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P. O. Box 380379
East Hartford, Connecticut 06138-0379
Telephone (203) 528-9806
Fax (203) 528-0648

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

Seventh Quarterly Report

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MICHAEL A. SERIO
ERIK KROO
SYLVIE CHARPENAY
PETER R. SOLOMON

with contributions by:

RIPUDAMAN MALHOTRA (SRI)
DONALD MCMILLEN (SRI)

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

Arun Bose, Project Manager

by

ADVANCED FUEL RESEARCH, INC.

87 Church Street
East Hartford, CT 06108
(203) 528-9806

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LIQUEFACTION: CROSSLINKING AND CLEAVAGE REACTIONS**

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

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ABSTRACT

The work during the past quarter under Task 2 has focused on the investigation of FT-IR methods for measuring carboxyl and phenolic functions. Fourier transform infrared (FT-IR) spectra of coal contain a wealth of information that can be utilized in the development of quantitative analysis routines based on least squares curvefitting. In this work, we have modified the technique of Solomon et al. by allowing the curvefitting algorithm to determine the positions of those bands prone to shifting. Reduced spectral ranges were used in order to accommodate the increased number of parameters to be determined. The initial parameters for the curvefitting algorithm (number of bands, band assignments) were set using data available in the literature. Because of the importance of the carboxylate groups in retrogressive reactions, recent efforts have focused on the C=O stretching region. Raw and modified coal samples (acid washed, demineralized, and cation exchanged) were analyzed in order to validate the proposed band assignments in the C=O stretching region. This parameter set differentiates free carbonyl (B2) and hydrogen-bonded carbonyl (B4) from carboxylic acid carbonyl (B3) and carboxylate (B7). One test of these assignments, which are based on literature data, is to plot B3 versus B7. This should be linear, assuming that the sum of the free carboxyl and carboxylate groups is constant and that the intensity of the overlapped aromatic ring band in B7 is also constant. This relationship was found to hold for a set of raw, acid washed, and acid washed/cation-exchanged Zap coals.

The work under Task 3 has involved (1) completion of the synthesis of the -C-C-O- linked, methoxy substituted lignin-network polymer, $\text{---}[\text{C}_6\text{H}_3(\text{o-OMe})\text{-O-CH}_2\text{CH}_2]_n\text{---}$ polymer, (2) Analysis of the polymer via depolymerization under pyrolysis-FIMS (Py-FIMS) conditions, and (3) testing of several routes to selective cleavage of the O-Methyl bond so that the relative crosslinking tendencies of the methylated and unmethylated versions of the polymer could be determined.

Work was completed on the ACS Denver paper, titled "The Effects of Moisture and Cations on liquefaction of Low Rank Coals." In addition, three abstracts were prepared for the International Conference on Coal Science (Banff, Alberta, CANADA, September 12-17, 1993) based on the work done under this project. The first is titled "The Role of Cations in Retrogressive Reactions During Pyrolysis and Liquefaction," which concerns the work done on coals and modified coals. The second is titled "Application of a Spectral Deconvolution Technique to Coal FT-IR Spectra," which concerns the use of FT-IR methods for measurement of carboxyl and hydroxyl functions. The third paper is titled "Pyrolysis Pathways and Kinetics of Polymeric Models for Low-Rank Coals" which focuses on the thermal decomposition chemistry of the β -ether-linked lignin model polymers.

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 1 - WORK PLAN

This task is complete.

III. TASK 2 - STUDIES WITH COALS AND MODIFIED COALS

The work during the past quarter under Task 2 has focused on the investigation of FT-IR methods for measuring carboxyl and phenolic functions. Fourier transform infrared (FT-IR) spectra of coal contain a wealth of information that can be utilized in the development of quantitative analysis routines based on least squares curvefitting. However, since the exact composition of the coal is not known, the selection of parameters, such as the number, position, and width of the bands, is not straightforward. The application of Fourier self-deconvolution, maximum likelihood restoration, and the calculation of derivative spectra has been shown capable of narrowing bandwidths in order to facilitate the selection of these parameters (1,2). However, these techniques provide poor results for spectra with highly overlapped bands, baseline errors or high noise levels (1,2). Although coal spectra typically exhibit these shortcomings, some of these approaches have been utilized (3,4). As an alternative to the approach mentioned above, Solomon et al. (5,6) defined a set of 24 Gaussian bands with fixed positions and widths that could reproduce coal spectra within the experimental error. Although good correlations were observed for coal samples of different rank, the use of fixed band positions prevents the observation of band shifts induced by changing inter- and intramolecular interactions in the coal structure.

