	0.19	—
demin. + Ba ⁺⁺ (pH12.5)	7	5	2	89	3.9	0.09	3.4	0.23	0.02	0.12	0.04

TABLE III-2 - Liquefaction Results of Moisturized Modified Coal Samples*

Coal (Type/Preparation)	Toluene Solubles			Toluene Insolubles	Gas						
	Total	Oils	Asphaltene		Total	H ₂	CO ₂	CO	CH ₄	C ₂ H ₆	C ₂ H ₄
Zap, moisturized											
demin.	56±5	28±2	28±7	40±5	4.3	—	3.9	0.18	0.01	0.10	—
demin. + K ⁺ (pH8)	25	20	5	66	9.5	—	8.9	0.40	0.04	0.14	—
demin. + Ca ⁺⁺ (pH8)	29	18	11	66	4.5	—	4.1	0.20	0.12	0.08	—
demin. + Ba ⁺⁺ (pH8)	17	8	9	74	8.5	—	7.4	0.88	0.15	0.08	0.01
demin. + K ⁺ (pH12.5)	28	10	18	57	15.3	—	14.9	0.13	0.13	0.12	0.02
demin. + Ca ⁺⁺ (pH12.5)	10	9	2	87	2.2	—	1.9	0.24	0.01	0.05	—
demin. + Ba ⁺⁺ (pH12.5)	13	3	10	76	10.7	—	10.1	0.45	0.10	0.10	—
Wyodak, moisturized											
demin.	57	11	46	38	4.7	0.05	4.0	0.32	0.11	0.14	—
demin. + K ⁺ (pH8)	55	29	26	32	12.8	0.01	12.0	0.33	0.17	0.23	0.02
demin. + Ca ⁺⁺ (pH8)	32	13	19	63	4.7	—	4.3	0.22	0.06	0.08	0.01
demin. + Ba ⁺⁺ (pH8)	25	7	18	67	8.7	—	6.8	1.93	0.11	0.06	—
demin. + Ba ⁺⁺ (pH12.5)	26	15	12	67	7.0	0.01	6.7	0.27	0.01	0.01	0.02

* Conditions: 440 °C, 30 min., dihydrophenanthrene solvent (0.5 g coal; 3 g solvent)

added water for the demineralized coals. The ability of water to interact with cations and affect the course of the thermal decomposition behavior is consistent with results that have been observed in hydrothermal treatment of coal, which mimics the geological aging process in many respects.

Table III-3 Effect of Added Water on Liquefaction of Raw and Demineralized Argonne Zap Coal.

Temp. Level (°C)	Water Addition	Toluene Solubles wt.%, daf		CO ₂ Yields wt.%, daf	
		Raw	Demin.	Raw	Demin.
350	yes	13	0	0.0	1.1
	no	1	27	5.4	2.4
375	yes	23	19	2.4	1.5
	no	11	40	5.2	2.2
400	yes	31	24	5.2	0.8
	no	30	58	4.1	4.2

Analysis of MBI Samples - Upon the recommendation of Malvina Farcasiu, a sample of demineralized (DMN) Argonne Wyodak coal was prepared for the Michigan Biotechnology Institute (MBI). This was subjected to biological pretreatment for removal of carboxyl groups (4) and sent back to us along with samples of biopretreated raw coal and a control sample. The control sample was a raw Wyodak sample which had been added to the growth medium but which was not inoculated with bacteria. At AFR, the five samples were subjected to FT-IR pellet analysis, TG-FTIR analysis, SEM/x-ray analysis, and liquefaction experiments in a donor solvent.

The results for the curve resolving of the carbonyl region of the FT-IR spectra are shown in Table III-4. The results from the liquefaction experiments are shown in Table III-5.

Table III-4 shows the data for the carboxylic acid carbonyl and the sum of the free and hydrogen bonded or conjugated carbonyls. The COOH concentration measurements were somewhat variable when duplicate pellets were measured, but indicate a slight decrease in the carboxyl concentration as a result of biotreatment of the raw coal. A surprising result was the apparent increase in the COOH concentration for the DMN, biotreated sample when compared to the normal DMN sample. Unfortunately there was no control done for the DMN sample so it cannot be established if this was due to the addition of the acidic growth medium. However, this is a likely explanation. The changes in the sum of the free and H-bonded carbonyls for the control sample

Table III-4 FT-IR Analysis of Carbonyl Region for Normal and Biotreated Samples

Coal	Peak heights (arbitrary units)	
	COOH	C = O*
Raw	0.06	0.08
DMN	0.09	0.11
Raw, control	0.05	0.25
Raw, biotreated	0.04	0.21
Raw, biotreated	0.04	0.25
DMN, biotreated	0.15	0.14
DMN, biotreated	0.19	0.18

