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DE93 004931

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

Fifth Quarterly Report

#523085

For the Period

April 1, 1992 to June 30, 1992

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Work Performed Under Contract No. DE-AC22-91-PC91026

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LIQUEFACTION: CROSSLINKING AND CLEAVAGE REACTIONS**

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

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SEP 1 1992

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ABSTRACT

Preparation and Characterization of Ion-Exchanged Coals - Preparation of ion-exchanged (including barium, calcium and potassium) demineralized Zap and Wyodak has been completed. Both vacuum dried and moist samples were prepared, using procedures described previously. The modified samples were subjected to functional group analysis as KBr pellets with FT-IR, and programmed pyrolysis analysis with TG-FTIR. Liquefaction experiments of these samples were also performed and products were analyzed. The data show that both the pyrolytic tar and liquefaction yields decrease with the extent of ion-exchange, i.e., in the order of (demineralized) > (ion-exchanged at pH 8) > (ion-exchanged at pH 12.5).

For the pyrolysis of vacuum dried samples, the tar yield was higher for the potassium-exchanged coals than the calcium and barium-exchanged samples, suggesting that bivalent cations tighten the coal structure by cross-linking coal fragments and make it more difficult for tar molecules to escape. The liquefaction results show that the potassium-exchanged samples have higher liquefaction yields (especially asphaltenes) than for the barium- and calcium-exchanged samples. This can probably be attributed to the same reason for the high pyrolytic tar yield, i.e., that bivalent cations can serve as a cross-linking agents to tighten the coal structure.

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. Preliminary results show that the moisture content can reach that of the raw samples by remoisturization for Zap, but not for Wyodak. Furthermore, the chemical structure of the coal samples seems to have been changed by remoisturization, since different CO₂ evolution behaviors were observed. In almost every case, the asphaltene yield was increased with moisturization except for the pH 8 Zap, in which case the asphaltene yield was slightly reduced. Interestingly enough, the oil yield was reduced for most of the modified samples with moisturization, except for the demineralized Zap and the pH 12.6 Wyodak. The indication from the above results is that moisturization favors the formation of the larger molecular weight asphaltenes in liquefaction, while the formation of the smaller molecular weight oils was less favored.

It is usually shown that the trends for improved liquefaction yields parallel those for improved tar yields in pyrolysis. However, it was found in this study that the influences of moisturization on the yields of pyrolytic tars and liquefaction toluene soluble yields are different in that moisturization does not appear to have a significant effect on tar yields. This indicates that moisture plays different roles for the formation of tars in pyrolysis and coal liquids in liquefaction. 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. This aspect requires further investigation.

Preparation and Characterization of Methylated Coals - The methylation of a demineralized Zap Lignite sample was performed using a modification of the alkylation procedure we have previously employed. The principal modifications were the addition of a second aliquot of base and alkylating agent to increase the extent of alkylation in a single stage reaction, and the extraction with methanol-water mixtures to more thoroughly remove tetrabutylammonium hydroxide and iodide from the product mixture. These modifications resulted in a methylated coal having very little nitrogen incorporation from the tetralkyl amine base, no incorporation of halogen, and a much more nearly correct ratio of incorporated carbon and hydrogen than we had previously achieved with this coal.

Preparation and Characterization of C-C-O Polymers - The preparation of moderate molecular weight C-C-O polymers ($n = 10$ to 30) has been further optimized. The synthesis of the 4-hydroxyphenethyl halide needed for the phase-transfer-catalyzed polymerization has been shortened from three separated procedures to a sequence of three reactions carried out effectively in a single step. NMR, GPC, and pyrolysis-FIMS analyses of the polymer subsequently produced from this iodide show it to have a weight-average molecular weight of somewhat over 4000 ($n = \sim 35$), to have the desired phenyl-O-C-C- structure and to be contaminated with $\leq 5\%$ of related olefins and *n*-butyl amine. Pyrolysis-FIMS analysis supports the purity of the polymer and reveals that coordinated cleavage or unzipping appears to be very facile at about 380°C . This coordinated cleavage does not result from any radical pathway we can identify at this time, but it is strikingly reminiscent of the cleavage reported for lignins themselves (and not understood in those systems either).

Decarboxylation Studies with Model Compounds - Decarboxylation of phenyl-substituted alkane carboxylic acids were examined using the model compound phenylacetic acid. Its behavior was examined under a variety of conditions to probe the effects of added radical scavenger, base, and the electron transfer agent Fe_3O_4 . Both decarboxylation and coupling were faster than with benzoic acid. Consonant with the results with benzoic acids, added scavenger decreased the degree of coupling in the absence of Fe_3O_4 . Surprisingly, however, the addition of scavenger in the presence of Fe_3O_4 led to a 4-5 fold increase in the formation of the coupling product 1,3-diphenylacetone. This product accounted for about 40% of the reacted acid when this combination of reagents was present. In addition, since the analogous product was not identified in the benzoic acid system, this product indicates that some of the major coupling pathways of phenylacetic acid, and perhaps all alkane carboxylic acids, are significantly different than those of benzoic acids.