In this work, we have modified the technique of Solomon et al. (5,6) by allowing the curvefitting algorithm to determine the positions of those bands prone to shifting. Reduced spectral ranges were used in order to accommodate the increased number of parameters to be determined. The initial parameters for the curvefitting algorithm (number of bands, band assignments) were set using data available in the literature. The key to this approach is that known modifications were made to the hydroxyl and carboxyl functional groups within the coal structure in order to test the curvefitting

results. Because of the importance of the carboxylate groups in retrogressive reactions, recent efforts have focused on the C=O stretching region. Raw and modified coal samples (acid washed, demineralized, and cation exchanged) were analyzed in order to validate the proposed band assignments in the C=O stretching region given in Table III-1. This parameter set differentiates free carbonyl (B2) and hydrogen-bonded carbonyl (B4) from carboxylic acid carbonyl (B3) and carboxylate (B7). One test of these assignments, which are based on literature data, is to plot B3 versus B7. This should be linear, assuming that the sum of the free carboxyl and carboxylate groups is constant and that the intensity of the overlapped aromatic ring band in B7 is also constant. This relationship was found to hold for a set of raw, acid washed, and acid washed/cation-exchanged Zap coals, as shown in Figure III-1.

band #	position	Assignment
B1	*1772	
B2	*1738	C=O
B3	1708	COOH
B4	1690	C=O..H
B5	1650	broad water band
B6	1600	arom.str. 1
B7	*1575	COO-, arom.str. 2
B8	1508	
B9	1454	

Table III-1. Band positions and assignments used for input parameters for the C=O stretching region (*indicates fixed band position)

Acid washing the raw Zap samples results in an increase in the COOH/COO-band intensity ratio. Cation exchanging the acid washed samples returns the COOH/COO-ratio to approximately the same value observed for the raw coal. This is demonstrated more quantitatively in Figure III-2. Coal samples with a relatively wide range of COOH/COO-ratios were prepared by cation exchanging demineralized coal samples using different cations under varying conditions (7). Clearly a linear relationship between the intensities of the carboxylic acid band and the carboxylate band is demonstrated. The difference between the raw (Figure III-1) and demineralized (Figure III-2) coals possibly reflects the interaction of mineral matter with the carboxyl group.

Figure III-1. Relationship of Carboxylic Acid and Carboxylate Band Intensities for Raw, Acid Washed, and Acid Washed-Cation Exchanged Zap Coals.

Figure III-2. Relationship of Carboxylic Acid and Carboxylate Band Intensities for Demineralized and Demineralized-Cation Exchanged Zap Coals.

IV. TASK 3 - STUDIES WITH POLYMERIC MODEL SYSTEMS

INTRODUCTION

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 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 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 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 unanalyzable. 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 in the sixth and seventh 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 (8) 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. (9) 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

Preparation of the $\text{—[C}_6\text{H}_3(\text{o-Me})\text{CH}_2\text{CH}_2\text{O-]}_n\text{—}$ Polymer

In October we prepared two small test batches of the methoxy substituted model polymer ($\text{—[C}_6\text{H}_3(\text{o-OMe})\text{CH}_2\text{CH}_2\text{O-]}_n\text{—}$), using reaction times of 3 and 5 days. Both of these polymers were largely soluble in CDCl_3 , though they were surprisingly somewhat less soluble in THF. We have obtained the ^1H and ^{13}C solution phase NMR spectra; these spectra show the polymers to have <5% impurities.