* Sum of free and H-bonded forms

Table III-5 Liquefaction Yields (DAF%) for Normal and Biotreated Samples

Coal	Tol. sol.	Oils	Asph.	CO ₂	CO	CH ₄
*Raw	34	19	15	0.8	0.1	0.03
*DMN	54	22	32	2.2	0.3	0.1
*DMN + H ⁺	36	14	22	0.0	0.2	0.04
Raw, Control	38	24	14	3.9	0.3	0.05
Raw, biotreated	41	26	15	0.6	0.3	0.11
DMN, biotreated	42	25	17	0.5	0.3	0.12

* Liquefaction done in dihydrophenanthrene

suggests that significant changes have taken place as a result of the processing which is done prior to the biological activity. This is a major difficulty in interpreting these results.

The liquefaction experiments were carried out at 400° C for 30 min. with 6:1 tetralin: coal. Table III-5 shows the results of these experiments on the MBI samples along with values for the raw Argonne Wyodak coal. The biotreatment of the raw coal leads to only modest increases in the liquefaction yields. The biotreatment of the demineralized coal actually resulted in yields lower than expected from the normal demineralized coal. However, we have found that residual acid (from incomplete washing) can significantly reduce the solubles yields, as indicated in Table III-5. Consequently, the benefit of the biotreatment may have been offset by the addition of the acidic nutrient media to the coal.

In the case of the biotreated raw coal, there was a modest reduction in the CO₂ yield in liquefaction due to biotreatment which is consistent with the modest reduction in carboxyl groups. However, there was a very large increase for the raw control sample which was not reflected in a large increase in carboxyl group content (see Table III-4). In addition, the results for the DMN samples are hard to reconcile since the trends for CO₂ yields and carboxyl content are in opposite directions. We have found that the CO₂ yield in liquefaction is very sensitive to the liquefaction conditions and can also be influenced by secondary reactions. Another factor, in this case, is the unknown effect of the addition of the nutrient media.

The results for the TG-FTIR analysis and SEM/x-ray analysis are given in Tables III-6 and III-7 respectively. The results for the tar yields from programmed pyrolysis in the TG-FTIR are largely consistent with the results from the liquefaction experiments, i.e., there appeared to be a modest benefit to biotreating the raw coal and a significant detriment to biotreating the demineralized coal. Again, the lack of a control for the demineralized sample makes the interpretation of the latter results more difficult. It was noted by the investigators at MBI that maintaining an optimum pH for the demineralized samples was more difficult.

There was a decrease in CO₂ yield from TG-FTIR for the biotreated samples, but not as large as the decrease in the CO₂ yield for the normal demineralized sample (see Table III-6). These changes do not correlate with the change in the free carboxyl content reported in Table III-4. This is not surprising in light of the fact that it is the cation-exchanged (carboxylate) form which is more likely to produce CO₂ upon pyrolysis. It is also true that model polymers which have no carboxyl group content will produce CO₂ upon pyrolysis, probably due to secondary reactions of CO and H₂O (5).

The results for the SEM/x-ray analysis of the normal and biotreated samples are given in Table III-7. Since this system is in need of recalibration, these numbers should not be considered absolute.

TABLE III-6 - SUMMARY OF TG-FTIR RESULTS ON NORMAL AND BIOTREATED WYODAK SAMPLES

SAMPLE IDENTIFICATION

SPECIES	RAW	RAW, CONTROL	RAW, BIOTREATED (#5)	RAW, BIOTREATED (#13)	DMN	DMN BIOTREATED (DRI)	DMN BIOTREATED (DLI)
% Char, DAF	54	54	52	53	50	53	54
% Ash, AR	7	7	8	10	0	5	2
% M, AR	25	10	6	8	2	3	4
Tars, DAF	15	18	21	21	30	20	21
CH ₄ , DAF	2.2	2.3	2.1	1.8	2.8	2.4	2.2
H ₂ O, DAF	12	10	11	11	5	14	11
CO ₂ , DAF	5.4	4.7	4.6	4.4	2.4	4.4	4.0
CO, DAF	13.4	10.7	10.1	8.2	9.6	7.4	7.0
ΣO, DAF*	21	18	19	18	12	19	17