The reaction of the activated acid *o*-Anisic acid (2-methoxybenzoic acid) in the presence of Fe_3O_4 was also examined. Xanthenes were formed in about 9% yield under some conditions. These products were demonstrated to stem from the reactions of cresol with either phenol or itself, rather than directly from *o*-Anisic acid (the phenols are decarboxylation products of *o*-Anisic acid). It is apparently the juxtaposition of the methyl and hydroxy groups that leads to the retrograde reactivity. These results suggest that phenolic groups could play a major, or even dominant role in the retrograde reactions

that occur during coal liquefaction in the temperature regime associated with CO₂ loss. Since such structures may be present in the coal matrix even prior to decarboxylation, what remains unclear is exactly to what degree such reactions necessarily arise as a consequence of decarboxylation.

Data Integration and Reporting - The annual report was completed. A preliminary assessment of the effects of cation exchange on pyrolysis and liquefaction yields was completed. Work began on using the FG-DVC liquefaction model to predict the results of liquefaction experiments for modified coals.

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

A. Preparation and Analysis of Ion-Exchanged Coals

Preparation of ion-exchanged (including barium, calcium and potassium) demineralized Zap and Wyodak has been completed. Both vacuum dried and moist samples were prepared, using procedures described previously. As usual, the modified samples were subjected to functional group analysis as KBr pellets with FT-IR, and programmed pyrolysis analysis with TG-FTIR. Liquefaction experiments of these samples were also performed and products were analyzed. The pyrolysis and liquefaction results are summarized in Tables III-1 to III-4.

The data in Tables III-1 to III-4 show that both the pyrolytic tar and liquefaction yields decrease with the extent of ion-exchange, i.e., in the order of (demineralized) > (ion-exchanged at pH 8) > (ion-exchanged at pH 12.5). However, it is realized that this is not a fair comparison for the samples exchanged at pH 12.5, since considerable amounts of humic acids were observed to dissolve in the high pH value solutions. The dissolution of coals in the aqueous alkaline solutions may be due to the breaking of ester bonds in coal, i.e., $\text{RCOOR}' + \text{OH}^- \rightarrow \text{RCOO}^- + \text{R}'\text{OH}$. This coal dissolution mechanism was also proposed by other workers (van Bodegom et al., 1984). The solubility of coal in alkaline solutions varies with the cations contained in the solution. The color difference of the calcium and potassium solutions after ion-exchange at high pH is striking, in that the potassium solution has a much darker color, indicating much more coal dissolved in the monovalent cation (K^+ here) solution than the bivalent cation (Ca^{++} here) solution. A photograph of the two solutions is shown in Fig. III-1. A possible reason is the fact that Ca^{++} ions can act as cross-links between two acid groups of different coal fragments (van Bodegom et al., 1984), whereas K^+ can only interact

TABLE III-1 - Pyrolysis Results of Vac. Dry Modified Coal Samples										
Coal (Type/Preparation)	Proximate Analysis (wt.%, as rec.)				Pyrolysis Products (wt.%, daf)					
	Ash	Moisture	Fixed C	Volatiles	Char	Tars	CO ₂	CO	H ₂ O	CH ₄
Zap Lignite, Vac. Dry										
demin.	2	4	51	44	54	20	4.8	10.4	8.4	2.7
demin. + K ⁺ (pH8)	7	6	50	37	57	11	8.6	9.9	16.0	1.9
demin. + Ca ⁺⁺ (pH8)	7	5	51	37	58	9.5	8.6	13.5	10.3	2.4
demin. + Ba ⁺⁺ (pH8)	15	5	44	36	55	5.5	11.7	15.8	18.6	2.6
demin. + K ⁺ (pH12.5)	16	6	45	34	57	4.9	9.9	12.4	13.5	1.6
demin. + Ca ⁺⁺ (pH12.5)	25	7	34	33	51	3.8	8.2	22.6	12.6	2.0
demin. + Ba ⁺⁺ (pH12.5)	38	9	28	26	52	2.9	10.5	24.1	15.5	2.6
Wyodak, Vac. Dry										
demin.	0	2	49	49	50	30	2.5	9.6	4.7	2.8
demin. + K ⁺ (pH8)	4	4	52	40	57	16	8.3	9.0	13.1	2.1
demin. + Ca ⁺⁺ (pH8)	6	4	49	41	55	14	6.1	11.6	9.8	2.7
demin. + Ba ⁺⁺ (pH8)	15	4	44	37	54	14	8.8	13.6	12.4	2.9
demin. + Ba ⁺⁺ (pH12.6)	36	6	30	28	51	13	6.4	19.6	10.6	2.9

TABLE III-2 - Pyrolysis Results of Moisturized Modified Coal Samples										
Coal (Type/Preparation)	Proximate Analysis (wt.%, as rec.)				Pyrolysis Products (wt.%, daf)					
	Ash	Moisture	Fixed C	Volatile	Char	Tars	CO ₂	CO	H ₂ O	CH ₄
Zap, Moisturized										
demin.	2	15	41	42	50	16	6.5	16.8	11.1	2.8
demin. + K+ (pH8)	7	20	41	31	57	12	8.2	11.6	7.9	1.6
demin. + Ca++ (pH8)	6	21	40	33	55	11	7.0	16.0	4.9	2.3
demin. + Ba++ (pH8)	13	24	33	30	53	9	10.0	15.6	13.7	2.0
demin. + K+ (pH12.5)	10	29	32	29	53	5	14.7	13.0	8.1	1.4
demin. + Ca++ (pH12.5)	19	22	27	31	47	6	12.0	27.1	4.1	1.9
demin. + Ba++ (pH12.5)	31	24	18	27	40	5	14.6	27.3	14.2	2.2
Wyodak, Moisturized										
demin.	0	15	41	45	48	25	5.3	11.1	12.4	2.9
demin. + K+ (pH8)	14	17	33	36	48	15	10.4	12.6	12.5	2.2
demin. + Ca++ (pH8)	4	17	42	37	53	15	7.7	13.7	8.3	2.7
demin. + Ba++ (pH8)	13	20	35	32	52	17	6.4	14.5	11.7	2.4
demin. + Ba++ (pH12.6)	28	25	19	28	40	11	12.8	27.2	8.0	2.5