Pyrolysis-FIMS of the -C-C-O- polymers

General Features and Mechanistic Expectations. The pyrolysis-FI mass spectrum for the three-day preparation of $\text{—[C}_6\text{H}_3(\text{o-OMe})\text{CH}_2\text{CH}_2\text{O-]}_n\text{—}$, shown in Figure IV-1, is similar in general terms to those for the $\text{—[PhCH}_2\text{CH}_2\text{O-]}_n\text{—}$ polymer preparations shown in the last quarterly report (reproduced here as Figure IV-2). However, there are interesting differences that indicate variations in pyrolytic behavior. All the spectra show a series of oligomers (more precisely, a series of oligomers with a double bond in one of the ethylene groups, presumably preferentially the terminal $\text{-CH}_2=\text{CH}_2$ grouping) that would be expected from simple non-reductive cleavage. In all

Figure IV-1. Pyrolysis-FI Mass Spectrum for $-\text{[C}_6\text{H}_3(\text{o-OMe})\text{CH}_2\text{CH}_2\text{-O]}_n\text{-Polymer}$.

Figure IV-2. Pyrolysis-FI Mass Spectrum for $-\text{[PhCH}_2\text{CH}_2\text{-O]}_n\text{-Polymer}$.

cases, a dominance of monomer over dimer, trimer, etc., *from the onset of decomposition through its completion* indicates that the linkages are being cleaved in a coordinated, or unzipping manner. We can qualitatively rationalize this unzipping by postulating that the radical-chain H-abstraction— β -scission processes that account for the decomposition of monomeric -C-C-O- linked structures would here lead to the chain transfer H-abstraction reactions occurring preferentially on the end unit. This sequence is illustrated in Scheme 1.

Scheme 1. Possible radical-chain unzipping sequence for -C-C-O- polymers.

Autoacceleratory Character of the Decomposition. In view of the probable coiled configurations of these linear polymers, and thus the likely proximity of many interior chain positions, rationalization of the pronounced unzipping tendency simply in terms of a radical chain mechanism does not appear really satisfactory. In any case, central bond cleavage is clearly a chain or an autocatalytic process, such that once cleavage begins at about 300°C, it proceeds progressively more rapidly, leading to essentially complete volatilization by 350°C. This behavior is illustrated by the vacuum "evaporation" curves shown in Figures IV-3 and IV-4, depicting the temperature dependence of volatiles formation observed during acquisition of the spectra in Figures IV-1 and IV-2, respectively. While both curves are very steep after the threshold is passed at about 300°C, the curve in Figure IV-3 for the $-\text{C}_6\text{H}_3(\text{o}-\text{OMe})\text{CH}_2\text{CH}_2-\text{O}-$ polymer is drastically "overhung." In other words, the ion current rose so quickly once the decomposition threshold was passed (at $\sim 300^\circ\text{C}$) that the probe temperature had to be decreased substantially to keep from exceeding the ion counting capability of the instrument. We note that the threshold itself actually does *not* occur at a significantly lower temperature than for the $-\text{PhCH}_2\text{CH}_2-\text{O}-$ polymer: in both cases the threshold appears between 300 and 350°C. However, once decomposition begins, it proceeds much more rapidly with the methoxy-substituted polymer. That is, there is a much more pronounced autocatalytic behavior with that material.

Figure IV-3. Vacuum Evaporation Curve for $-\text{[C}_6\text{H}_3(\text{o-OMe})\text{CH}_2\text{CH}_2\text{-O]}_n\text{-Polymer}$.

Figure IV-4. Vacuum Evaporation Curve for $-\text{[PhCH}_2\text{CH}_2\text{-O]}_n\text{-Polymer}$.

Our current thinking is that this striking autocatalysis may be indicating a new reaction pathway. The reasoning is as follows, proceeding in two steps from phenylphenethyl ether ($\text{PhCH}_2\text{CH}_2\text{-O-Ph}$, "PPE"), the simplest "dimer" unit one can consider a prototype for these β -ether lignin-like polymers. This prototype has been studied by several groups in recent years, notably Klein and Virk (8), Britt and Buchanan, (9) and Gilbert and Gajewski (10). This work has been authoritatively reviewed by Poutsma (11). The changes in bond strength one expects in going from PPE to the simple -C-C-O- polymer and then to the methoxy-substituted -C-C-O- polymer are shown in Table IV-1, together with the half-lives for decomposition. The bond strength estimates are made, in large part, on the basis of recent kinetic studies published by Stein for pyrolysis of anisole derivatives (12).