* Sum of oxygen in H₂O, CO, and CO₂

TABLE III-7 - SUMMARY OF SEM/X-RAY ANALYSIS RESULTS ON NORMAL AND BIOTREATED WYODAK SAMPLES

SAMPLE IDENTIFICATION

SPECIES (DRY WT. %)	RAW	RAW, CONTROL	RAW, BIOTREATED (#5)	RAW, BIOTREATED (#13)	DMN	DMN BIOTREATED (DRI)	DMN BIOTREATED (DLI)
% Ash	6.44	5.76	6.98	6.65	0.30	1.96	1.99
% Na	0.00	0.00	0.00	0.19	0.00	0.05	0.06
% Mg	0.23	0.00	0.00	0.00	0.03	0.09	0.10
% K	0.01	0.03	0.32	0.59	0.00	0.22	0.25
% Ca	1.09	1.17	1.10	0.74	0.04	0.18	0.18
% S (o)	0.36	0.47	0.54	0.48	0.35	0.47	0.53
% S (m)	0.19	0.18	0.17	0.11	0.13	0.17	0.16

The numbers for total ash content show the same general trends as the TG-FTIR values in Table III-6. The values for the calcium content, most of which is exchanged on carboxyl groups, do not appear to be affected much by biotreatment. As expected, these values are much lower for the demineralized samples. The values of organic or mineral sulfur are small to begin with and did not appear to be affected much by biotreatment.

In summary, the results from the various analyses indicate a modest benefit to the MBI biotreatment process for the raw coal and a negative result for the demineralized coal. In all cases, the best sample from a liquefaction standpoint was the normal demineralized coal. This is consistent with our other data from coal and model compound studies which suggest that carboxyl groups are not bad actors as far as retrogressive reactions are concerned but rather the cations which are exchanged on these groups. Consequently, efforts on biological pretreatment should be redirected toward removal of cations rather than carboxyl groups.

IV. TASK 3 - STUDIES WITH POLYMERIC MODEL SYSTEMS

INTRODUCTION

During the last three months this work has involved (a) completion of the series of decarboxylation /coupling studies we have performed on several prototypical aromatic- and aliphatic carboxylic acids, (b) completion of a larger scale synthesis of the $-(C_6H_4-O-CH_2CH_2)_n-$ polymer, and (c) completion of four of five steps in the preparation of the $-[C_6H_3(o-OMe)-O-CH_2CH_2]_n-$ polymer.

It has become increasingly clear in recent years not only that retrograde reactions substantially hinder the liquefaction of low-rank coals, but also that oxygen functional groups in the coal structure are major actors in these retrograde reactions. The evidence connecting oxygen groups to the formation of new, strong bonds, though convincing, is largely phenomenological in nature rather than mechanistic. Thus we know that crosslinking is correlated with the evolution of CO_2 and H_2O and therefore that carboxyl and/or phenolic groups are probably involved, but we do not know exactly how or why. In order to know how to best mitigate the retrograde reactions, it is necessary to better understand their mechanisms-i.e., to know what factors promote and inhibit these reactions.

Task 3 complements the other tasks in this project in that it seeks to help understand why certain pretreatments tested with real coals are found to mitigate retrograde reactions and thus help lead to improved or different pretreatments. The approach to achieving this goal is to prepare and study the behavior of polymeric coal models under liquefaction conditions. This will provide us not only with starting materials and products that are both better known than is possible with real coals, but also with structures and reaction conditions that are more relevant to the liquefaction of real coals

than are the typical "model compound" studies. Polymeric models should be more relevant to coals particularly with respect to mass-transport factors that come into play with insoluble starting materials. The difficulty is not to make them *too* relevant: If the polymers are too much like real coals, both they and their products will be un-analyzable. Therefore, judicious choices are necessary in the attempt to focus on those oxygen-containing structures that are likely to be key to retrograde reactions in low-rank coals.

The first objective of Task 3 is to prepare polymer models having phenolic, carboxylic, and/or aryl ether groups considered to be important in low rank coals. There are two aspects to the choice of appropriate polymers: the choice of the polymeric backbone and the choice of the functional groups. One approach is to focus on the chemistry of the chosen functional groups in a polymeric matrix by selecting a polymer backbone that is itself not subject to cleavage under the reaction conditions (e.g., polyaryls). The other approach is to choose a backbone that is presumed to be coal-relevant and seek to understand its behavior first without, and then with, appended, relevant oxygen functional groups. As discussed in the Annual Topical Report, we have worked on both of these approaches, using in the first case a refractory backbone of biaryl linkages (i.e., poly(phenylenes)), and in the second case a backbone having the major linkage type known to exist in lignins and presumed to be at least partially retained in low-rank coals. In Quarterly Report No. 5, we discussed the difficulties in the first approach and the progress made on the second. We have continued this quarter to focus on the second approach, involving synthesis of polymers connected by $-\text{CH}_2\text{CH}_2\text{O}-$ linkages.