TABLE III-3 - Liquefaction Results of Vac Dry 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 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-4 - 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			66	9.5	---	8.9	0.40	0.04	0.14	---
demin. + Ca ⁺⁺ (pH8)	29			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			57	15.3	---	14.9	0.13	0.10	0.12	0.02
demin. + Ca ⁺⁺ (pH12.5)	10			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			32	12.8	0.01	12.0	0.33	0.17	0.23	0.02
demin. + Ca ⁺⁺ (pH8)	32			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

Figure III-1. The Solutions after Ion-Exchange with Demineralized Zap Lignite. a) Calcium Acetate at pH 12.4; b) Potassium Chloride at pH 12.4

with one acidic site. The results also show that the barium solution extracted more coal than the calcium solution. It is likely that coal solubility in aqueous alkaline solutions increases with the size of the cations of the same valence. If this is true, the dissolution of coal in sodium solution would be expected to be less than that in the potassium solution. Preliminary results show that this is the case. However, this requires further confirmation. In summary, at similar pH values (~ 12.5), the amounts of Zap lignite extracted by 1 liter of the cation solutions in 20 hours increases in the order of $\text{Ca}^{++} < \text{Ba}^+ < \text{K}^+$.

It can be seen in Table III-1, for the pyrolysis of vacuum dried samples, that the tar yield was higher for the potassium-exchanged coals than the calcium and barium-exchanged samples, suggesting that bivalent cations tighten the coal structure by cross-linking coal fragments and make it difficult for larger tar molecules to escape (Wornat and Nelson, 1992). Also shown in Table III-1, the CO yield in pyrolysis for different ion-exchanged samples generally shows a trend opposite to that of the tar yield. The possible reasons for this have been discussed in the previous reports. The CH_4 yield also showed a trend opposite to that of the tar yield for the ion-exchanged samples. This has been generally reported in coal pyrolysis studies. By reincorporation into the solid matrix by more stable bonds, the tar precursors can yield volatiles only by cracking off of small side groups, hence the increased CH_4 yields with decreasing tar yields.

The liquefaction results in Table III-3 show that the potassium-exchanged samples have higher liquefaction yields (especially asphaltenes) than for the barium- and calcium-exchanged samples. This can probably be attributed to the same reason for the high pyrolytic tar yield, that bivalent cations can serve as a cross-linking agents to tighten the coal structure. Also, the gas evolution, especially CO_2 , was highest for the potassium-exchanged samples during liquefaction. The reason for this is not clear at this stage. It may be due to catalytic activity of the potassium. In previous work, higher CO_2 yields have generally been associated with lower liquefaction yields.

In considering the size effect of the cations on the pyrolytic tar and liquefaction yields, one should compare the data for the barium- and calcium-exchanged samples. It is interesting that the size of the cations has an opposite effect on the tar and liquefaction yields. In pyrolysis, the tar yield for the barium-exchanged samples is lower than that of the calcium-exchanged samples. This could be due to the larger size of barium, which hinders escape of tars in the coal particles. However, according to Table III-1, the char yield was not higher for the barium-exchanged samples, while the yields of oxygen-containing gases and CH_4 were higher. This suggests more severe cracking off of oxygen functions in the tars from the barium-exchanged samples due to a longer residence time in the coal particle. In liquefaction, the yield was higher for the barium-exchanged samples. The reason for this is not clear, but it may be related to the fact that more coal was dissolved in barium-containing alkaline solution than the calcium one.

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 reach that of the raw samples by remoisturization for Zap, but not for Wyodak. Furthermore, the chemical structure of the coal samples seems to have been changed by remoisturization, since different CO₂ evolution behaviors were observed. A comparison of the CO₂ evolution behavior for raw and remoisturized coal samples is given in Fig. III-2.

In almost every case, the asphaltene yield was increased with moisturization except for the pH 8 Zap, in which case the asphaltene yield was slightly reduced. Interestingly enough, the oil yield was reduced for most of the modified samples with moisturization, except for the demineralized Zap and the pH 12.6 Wyodak. The indication from the above results is that moisturization favors the formation of the larger molecular weight asphaltenes in liquefaction, while the formation of the smaller molecular weight oils was less favored.

It is usually shown that the trends for improved liquefaction yields parallel those for improved tar yields in pyrolysis. However, it was found in this study that the influences of moisturization on the yields of pyrolytic tars and liquefaction toluene soluble yields are different in that moisturization does not appear to have a significant effect on tar yields. This indicates that moisture plays different roles for the formation of tars in pyrolysis and coal liquids in liquefaction. 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. This aspect requires further investigation.

The results in Table III-3 and III-4 also show that the moist samples have a higher gas yield in liquefaction than the vacuum dried samples. The increase in gas yield is mainly from CO₂ and CO (especially CO₂), whereas the yields of hydrocarbon gases decrease with moisturization. One possible explanation for this result is that moisture may react with side chain structures in coal, which are the sources for the formation of oils and hydrocarbon gases during liquefaction, to form oxygen functions. The subsequent reaction of these oxygen functions produces more CO₂, CO and asphaltenes in the liquefaction of moist coals.