Table IV-1
Bond Strengths and Decomposition Rates for -C-C-O- Linked Aromatic Ring Systems

STRUCTURE	BDE ^a $\text{CH}_2\text{-O}$	BDE ^a ArC(H)-H	$t_{1/2}$ Obs (min)	
	kcal/mol	kcal/mol	300°C	350°C
$\text{PhCH}_2\text{CH}_2\text{OPh}$	60	85	4×10^4	2500
$\text{--[OPhCH}_2\text{CH}_2\text{OPhCH}_2\text{CH}_2\text{]}_n\text{--}$	59.6	~83	5 ^b (325°C)	
$\text{--[C}_6\text{H}_3(\text{o-OMe})\text{CH}_2\text{CH}_2\text{-O]}_n\text{--}$	55.7	~83	<1 ^b (325°C)	

a. Estimates based upon data and derived values in references 5 and 6. Because the differences are small, values have *not* been rounded to nearest kcal; even though *absolute* accuracy for any given estimate is probably only 1-2 kcal/mol, the relative accuracy should be substantially better.

b. Values taken from vacuum vaporization curves, based on fraction vaporized during the 300° to 350°C interval.

As reviewed by Poutsma, (11) the data for PPE indicate an H-abstraction — β -scission radical-chain decomposition that is initiated by $\text{CH}_2\text{-O}$ bond homolysis, and in which the H-abstraction chain-transfer step is the slowest of the two propagation steps, as shown above in Scheme 1.

Comparing first the behavior of the simple $\text{--[PhCH}_2\text{CH}_2\text{-O]}_n\text{--}$ polymer with PPE, we see that at 300°C, where $2.3RT = 2.62$ (in kcal/mol units), and therefore where every ~2.6 kcal/mol decrease in activation energy results in a factor of 10 in rate increase, there would be less than a two-fold increase in initiation rate and no more than a six-fold increase in propagation resulting from the 2 kcal/mol decrease in the enthalpic requirement of the H-abstraction step. Together these

assuming similar termination rates, would lead one to expect an about an order of an order of magnitude increase in overall rate. However, the observed rate went up by more than a factor of 500.

Moving to the $\text{—[C}_6\text{H}_3(\text{o-OMe})\text{CH}_2\text{CH}_2\text{—O—]}_n\text{—}$ polymer, we see that a ~ 4 kcal/mol decrease in $\text{CH}_2\text{—O}$ bond strength should increase the rate of initiation by a factor of about ten as compared to the $\text{—[PhCH}_2\text{CH}_2\text{—O—]}_n\text{—}$ polymer, but that there should be little further effect on the H-abstraction propagation step, because the added methoxy group is meta- to the $\text{—CH}_2\text{—}$ group. (The $\text{CH}_2\text{—O}$ β -scission will be accelerated by ortho-methoxy substitution, but in the decomposition of β -phenethyl ether itself, the β -scission has been shown (11) to be, by a substantial margin, to *not* be the rate-limiting propagation step. Therefore, a decrease in $\text{CH}_2\text{—O}$ bond strength should have little impact on the overall propagation rate.) Faster initiation without faster propagation should tend to lower the onset temperature but decrease the steepness of the vaporization curve in Figure IV-3. Since this clearly is not what happened with the methoxy polymer as compared with the simple $\text{—[PhCH}_2\text{CH}_2\text{—O—]}_n\text{—}$ polymer, it appears that a new mechanism may be intervening as this system is made polymeric and progressively more lignin-like.

This conclusion, of course, is at this stage highly speculative; however, it is consistent with the fact that the bond cleavage lifetimes observed for both polymers are substantially shorter than those reported for β -phenylphenethyl ether ($\text{Ph—O—CH}_2\text{CH}_2\text{Ph}$). To summarize, the terminal hydroxy group, as it apparently does with lignins, seems to activate the adjacent —C—C—O— linkage to an extent not readily explained by the radical-chain chemistry considered sufficient for the simple ether itself. Furthermore, the addition of a methoxy group ortho- to the O—Ar attachment additionally enhances the reaction rate in a way that is not readily explained by the expected radical-chain chemistry.