The O-C-C " β -ether" connection between adjacent aromatic rings is the most abundant linkage in lignins, from both angiosperm and gymnosperm sources. In the absence of evidence to the contrary, we have begun by assuming that some significant fraction of these linkages survive into the low-rank coals. If these linkages are important in lignites and subbituminous coals, they provide a very interesting situation. The β -ether linkage is known to be quite labile, via a free radical chain reaction, under coal liquefaction conditions (6). In its simplest form, in phenylphenethyl ether ($\text{C}_6\text{H}_5\text{-O-CH}_2\text{-CH}_2\text{-C}_6\text{H}_5$), the β -ether linkage has a half life at 400°C of 120 minutes, forming styrene and phenol (7). Thus one might speculate that if lignite were composed substantially of such linkages, it would simply fall to pieces under liquefaction conditions *unless* retrograde reactions were very facile. Indeed, in the previous contract, we found that two different polymers presumably consisting largely of the β -ether linkage, showed both facile cleavage *and* extensive crosslinking. However, this observation was clouded by the fact that side reactions could not readily be eliminated in the polymer, synthesis (using mercuric trifluoroacetate of 4-allylphenol and eugenol (2-methoxy-4-allylphenol)), and we were never able to obtain polymers that gave the correct elemental analysis. For this reason, more extensive study and interpretation of those earlier polymer preparations was judged to be premature.

WORK PERFORMED

Synthesis of $-(\text{Ar-OCH}_2\text{CH}_2)_n$ Polymers - In the current work, we have successfully developed a new route to these C-C-O polymers, and we believe they re-emerge as the better vehicle for addressing, in a polymeric context, the question of the effect of decarboxylation and other factors on crosslinking in low-rank coals. We felt last quarter, in fact, that we had come to a satisfactory optimization of this new synthetic route with a single-reaction vessel preparation which would go all the way from the starting 4-hydroxyphenethyl alcohol to the 4-hydroxyphenethyl iodide by using three equivalents of trimethylsilyl iodide. However, this conclusion was premature: we found out in this quarter that the final step - polymerization of the iodide - proceeds with poor yield because base-catalyzed elimination of HI is the major pathway. In the current quarter we have made what we believe is the last change in this synthesis, switching to the use of trimethylsilyl bromide. This reaction sequence is outlined in Scheme 1.

Scheme 1. Shortened synthesis of 4-hydroxyphenethyl bromide with trimethylsilyl bromide.

The 4-hydroxyphenethyl bromide is isolated and the phase-transfer catalysis approach discussed in the annual topical report is used to produce the C-C-O bridged polymer.

Larger Scale Preparation of the $-(\text{C}_6\text{H}_4-\text{O}-\text{CH}_2\text{CH}_2)_n$ Polymer - The first attempted larger scale synthesis of the basic β -ether- bridged polymer involved the use of trimethylsilyl iodide, as indicated above. Starting with 5 grams of the 4-hydroxyphenethyl alcohol, we obtained the $-(\text{C}_6\text{H}_4-\text{O}-\text{CH}_2\text{CH}_2)_n$ polymer in good purity (by solution-phase ^{13}C - and proton- NMR), but in a yield of only ~16%. This gave us only about 700 mg of purified material, not enough even to perform one liquefaction experiment at the 1-gram scale now used at AFR. Since increasing the scale even to 10 grams would not give enough for more than 1 liquefaction experiment, and increasing the scale further can introduce other problems that would then have to be worked out, we decided to try another variation of the same basic approach.

Because the polymerization of an earlier step-wise preparation of 4-hydroxy-phenethylbromide had been quite efficient (though the bromide itself had been rather difficult to obtain), we tried a final

variation in which the trimethylsilyl iodide was replaced by trimethylsilyl bromide. Starting with 5.0 grams of the 4-hydroxyphenethyl alcohol, we obtained 3.1 grams of the solid polymer (90% yield). The yield was not only very good, but this preparation appears to be substantially higher in molecular weight than our previous preparations. It is completely insoluble in methylene chloride, THF, DMSO, and DMF. The structure and purity of this and the earlier soluble preparations of this polymer are discussed below in the section entitled "GPC, NMR, and FIMS Analysis of the Polymer Preparations." In brief, this higher molecular weight, insoluble polymer preparation has passed all the structure and purity tests to which it has been subjected. At this point, the only remaining test for this latest product is elemental analysis. Presuming that it also passes this test, the 3.1 grams in the latest batch constitutes enough high molecular weight polymer for AFR to perform several liquefaction tests along with the normal TG-FTIR and FIMS analyses. Although the use of an insoluble polymer presents a difficulty in that we cannot characterize the starting molecular weight distribution, it does provide a polymeric material whose behavior should be more relevant to the originally insoluble portion of low-rank coals than would be our earlier lower molecular weight soluble polymer preparations.