B. Preparation and Analysis of Methylated Samples

As part of the study of the effect of coal modification, the preparation of alkylated coals has been carried out at SRI. A 15 gram sample of de-mineralized Argonne Zap Lignite was prepared at AFR and sent to SRI. The methylation of this coal in a single batch was begun using a slight modification of the procedure employed in the earlier phase of this project. A portion of the "fully" methylated

Figure III-2. CO₂ Evolution During Coal Pyrolysis. a) Raw Zap; b) Remoisturized Zap; c) Raw Wyodak; d) Remoisturized Wyodak.

coal will be subjected to either ether cleavage or ester hydrolysis to generate a sample in which only one type of acidic oxygen is methylated. The major purpose of this combination of demineralization and complete and partial methylation is of course to determine the effect of methylation per-se, and to see if it accomplishes substantially different things than the demineralization.

The major modifications in the alkylation procedure were the addition of second aliquots of tetrabutylammonium hydroxide and methyl iodide and soxhlet extraction with a water-methanol mixture during the work-up of the methylated coal. These changes were made after consulting with Dr. Leon Stock of the University of Chicago and Dr. A. C. Buchanan of Oak Ridge National Laboratory. In brief, the rationale was that methanolic water both improves the wetting of the coal and has higher solubility for tetrabutylammonium iodide. This rationale seems to have merit, since the nominal uptake of nitrogen (0.09/100C) was only one fifth of that observed in our previous large scale methylation of Zap lignite. We began the methylation procedure with 13.17 grams of demineralized dried coal, and recovered 13.2 grams of the methylated product. Samples of the alkylated and unalkylated coal were sent for elemental analysis. The results of the elemental analyses are shown in Table III-5.

As Table III-5 shows, the increase in nitrogen is small, and the change in total halide is insignificant. The empirical formula for the unmethylated (but demineralized) Zap is $C_{100}H_{85.6}N_{1.17}O_{26.4}$ and that for the methylated product (assuming that oxygen stayed constant during methylation and workup) is $C_{116.8}H_{109.9}N_{1.26}O_{26.4}$. Since the empirical formula is only a set of ratios it is necessary to assume an absolute change (or lack of one) for some element in order to stipulate the absolute change in carbon and hydrogen. The assumption that oxygen does not change gives an empirical formula that corresponds to a ΔC of 16.8 and a ΔH of 24.3, or a shortage of 9.3 hydrogens. These values change slightly if it is assumed that the nominal increase of 0.09 in nitrogen is real and that part of the observed increases in carbon and hydrogen are due to incorporation of the tetrabutyl ammonium group. If, on the other hand, we assume that sulfur is the most likely to have neither decreased nor increased during the methylation procedures and therefore hold it constant during the calculation of the empirical formula, we arrive at a formula (Table III-5) that corresponds to a ΔC of 7.0, a ΔH of 15.08, and a ΔN of 0.01. The carbon and hydrogen proportions are now exactly correct, though the apparent degree of methylation is less. In any case, the uptake of nitrogen and apparent shortage of incorporated hydrogens during this methylation are much less than they were in the previous large scale methylation of Zap. In that earlier alkylation, the observed increase in hydrogen was only 43% of that expected based on the nominal increase in carbon. With this demineralized coal and new alkylation procedure, the increase in hydrogen was 69% of that expected based on the increase in carbon, even for the "worst" case, where oxygen is held constant and the carbon and hydrogen are adjusted assuming the nominal increase in nitrogen comes from incorporation of tetrabutylammonium ion. Thus, depending on the bases chosen for comparing the elemental compositions, we conclude that from 7 to 15 carbons were introduced, the increase in

hydrogen was from 70 to 100% of that expected based on the carbon increase, and that there was ≤ 0.09 N/100 C introduced.

TABLE III-5.

Elemental Analysis and Empirical Formulas for Demineralized Zap Lignite
Before and After Methylation

ELEMENT	NON-METHYLATED	METHYLATED
C	71.19	71.14
H	5.08	5.60
O	25.02	21.55
N	0.97	0.90
S	0.81	0.76
Total halide	200	210
Ash	0.16	0.56
Empirical Formula	$C_{100}H_{85.6}N_{1.17}S_{0.426}O_{26.4}$	$C_{116.8}H_{94.06}N_{1.08}S_{0.398}O_{0.426}$
Emp. For. (Constant Oxygen)		$C_{116.8}H_{109.9}N_{1.26}S_{0.465}O_{26.4}$
Emp. For. (Const. O,N)		$C_{115.3}H_{106.6}N_{(1.17)}O_{26.4}$
Emp. For. (Const. S)		$C_{107.0}H_{100.7}N_{1.16}O_{24.19}$

IV. TASK 3 - STUDIES WITH POLYMERIC MODEL SYSTEMS

A. Introduction and Objectives

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 CO₂ and H₂O and therefore that carboxyl and/or phenolic groups are involved, but we do not know exactly how or why. In order 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 reaction 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. 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 unanalyzable. Therefore, judicious choices are necessary in the attempt to focus on those oxygen-containing structures that are 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. 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. We have made the most progress in the second approach, including background studies on the behavior of carboxylic acids under coal liquefaction conditions. By contrast, we have found that the preparation *and characterization* of even low

molecular weight poly aryls (such as hexa- and octa- phenyls) is a task that faces severe difficulties because of the solubility limitations of these polymers. No additional work was performed on this approach during the fifth quarter. In this report, we describe the progress made since the Annual Topical Report on the synthesis of polymers connected by the β -ether bonding ($-\text{CH}_2\text{CH}_2\text{O}-$) that is known to dominate the inter-cluster linkages in most lignins. We also briefly summarize the additional work performed to elucidate the coupling behavior of carboxylic acid groups likely to be present in low-rank coals and the methylation of demineralized Zap lignite.