Generation of Satellite Peaks from Loss and Addition of Methyl Groups. Another prominent difference between the Py-FIMS of the unsubstituted and methoxy-substituted —C—C—O— polymers lies in the different levels of satellites they generate at $\pm n(14)$ mass units from each of the main oligomer peaks. This difference can easily be seen by comparison of the spectrum in Figure IV-1 for $\text{—[C}_6\text{H}_3(\text{o-OMe})\text{CH}_2\text{CH}_2\text{—O—]}_n\text{—}$ with that in Figure IV-2 for the $\text{—[PhCH}_2\text{CH}_2\text{—O—]}_n\text{—}$ polymer. Qualitatively it is not surprising that the satellite peaks at -14 and -28 are more prominent with the methoxy-substituted polymer, given that the ArO—Me bond is moderately weak, but the size of these satellites is a quantitative surprise. The -14 satellites could be formed by simple homolysis of one of the ArO—Me bonds in the methoxy polymer, but since literature data suggest O—Me bond in the OH-terminated aromatic ring (est. BDE = ~ 60 kcal/mol) should exhibit a homolysis half-life of about 20,000 minutes at 300°C and 400 minutes at 350°C , the roughly 12 minutes required to go from 300 to 350°C and generate the volatiles would appear to be insufficient

to allow roughly one out of every five monomer units to have lost a methyl group. Therefore, we tentatively conclude that the loss of methyl groups is somehow coupled to cleavage of the central linkage.

The rather small variation in intensity of the satellite peaks relative to their respective "parent" oligomer peaks shown in Figure IV-1 is something we do expect to see. Since in all interior units of any oligomer, the O-Me bond strength is about 3 kcal/mol higher (with 300- and 400°C- half-lives of 300,000 and 4,000 minutes, respectively) , we do expect, in oligomer units below $n = \sim 10$, to have most of the O-Me cleavage occur on the terminal ring system. In accord with this expectation, the intensity of satellites at - 14 Daltons in Figure IV-1 increases from roughly 20% of the oligomer parent in the monomer to only about 40% of the parent in the hexamer.

The additional implication of observing rather little methyl loss except from the terminal unit is that notwithstanding its moderately weak bond, most of the O-Me aralkyl ether bonds can, *under appropriate conversion conditions*, perhaps remain intact long enough to provide crosslink protection for the dihydroxy aromatic units. This presumably explains why there was 100% vaporization during Py-FIMS of the $—[C_6H_3(o-OMe)CH_2CH_2-O]_n—$ polymer, but the presumption needs to be tested (see below).

Extent of Cleavage by Hydrodealkylation. One other very noticeable difference between the $—[PhCH_2CH_2-O]_n—$ and $—[C_6H_3(o-OMe)CH_2CH_2-O]_n—$ polymers is the much larger intensity of the peak corresponding to dealkylated monomer (i.e, to phenol in the former case, and methoxy phenol, or guaiacol, in the latter case) in the polymer *not* having the methoxy substitution. Thus the m/z 94 peak in Figure IV-2 is much larger than the m/z 124 peak in Figure IV-1. As we have previously noted, formation of phenol (or guaiacol) requires not only cleavage of the C-O linkages on either side of a given aromatic ring (a non-hydrogenative, or non-reductive, cleavage), but also a hydrodealkylation or hydrogenolysis to remove the two-carbon chain, as shown below.

Scheme 2. Required bond cleavages to form dealkylated monomer.

The ultimate origin of the hydrogen necessary to form the dealkylated or otherwise reduced oligomers is not evident in the FI mass spectrum of Figure IV-2. That is, the sum of hydrodealkylated and reduced oligomers, at least up to $n = 3$, is about ten times the sum of oxidized oligomers. Presumably the necessary additional hydrogen has come from the 20% of the —[PhCH₂CH₂O]_n— that failed to volatilize under the pyrolysis-FIMS conditions. Such disproportionation phenomena are quite common in pyrolytic processes, such as the hydrotreating of petroleum- or coal-derived resids, although the detailed mechanisms are generally unclear (13).