Preparation of the $-(C_6H_3(o-Me)-O-CH_2CH_2)_n-$ Polymer- The -O-C-C- linked polymer with a methoxy located ortho- to the bridge oxygen contains what is probably the most common lignin linkage type. Furthermore, it is undoubtedly a more reactive structure (presumably both with respect to cleavage and to crosslinking) than is $-(C_6H_4-O-CH_2CH_2)_n-$ itself. Therefore, we consider the methoxy-substituted polymer to be the model system that will reveal the most about the chemistry of low-rank coals. We chose to synthesize $-(C_6H_4-O-CH_2CH_2)_n-$ first anticipating both that the chemical behavior of the more complex polymer will be less informative if it is observed in isolation, and that we would learn useful lessons in the synthesis of the simpler polymer. The synthesis of the methoxy-substituted polymer has thus far shown the second expectation to be correct. We have now performed four of the five steps necessary to obtain the polymer, leaving only the polymerization step itself. For this slightly more complex polymer, we could not combine the three ether-formation, halide formation, ether cleavage steps, because the pre-existing -OMe group would itself have been cleaved. We have had instead to carry out each of the steps

individually, as shown below in Scheme 2.

Scheme 2. Synthetic route to the $-\text{[C}_6\text{H}_3(\text{o-Me})\text{-O-CH}_2\text{CH}_2\text{]}_n\text{-}$ precursor.

We have, however, been able to obtain the products of each of the individual steps in Scheme 2 in high yield. After each of the first three steps we have isolated the product and characterized it by solution-phase NMR. This technique has provided a convenient monitor of the extent to which the desired transformation(s) have been achieved. The chemical shifts of the methylene protons on the bridge carbon connected to oxygen (the "β-ether" carbon) provide the most direct assessment of the extent of transformation. The chemical shifts allow one to readily distinguish between -CH₂OH, -CH₂OTs, and -CH₂Br, and -CH₂-OPh at 3.85, 4.3, 3.4, and 4.15 ppm relative to TMS, respectively. By this criterion, the products of the first three steps all were of satisfactory purity.

The 4-hydroxyphenethyl bromide product of the catalytic hydrogenolysis in Step 4 will be purified by column chromatography, since thin-layer chromatography shows it to have two components. Even if it didn't have two components, the difficulty of purifying the insoluble polymer to be made in the next step dictates that we begin the polymerization with an intermediate of suitable purity. After purification, we will subject about 5% (ca. 200 mg) of intermediate IV to the polymerization conditions we have found suitable for its unmethoxylated analog. If these prove suitable for this material also, we will subject the entire remaining portion of the bromide to the phase-transfer catalysis polymerization so that we have a single sample for the various analyses and coal conversion tests.

GPC, NMR, and FIMS Analysis of the Polymer Preparations - For all of the earlier $-(\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_2)_n\text{-}$ preparations that have been at least partly soluble in THF, solution-phase NMR has been the analytical tool of choice for structural determination. It is also a good measure of impurity above about the 3% level (for impurities that contain C and H). Clear distinction can be

made between the proton- and carbon- types in the starting materials and various products, including the most probable side products, such as olefins. NMR results for the soluble polymer preparations were discussed in Quarterly Report No. 5, and will not be repeated here except to say that these NMR supported the expected polymer structure and a level of impurity (apart from traces of tributylamine) of less than about 5%. GPC indicated weight average molecular weights (for those portions soluble in THF) ranging from about 2000 to 4000.

Since no solution-phase NMR is possible for the insoluble product we obtained in our most recent larger-scale synthesis of $-(C_6H_4OCH_2CH_2)_n-$, comparison of the IR absorption spectrum with those of previously confirmed, lower molecular weight, soluble polymer preparations offered the simplest basis for structural confirmation. Notwithstanding any differences in molecular weight, the IR spectra should be essentially identical, *if* the current preparation indeed has the anticipated structure. In fact, the FTIR spectrum of this batch is essentially identical with that of the previous batch (except for the intensity of one absorption at $\sim 1460\text{cm}^{-1}$), for which solution-phase NMR was confirmatory both for structure and purity.

The similarity in IR spectra was sufficient to warrant the next step - analysis by pyrolysis-FIMS to observe the thermal fragmentation behavior and perhaps obtain some information on the molecular weight distribution. This FIMS analysis was performed and the spectrum of the new insoluble polymer is shown in Figure IV-1. For comparison, that of one of the earlier, soluble polymer preparations is shown in Figure IV-2. The FIMS-"volatile" fractions were 79 and 89%, respectively. The FIMS spectra are clearly quite similar, both being dominated by oligomeric fragments at 120, 240, 360, 480, 600, and 720 mass units (representing $-(C_6H_4OCH_2CH_2)_n-$ with one double bond somewhere in the molecule, most often presumably in the terminal alkyl group). The intensity-temperature profiles for these masses clearly indicate no significant fraction of any of these peaks is present as such in the original polymer: they are all generated by thermal decomposition in the temperature-programmed FI source.