B. Work Performed

1. Synthesis of C-C-O Polymers

The O-C-C " β -ether" linkage 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 assumed 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. 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 (Gilbert and Gajewski, 1982). 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 polymer preparations was judged to be premature.

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. In the current quarter, we have further optimized the synthesis route, collapsing three separate steps into a single, one-reaction-vessel process. The three-step generation of 4-hydroxyphenethyl bromide (or its analogs) that we described in the Annual Topical Report has been replaced by the reaction of 4-hydroxyphenethyl alcohol in three equivalents of trimethylsilyliodide. As shown below, these reactants first generate trimethylsilyl ethers from both the phenolic- and aliphatic-OH. The extra equivalent of trimethylsilyliodide then generates the alkyl iodide from the alkyl ether, leaving the aryl ether (which is not subject to nucleophilic displacement) intact. In the workup, the latter ether is

cleaved with mild acid, and the net result is the generation of 4-hydroxyphenethyl iodide in a single reaction vessel in high yield.

Scheme 1. One-Step Synthesis of 4-hydroxyphenethyl iodide.

The 4-hydroxyphenethyl iodide was isolated and the phase-transfer catalysis approach discussed in the Annual Report was used to produce the C-C-O bridged polymer.

NMR and GPC Analysis - Both proton and ^{13}C NMR analysis show the new polymer preparation to have essentially nothing other than the expected functional groups. The likely and/or expected impurities (analogous oligomeric olefins and traces of tri-*n*-butylamine) are present to a level of $\leq 5\%$. We have now obtained gel permeation chromatography (GPC) analysis, using THF as the solvent, for a new preparation of the $-(\text{Ph}-\text{O}-\text{CH}_2\text{CH}_2)_n-$ polymer. This analysis shows a single peak running roughly from 100 to 100,000 with a number-average molecular weight of 1230 and a weight average value of 4216. This value only pertains, of course, to the portion of the polymer that was actually in solution in the GPC solvent. The THF solution was slightly turbid at the concentration level used. Since it was completely clear at lower concentrations of the polymer, we assume the solubility limit had been reached for some of the higher molecular weight oligomers. We estimate the fraction of the sample thus not included in the molecular weight distribution to be less than 10%. Since the weight-average molecular weight of ~ 4200 corresponds to 35 monomer units, even limited fractionation to remove the lower molecular weight portion would provide a substrate for conversion studies where the majority of the product fragments would have come from chains in excess of 40 monomer units. While this is probably not enough in a linear polymer to provide a substrate solubility similar to that of low-rank coals (i.e., insoluble in the liquefaction solvent at 400°C and time zero), it should be enough to provide substantial tangling of polymer chains and some of the impact on mass transport and crosslinking that one expects from a polymeric system. Given the need to characterize the polymer before liquefaction studies, a polymer wholly insoluble in THF or other practical GPC solvent is not necessarily desirable.

FIMS Analysis - Analysis of the whole polymer sample by field ionization mass spectrometry (FIMS) provides results consistent with the NMR and GPC analyses, and begins to provide a view of the thermal behavior of this structural analog of low rank coals. The most prominent peak in the pyrolysis-FI mass spectrum is that at m/z 120, followed (with decreasing intensity) by those at m/z 240, 360, 480, etc., corresponding to the thermal fragments $\text{CH}_2=\text{CH}-(\text{Ph}-\text{OCH}_2\text{CH}_2)_n-\text{PhOH}$. Cresol and phenol are also prominent, as are peaks at m/z 185 and 184 due to tri-*n*-butylamine. (The latter constitute a little less than 5% of the total ion intensity, consistent with the NMR analysis.)

Examination of the temporal profile of the series of peaks beginning at m/z 120 shows that at least up through m/z 720 they all result primarily from thermal cleavage reactions, which reach a maximum in the 360 to 400°C window. Furthermore, from the beginning of rapid cleavage at about 340 to 360°C through to its completion at ca. 430°C, the monomer at m/z 120 is by far the dominant oligomer, indicating either that there is an "unzipping" process (i.e., that the cleavage of one linkage is correlated with the cleavage of the adjacent linkage) and/or that there is extensive crosslinking. Since the fraction volatilized during FIMS analysis was 89%, it appears that crosslinking is not very competitive with bond cleavage, or at least that it does not prevent bond cleavage from being essentially completed. It is interesting to compare these results with those obtained in the previous phase of this contract using more poorly defined samples of this class of polymers (obtained by an entirely different synthetic route). In those previous results, thermal generation of the monomer unit was also dominant, but the fraction volatilized in FIMS analysis was much lower. The "liquefaction" yields were also rather low (ca. 50%) for a polymer that fragmented so readily. A major question is whether the apparent lack of crosslinking reaction is primarily the result of mass transport -(i.e., physical-) factors, or whether it is the result of chemical differences. Thus it will be interesting to determine liquefaction yields not only for the new polymer preparation, but also for the analog with ring-methoxy substitution ortho to the oxygen connection ($-(\text{Ph}[\text{OCH}_3]-\text{O}-\text{CH}_2\text{CH}_2)_n-$). We consider the latter to actually be the better representative of low rank coals; furthermore, it has the di-hydroxy configuration known to increase proclivity to retrograde reactions.

The correlated bond cleavage we see here appears similar to that reported (but not understood) for lignins, which are dominated by the so-called β -ether linkage, but which have still intact aliphatic alcohol groups. We have discussed this behavior of lignins with Bob Evans and coworkers at the National Renewable Energy Research Laboratory (NREL) in Golden, Colorado and have agreed to supply them a small amount of this polymer model for study in their molecular-beam-sampled pyrolysis apparatus.

2. The Behavior of Carboxyl Functions in a Coal Liquefaction Environment

Decarboxylation of Phenyl-Substituted Alkane Carboxylic Acids - The last category of decarboxylation experiments we have performed is that of alkylaromatic systems in which the carboxylic acid group is bonded to an aliphatic carbon. Since we do not know the distribution of

carboxylic acid types in these coals, and since the oxidation of non-benzylic alcohol carbons in the original lignin structure is an alternative to oxidation of benzylic carbons to substituted benzoic acids, we have performed some experiments with phenylacetic acid, chosen as a reasonable prototype for all acids having the carboxyl carbon β - or further from the aromatic ring. Initial experiments with this category were described in the Annual Topical Report. Those results will be briefly summarized here, followed by a description of the limited set of experiments performed since then, whose objective was to complete, to the extent possible, an outline of how aromatic and aliphatic carboxylic acids may contribute to retrograde reactions of low rank coals.

In the Annual Topical Report we reported that decarboxylation of phenylacetic acid in tetralin proceeds with a rate about 6 times that of benzoic acid but slower than that of acids activated by e.g., an ortho or para hydroxy. Decarboxylation was found to have been accelerated by the combination of base and the electron-transfer agent cupric acetate, although surprisingly to a lesser degree than observed for benzoic acid. Finally, the gas chromatograms of the product mixture gave evidence for greater coupling than with benzoic or the activated acids, but the products had not been identified at that time. We now have more complete information and have summarized in Table IV-1 the results of a series of experiments in which we have probed the effects of radical scavenger, base, and the 1-electron oxidant Fe_3O_4 on the conversion and coupling reactions of phenylacetic acid.

The electron transfer agent Fe_3O_4 was found to have a large effect on the reaction and so, in order to simplify the discussion, we will begin with a description of the results in experiments without this additive. In the absence of Fe_3O_4 , toluene, the primary decarboxylation product, is formed in 27% yield after 1 hour in naphthalene at 400°C . As the naphthalene is replaced by the hydrogen donor tetralin, the yield of toluene gradually decreases until it is present in 20% yield when pure tetralin is used. Several coupling products were also identified, including 1,3-diphenylacetone (DPA), bibenzyl, t-stilbene, benzylnaphthalenes, and phenylnaphthalenes. The yield of the major coupling product, DPA, decreases from 5.6% yield in naphthalene to 1.3% in tetralin. By contrast, replacement of naphthalene by tetralin increases benzylnaphthalene formation from 0.05% to 0.5%. The net effect of the hydrogen donor remains favorable, however, decreasing the ratio of (% coupling/% reaction) from 13 to 5%.

Most of the above results are explainable by the general mechanistic picture of decarboxylation that was presented in the Annual Topical Report, that is that decarboxylation proceeds primarily through the carboxylate anion, at least for unactivated species in the absence of electron transfer agents. The 25% decrease in toluene formation as the solvent is changed from naphthalene to the radical scavenger tetralin could indicate that some portion of the reaction involves radical species, but it could also reflect slightly different abilities of the two compounds to solvate the anion intermediate. In any case, radicals do play some role, since bibenzyl and t-stilbene are apparently primary and

Table IV-1

**Effects of Radical Scavenger and 1-Electron Oxidant on Coupling and Decarboxylation
of Phenylacetic Acid During Reaction at 400 °C for 1 Hour**

Exp	Reactants (mol%) ^a	Results (as a % of starting PAA ^a)						
		%Unr. Acid	Toluene	BB+SB ^{b,c}	DPA ^{b,c}	Bz-Naph ^b	Ph-Naph ^b	%Coup./ %Reaction ^d
1	PAA/Naph 10.9/89.1	57.1	27.2	0.41	5.6	0.047	0.065	13.3
2	PAA/Naph/Tet 11.1/77.9/11.0	65.0	27.3	<0.15	5.3	0.23	<0.05	15.8
3	PAA/Naph/Tet 9.9/20.5/69.6	72.3	21.1	<0.15	2.6	0.46	<0.05	11.0
4	PAA/Tet 10.3/89.7	67.2	19.7	<0.15	1.3	0.48	<0.05	5.4
5	PAA/Naph/Pyridine 9.8/79.0/11.2	61.3	31.6	0.39	5.1	0.052	<0.15	14.3
6	PAA/Naph/Fe ₃ O ₄ 9.8/79.9/10.3	34.7	35.7	7.2	5.5	3.3	2.4	28.2
7	PAA/Naph/Tet/Fe ₃ O ₄ 9.9/70.7/9.5/9.9	31.6	35.3	4.8	20.9	1.7	0.52	43.2
8	PAA/Naph/Tet/Fe ₃ O ₄ 9.9/44.5/35.6/10.0	35.2	32.7	2.5	23.8	1.1	0.17	42.5
9	PAA/Tet/Fe ₃ O ₄ 10.0/80.0/10.0	42.0	29.2	1.1	23.6	0.62	<0.05	43.7

^aPAA = phenylacetic acid; Naph = Naphthalene; Tet = Tetralin

^bBB = Bibenzyl; t-SB = trans-stilbene; Bz-Naph = 1 and 2-benzyl naphthalenes; Ph-Naph = 1 and 2-phenyl naphthalenes.