The relative intensities of the main peaks in the two spectra are quite similar. The most apparent difference is that the insoluble polymer spectrum (Figure IV-1) is considerably "cleaner", having much lower intensities of the various peaks in between the main fragments. For example, the satellites that vary from the main peaks by $+n(12)$, $+n(14)$, and -2 have only 1/3 to 1/2 the relative intensity in Figure IV-1 that they have in Figure IV-2. Also the peak at m/z 185, due to unremoved tri-*n*-butyl amine is only about 1/10 of that in the earlier preparation (Figure IV-2). The lower level of miscellaneous impurities is also reflected in the vacuum evaporation curves, where less than about 2% of the detected volatiles from the recent preparation appear by 250°C , as compared to about 6-7% with the older polymer. In Figure IV-1, there are two unidentified peaks at m/z 161 and 271 accounting together for about 2% of the total ion intensity. Bromine appears to be completely absent, as indicated by the absence of any twin peaks attributable to structures

A29701.SUM T = 28 TO 600 DEG C N AV MW=232 WT AV MW=347
 AR CCO NEW POLYMER (INSOL SOLID) ¹³C 1-11

Figure 1. Pyrolysis-FI mass spectrum of Insoluble $-(\text{PhOCH}_2\text{CH}_2)_n-$ polymer preparation.

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SRI FIMS V2.0

B19601.SUM T = 58 TO 600 DEG C N AV MW=326 WT AV MW=497

¹³C 2-11

POLIMER (RIPU)

Figure 2. Pyrolysis-FI mass spectrum of THF-soluble $-(\text{PhOCH}_2\text{CH}_2)_n-$ polymer preparation.

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containing the equal-abundance isomers of bromine. It thus appears from the IR and FIMS spectra that on the basis of purity and confirmed structure this polymer will be suitable for meaningful liquefaction and other conversion studies. We anticipate that elemental analysis will support this judgment.

The Py-FIMS analyses already allow us to draw some interesting, if still tentative, conclusions about thermal behavior of these materials. It should be noted that the satellites at +12, +14, and -2 are not impurities as such. They, like the main peaks, are not present in the original polymer, but are produced in the thermal decomposition process that sets in about 350°C. For some reason there are more transalkylation and other interconversion reactions taking place with the more impure polymer, thus amplifying further its appearance of impurity. While these subtle differences may ultimately tell us more about the chemistry of fragmentation and crosslinking of these polymers, the spectra are much more similar than they are different. The basic conclusion is that, notwithstanding significant differences in residual tributylamine and differences in molecular weight, the two polymers show the same pyrolytic behavior.

However, the large FIMS-volatile fractions in both of these cases (79% and 89% for Figures IV-1 and IV-2, respectively), together with the similar distribution of oligomeric fragments, suggests that liquefaction yields of the polymer itself will be very high. The monomeric fragment as m/z 120 is the most abundant fragment not only in the sum spectra, but also in the individual spectra recorded as the probe temperature is rising. Below 250°C, there is virtually no intensity at m/z 120, 240, etc. Any organic structure of mass 120 (or even 240) will vaporize long before 250°C. At about 300°C, the onset of thermal decomposition is reached and all of these fragments appear. Even at the onset of decomposition, the intensity of the monomeric fragment is at least twice the intensity of any of the other fragments. This means that either there is coordinated bond cleavage (i.e., unzipping), or that the polymer is so heavily crosslinked (or becomes so during heating) that only very small pieces, mainly monomer, are released during pyrolysis. The results described here strongly suggest that the former conclusion is correct: bond scission is coordinated rather than random. If crosslinking were competitive with what clearly is facile bond scission, then the volatile fractions would not be so high, and the higher molecular weight polymer preparation would presumably be subject to much more crosslinking than its lower molecular weight cousin.

The apparent absence of competitive crosslinking for the $-(C_6H_4-O-CH_2CH_2)_n-$ polymer is in marked contrast to the polyeugenol (nominal structure $-[C_6H_3(o-Me)-O-CH(CH_3)CH_2]_n-$) that we prepared and studied briefly in the previous contract. With that polymeric model of low-rank coal, we saw facile thermal generation of monomeric and other small fragments, but rapid crosslinking, as evidenced by low yields not only in pyrolysis but also from liquefaction in a very good hydrogen-donor solvent. Since there were side reactions we were unable to eliminate in the polyeugenol preparation, as reflected in unsatisfactory analytical results, we cannot now say whether the

incorporation of the o-OMe group or an originally crosslinked structure was the cause of the low yields. Thus it is important to compare the conversion behavior of the $-(C_6H_4-O-CH_2CH_2)_n-$ polymer discussed here and of a well characterized sample of $-[C_6H_3(o-Me)-O-CH_2CH_2]_n-$, whose preparation we are now completing.