^cThese species stem from two units of phenylacetic acid; given percentages are *twice* the mol%.

^dBased on identified coupling products and unreacted phenylacetic acid.

secondary recombination products of the relatively stable benzyl radical, an intermediate whose presence is also consistent with the formation of benzylnaphthalenes. The above products are formed in small amounts only ($< 0.5\%$), however, and it may well be that the benzyl radicals stem from toluene, rather than directly from the decarboxylation of phenylacetic acid.

The most difficult products to explain are phenylnaphthalene and 1,3-diphenylacetone (DPA). Although the former is only a trace product under the present conditions, it would seem to indicate the formation of some phenyl radicals in the system, which is not easy to understand. Further, as will be discussed, this species becomes significantly more important in the presence of Fe_3O_4 . The formation of 1,3-diphenylacetone is also not well understood at this time and will be discussed later. For the present we note only that the analogous product from benzoic acid, benzophenone, was not observed. This suggests that the $\alpha\text{-CH}_2$ of phenylacetic acid is involved in the formation of this product. Note also that DPA is the only coupling compound identified thus far where the carboxylate oxygen has been partially retained in the retrograde product.

Effect of added base - A slight increase of 16 % in the rate of decarboxylation was effected by the addition of 11 m% of pyridine to the phenylacetic acid/naphthalene mixture (see Table IV-1, expts. 1 and 5). This is a much smaller increase than was observed with benzoic acid, where a 300% increase was observed (see the Annual Topical Report). In the benzoic acid case, it was thought that the function of base was to increase the concentration of the carboxylate anion which was the species postulated to undergo decarboxylation. Why base would be much less effective in the case of phenylacetic acid is not presently understood. Rates of coupling reaction were essentially unaffected by the addition of the pyridine.

Effect of added Fe_3O_4 - Consistent with previous results on benzoic acid, addition of 10 m% of the electron transfer agent Fe_3O_4 to the phenylacetic acid/naphthalene mixture leads to more reaction and more coupling. The primary decarboxylation product toluene shows about a 30% increase in its rate of formation when compared to the naphthalene only case. The effects on coupling products are more dramatic, with the sum of bibenzyl and t-stilbene increasing by a factor of 18 and the products benzylnaphthalene and phenylnaphthalene by factors of 70 and 36, respectively. These results are consistent with our previous postulate that iron oxide leads to the generation of radicals in the system. We had suggested that the carboxylate anion was oxidized to the carboxyl radical, which then loses CO_2 to generate the corresponding radical. In the present instance this would lead to benzyl radical, thus explaining the large increase in the expected products from this intermediate (bibenzyl, t-stilbene, and benzylnaphthalene). It is less clear how Fe_3O_4 induces the formation of phenyl radicals, which presumably are responsible for the formation of phenylnaphthalene. In any case, addition of the radical scavenger tetralin to the system has the expected effect on these products, reducing their rates of formation. Most severely affected are phenylnaphthalenes, which drop from a 2.4% yield in naphthalene solvent to $< 0.05\%$ in pure tetralin. This is suggestive of very

efficient scavenging of C_6H_5 by tetralin, a not unexpected result given that the C-H bond in benzene is > 20 kcal/mol stronger than that in tetralin. Judging from the products from benzyl radical, tetralin is effective but somewhat less so in scavenging such resonance stabilized radicals with their more similar C-H bond strengths.

The most surprising result concerns the coupling product DPA. In pure naphthalene solvent, the addition of 10 m% of Fe_3O_4 to the mixture had no effect on DPA formation (Table IV-1, expts. 1 and 6), which remained constant at 5.5%. However, when 10 m% of the naphthalene was replaced by tetralin the DPA production increased four-fold, accounting for 21% of the starting acid. Further addition of tetralin then had only a small effect, with the yield of DPA remaining a constant 23-24%. This behavior is quite different from that observed in the absence of Fe_3O_4 , where the shift from naphthalene to tetralin smoothly reduced DPA formation from 5.5 to 1.1%. The dramatic effect of the combination of tetralin/ Fe_3O_4 on the formation of this product is presently not understood. One possibility is that the tetryl radicals in the system are donating an electron to the Fe_3O_4 and it is the reduced form of Fe_3O_4 that is catalyzing the formation of DPA. It is not clear, however, why carboxylate anions or benzyl radicals, both of which are present even when pure naphthalene is the solvent, would not be just as effective in this regard.