The Decarboxylation and Coupling of Aromatic and Aliphatic Acids - During this quarter, we completed our survey of the decarboxylation and coupling of some prototypical monomeric carboxylic acids under "liquefaction" conditions. The bulk of these results were discussed in the previous quarterly report and in the American Chemical Society Fuel Division preprint (8). The experiments performed this quarter involved testing the effect of iron sulfide as another iron salt of potential importance in crosslinking during the heating of coals. We also tested the effect of water on the behavior of phenylacetic acid. We found that the addition of FeS to benzoic acid in naphthalene increased the decarboxylation (during 1 hr at 400°C) from 4.5% to 45.5%. However, the coupling (to phenylnaphthalene, expressed as a % of the decarboxylation that yielded coupling) increased only from 2.5% to 5.7%. The increase in decarboxylation is several times greater than that observed with Fe_3O_4 , but the increase in coupling to about 6% is much less than the ~50% seen with Fe_3O_4 . Thus the principal general conclusion to be drawn from the relative impact of FeS is that the lower iron sulfides, which have long been considered to have a net benefit on liquefaction, are not likely to be a cause of retrograde reaction during coal heating. For completeness, we plan to perform one or two experiments also with the forms present in the original coals (FeS_2 , pyrite or marcasite).

In the decarboxylation of phenylacetic acid, we found the addition of water substantially suppressed the formation of dibenzylketone from the decarboxylation of phenylacetic acid in naphthalene. We believe, for the following reasons, that this to be a true chemical effect rather than a simple dilution effect. First, a chemical effect is expected: if the ketone formation is the result of the formation of phenylketene via the acid anhydride, as we have speculated, then water would inhibit the formation of the anhydride and/or react with the ketene to regenerate the original acid. Second, the extent of the suppression is several times greater than would be expected from a decreased concentration of acid, assuming a coupling that has a net second-order dependence on acid and that the acid and water were completely miscible. It would probably be appropriate to prepare the calcium salt of phenylacetic acid to observe its decarboxylation behavior. Heating of the neat calcium salts of aliphatic acids is known to generate ketone coupling products $[Ca^{++}(RCO_2^-)_2 \rightarrow R(C=O)R]$, so behavior of calcium phenylacetate and calcium hydrocinnamate $[Ca^{++}(PhCH_2CH_2CO_2^-)_2]$ may be as relevant to coupling during the heating of coals as the behavior of alkaline earth salts of aromatic acids. We have no specific plans at this point to perform such experiments, but they should perhaps be considered after those with the calcium salts of aromatic acids are completed.

We have prepared, purified, and tested the behavior of the calcium salts of benzoic acid and anisic acid $[\text{Ca}^+\text{C}_6\text{H}_4(\text{o}-\text{OCH}_3)\text{CO}_2^-]$ when heated, both in a poor "liquefaction" medium and neat. In brief, the results are that the decomposition of the calcium salts does *not* substantially increase the tendency for crosslinking to occur in association with decarboxylation. We have prepared but not yet purified the calcium salt of vanillic acid $[\text{Ca}^+\text{C}_6\text{H}_4(\text{o}-\text{OCH}_3)(\text{p}-\text{OH})\text{CO}_2^-]$, which is difficult to purify by crystallization from aqueous solution. The major remaining possibility we wish to test as a route to facile coupling of activated carboxylic acid species (such as anisic and vanillic acid-like structures) is route in which the presence of the acid in its salt form makes electrophilic displacement of the CO_2 group by a proton much less likely and allows instead for some other electrophile (such as $\text{HOC}_6\text{H}_4\text{CH}_2^+$) to perform the displacement, generating a new carbon-carbon linkage.

FUTURE WORK

The major portions of this task to be completed by SRI are the synthesis, characterization, and pyrolysis-FIMS analysis of the $-\text{[C}_6\text{H}_3(\text{o}-\text{Me})-\text{O}-\text{CH}_2\text{CH}_2\text{]}_n-$ polymer and the decarboxylation and coupling tests of calcium salts of activated acids in the presence of potential coal-derived carbon-centered electrophiles. As time and funds permit, we will attempt modification of either the $-(\text{C}_6\text{H}_4-\text{O}-\text{CH}_2\text{CH}_2)_n-$ or the $-\text{[C}_6\text{H}_3(\text{o}-\text{Me})-\text{O}-\text{CH}_2\text{CH}_2\text{]}_n-$ polymers to incorporate carboxylic acid groups. However, inasmuch as the remaining funds are limited and as the modified polymer synthesis and characterization will probably not be trivial, it is not likely that this variation can be completed. Furthermore, the results to date with the decarboxylation and coupling of monomeric acid systems all serve to point the retrograde reaction finger at hydroxy (and specifically poly-hydroxy) structures as the ones that are really responsible for the early retrograde reactions of low-rank coals. If this conjecture is supported by conversion studies of the $-(\text{C}_6\text{H}_4-\text{O}-\text{CH}_2\text{CH}_2)_n-$ polymer and the $-\text{[C}_6\text{H}_3(\text{o}-\text{Me})-\text{O}-\text{CH}_2\text{CH}_2\text{]}_n-$ polymer whose preparation is now being completed, then the need for testing of such carboxyl-substituted polymers will be lessened.

V. TASK 4 - DATA INTEGRATION AND REPORTING

Future Plans and Recommendations - Following Jeff Manion's presentation of the paper Decarboxylation and Coupling Reactions of Coal Structures at the ACS National Meeting in Washington D.C., (August 23-28, 1992) Ripu Malhotra, Don McMillen and Jeff Manion met with Mike Serio to discuss project results and future plans. The major points made and questions raised in that discussion are summarized below.

Preparation and Study of Polymeric Models - We believe that $-(\text{Ph}-\text{O}-\text{CH}_2\text{CH}_2)_n-$ and related polymers contain a linkage that, to the best of our knowledge, is more representative of what is likely to be present in low-rank (and perhaps bituminous) coals than that of any other

polymers that have yet been used for coal studies. Since more effort than we originally expected has been required to obtain this polymer with enough purity to draw meaningful mechanistic conclusions, we agreed that now that we have a good route to it, the first priority would be to obtain 5-10 g of $-(\text{Ph-O-CH}_2\text{CH}_2)_n-$. This will enable us to perform multiple liquefaction tests as well as to run other "conversion" tests (i.e., TG-FTIR and Pyrolysis-FIMS). The result of these experiments should be a good indicator of the chemical changes these structures undergo during pretreatment and liquefaction. The second priority would be to extend this to the structure that is presumably even more relevant to low-rank coals, namely the $-\text{[C}_6\text{H}_3(\text{o-CH}_3)\text{-O-CH}_2\text{CH}_2\text{]}_n-$ polymer. Only when these polymers have been successfully prepared in these amounts will we proceed to the task of third priority, namely further modification of one or both of the above structures to contain carboxylic acids. An additional reason for our suggestion of this prioritization is that results to date on the decarboxylation and coupling of aliphatic and aromatic carboxylic acids suggests, as summarized below, that coupling following decarboxylation may not be the major source of retrograde reactions during pretreatment and liquefaction.

Decarboxylation and Coupling of Aromatic and Aliphatic Acids - Our studies of decarboxylation under conditions relevant to coal conversion indicate at this point that (1) decarboxylation of unactivated acids is not responsible for the CO_2 evolution observed in the 300-350°C range and (2) decarboxylation of activated acids does not readily provide enough coupling to account for substantial crosslinking of coal structures. However, to complete these studies we need to perform more experiments with the calcium salts of both unactivated and activated acids under conditions relevant to the coal studies where decarboxylation has been correlated with crosslinking. These experiments will include the salts of benzoic p-hydroxy benzoic acid and o-methoxy benzoic acid. Reaction will be both in solvents and neat. With these experiments we will test two hypotheses that may explain the lack of coupling, we have observed thus far with presumably coal-like carboxylic acid structures.

First, we suggest that since decarboxylation of acids is activated by one or more electron-releasing groups such as -OH and -OMe and produces phenolic structures that we have already shown to be susceptible to coupling the real crosslinking may not result directly from the decarboxylation but secondarily from the activated phenols that are thereby produced. Second, since the decarboxylation of activated acids apparently proceeds via electrophilic attack of a proton on the aromatic carbon bearing the carboxylic acid group, decarboxylation with coupling *could* occur if attack were instead by a carbon-centered electrophile. In this scenario, the reason why preparation of calcium-exchanged coals yields more crosslinking could be that when the acids are present mainly in the calcium form, the ratio of protons to other electrophiles decreases and the ratio of clean decarboxylation to decarboxylation accompanied by coupling goes down. At present, this appears to be the best candidate explanation for reconciling the observed crosslinking and decarboxylation of coals with the surprising lack of crosslinking accompanying the decarboxylation

of pure activated acids.

VI. PLANS FOR SEVENTH QUARTER

- Continue work on FT-IR methods for measuring carboxyl and phenolic functions.
- Complete characterization of methylated coals.
- Complete preparation and characterization of $-\text{C}_6\text{H}_3(\text{o-Me})-\text{O}-(\text{H}_2\text{CH}_2)_n-$.
- Complete model compound experiments on carboxyl group behavior.
- Use FG-DVC liquefaction model to simulate results for modified coals.

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