Effect of Fe_3O_4 on Decarboxylation of Activated Carboxylic Acids - In the absence of electron transfer agents, our previous results (see the Annual Topical Report) showed that coupling of activated acids was a very minor process under reductive coal liquefaction conditions. However, because of the large effect of Fe_3O_4 on the coupling products that were observed with benzoic and phenylacetic acid, we thought it important to examine the behavior of the activated acid o-anisic acid (2-methoxybenzoic acid) in the presence of this electron transfer agent. As shown in Table IV-2, we find an 8.6% yield of xanthenes from o-AA in naphthalene when 10 m% of iron oxide is added. The question is how does this product arise? Is it a direct product of decarboxylation or is it formed from some species that has already lost CO_2 ? Phenol and Cresol are major decarboxylation products that we suspected could form reactive intermediates. As shown by the latter two experiments in Table IV-2, it is in fact these species that are responsible for the formation of xanthenes. The data demonstrate that the self-coupling of o-cresol gives methylxanthene (eq. 1) while the cross-coupling of phenol with o-cresol gives the

unmethylated parent. From a thermodynamic point of view, the net formation of water is very favorable and will help to drive the reaction. No product attributable to the self-coupling of phenol

Table IV-2

Fe₃O₄ INDUCED COUPLING OF DECARBOXYLATION PRODUCTS OF ANISIC ACID

Exp	Reactants (mol %) ^a	Results (as a % of starting material)					
		%Unr. Acid	Anisol	PhOH ⁴	o-Cresol	Xanth ^{a,b}	Me- Xanth ^{a,b}
1	o-AA/Naph/Fe ₃ O ₄ 12.8/77.7/9.9	<0.1	19.8	46.3	12.5	6.9	1.7
2	Cresol/Naph/Fe ₃ O ₄ 9.7/80.3/10.0	---	---	6.3	67.8	0.36	4.2
3	Cresol/PhOH/Naph/Fe ₃ O ₄ 8.0/8.2/75.5/8.3	---	---	81.7	73.9	4.6 ^c	2.1 ^c

^ao-AA = ortho-anisic acid (2-methoxybenzoic acid); Naph = Naphthalene; Cresol = ortho-Cresol, PhOH = phenol, Xanth = Xanthene; Me-Xanth = Methylxanthene (isomer undefined).

^bThese species stem from two units of phenylacetic acid; given percentages are *twice* the mol%.

^cGiven as a percentage of the *sum* of the starting phenols.

was found so it is apparent that the juxtaposed methyl and hydroxy groups are a structure that preferentially leads to coupling reactions under our conditions. With regard to coal liquefaction, it is apparent not only that such reactive structures may be generated during decarboxylation of activated acids, but also that they may pre-exist in the coal matrix and lead to retrograde reactions independent of decarboxylation reactions.

C. Summary and Conclusions

1. Model Polymer Synthesis

The preparation of moderate molecular weight C-C-O polymers ($n = 10$ to 30) has been further optimized. The synthesis of the 4-hydroxyphenethyl halide needed for the phase-transfer-catalyzed polymerization has been shortened from three separated procedures to a sequence of three reactions carried out effectively in a single step. NMR, GPC, and pyrolysis-FIMS analyses of the polymer subsequently produced from this iodide show it to have a weight-average molecular weight of somewhat over 4000 ($n = \sim 35$), to have the desired phenyl-O-C-C- structure and to be contaminated with $\leq 5\%$ of related olefins and *n*-butyl amine. Pyrolysis-FIMS analysis supports the purity of the polymer and reveals that coordinated cleavage or unzipping appears to be very facile at about 380°C . This coordinated cleavage does not result from any radical pathway we can identify at this time, but it is strikingly reminiscent of the cleavage reported for lignins themselves (and not understood in those systems either).

2. Decarboxylation and Coupling of Carboxylic Acids

Decarboxylation of phenyl-substituted alkane carboxylic acids were examined using the model compound phenylacetic acid. Its behavior was examined under a variety of conditions to probe the effects of added radical scavenger, base, and the electron transfer agent Fe_3O_4 . Both decarboxylation and coupling were faster than with benzoic acid. Consonant with the results with benzoic acids, added scavenger decreased the degree of coupling in the absence of Fe_3O_4 . Surprisingly, however, the addition of scavenger in the presence of Fe_3O_4 led to a 4-5 fold increase in the formation of the coupling product 1,3-diphenylacetone. This product accounted for about 40% of the reacted acid when this combination of reagents was present. In addition, since the analogous product was not identified in the benzoic acid system, this product indicates that some of the major coupling pathways of phenylacetic acid, and perhaps all alkane carboxylic acids, are significantly different than those of benzoic acids.

The reaction of the activated acid *o*-Anisic acid (2-methoxybenzoic acid) in the presence of Fe_3O_4 was also examined. Xanthenes were formed in about 9% yield under some conditions. These products were demonstrated to stem from the reactions of cresol with either phenol or itself, rather

than directly from o-Anisic acid (the phenols are decarboxylation products of o-Anisic acid). It is apparently the juxtaposition of the methyl and hydroxy groups that leads to the retrograde reactivity. These results suggest that phenolic groups could play a major, or even dominant role in the retrograde reactions that occur during coal liquefaction in the temperature regime associated with CO₂ loss. Since such structures may be present in the coal matrix even prior to decarboxylation, what remains unclear is exactly to what degree such reactions necessarily arise as a consequence of decarboxylation.

V. TASK 4 - DATA INTEGRATION AND REPORTING

The annual report was completed. A preliminary assessment of the effects of cation exchange on pyrolysis and liquefaction yields was completed. Work began on using the FG-DVC liquefaction model to predict the results of liquefaction experiments for modified coals.

VI. PLANS FOR SIXTH QUARTER

- Complete liquefaction experiments on cation exchanged coals.
- Complete preparation and characterization of methylated coals.
- Complete preparation and characterization of modified polymers.
- Continue to work on experiments and mechanisms of carboxyl group behavior.
- Continue to work on FG-DVC liquefaction model.

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