In the case of the —[C₆H₃(o-OMe)CH₂CH₂O]_n— polymer, there is much less hydrodealkylation. As can be seen in Figure IV-1, the ratio of guaiacol to HOC₆H₃(o-OMe)-CH=CH₂ is only about one-tenth of (0.14 vs 1.2) the ratio of phenol to HOPh-CH=CH₂ from —[PhCH₂CH₂O]_n— (Figure IV-2). We do not yet know whether this is because the methoxy substitution actually slows hydrogenolysis, or simply because it speeds up the competing cleavage of the O-C bonds in the main linkages. It is noteworthy that the —[C₆H₃(o-OMe)CH₂CH₂O]_n— polymer whose Py-FIMS spectrum is shown in Figure IV-1, was 100% (i.e., 97±3%) volatile. That is, there was very little hydrogen-poor char whose formation would have freed up the hydrogen necessary for widespread hydrogenolysis. This leads one to ask, once again, (13) the question, "To what extent (i.e., with what inevitability) is hydrogenolysis, which one wants, driven by crosslinking, which one does not want (at least in the coal liquefaction, heavy-oil processing contexts)?" In any case, a similar observation, namely that free phenolic groups on polymer models results in both more crosslinking *and* in more indiscriminate bond scission than results from their methylated analogs, can be drawn from pyrolysis-FIMS data for other polymer types published several years ago by Solomon and Squire (14).

Implications of -C-C-O- Polymer Decomposition Behavior. To summarize the thermal decomposition behavior, both the [PhCH₂CH₂O]_n— polymer and its methoxylated analog, —[C₆H₃(o-OMe)CH₂CH₂O]_n—, undergo rapid coordinated linkage cleavage, or unzipping, in the 300 to 350°C temperature region, yielding 80% or more volatile material under the temperature-programmed vacuum pyrolysis conditions of FIMS analysis. This general behavior was expected, inasmuch as the simplest element of these polymers, phenylphenethyl ether undergoes fairly rapid central bond cleavage in a radical-chain H-abstraction—β-scission process. However, the facility and pronounced autocatalytic depolymerization of the two new polymers was quantitatively unexpected. By the same token, the crosslinking, or retrograde reaction, has been rather less than we expected (and less than we observed last year with a more impure and potentially pre-crosslinked sample of the —[C₆H₃(o-OMe)CH₂CH₂O]_n— polymer). The surprising facility of depolymerization of the remnants of lignin most likely to be found in low-rank coals provides some tentative conclusions and raises further questions relevant to the liquefaction of low-rank coals. First, if crosslinking (in low-rank coals) is to be competitive with this type of depolymerization, the crosslinking must be exceedingly facile. Second, it follows then that *none* of the rather limited

crosslinking behavior we observed in our studies with various aromatic and aliphatic (and at least arguably coal-related) carboxylic acids was facile enough to support the long-standing speculation that decarboxylation instigated crosslinking is the major cause of retrograde reactions during preheating and/or liquefaction. Third, these results throw attention regarding the issue of retrograde reactions back to phenolic -OH as the major site/source of crosslinking and further emphasize the importance of comparing the conversion behavior of the $\text{---[C}_6\text{H}_3(\text{o-OMe})\text{CH}_2\text{CH}_2\text{-O]}_n\text{---}$ polymer with the unmethylated analog $\text{---[C}_6\text{H}_3(\text{o-OH})\text{CH}_2\text{CH}_2\text{-O]}_n\text{---}$. Fourth, the unexpected facility and autocatalytic nature of the $\text{---[C}_6\text{H}_3(\text{o-OMe})\text{CH}_2\text{CH}_2\text{-O]}_n\text{---}$ depolymerization, which cannot readily be explained by simple free radical pathways, raises the question of whether electron-transfer may be important in the decomposition of these model coal polymers, and if so, whether explicit attempts to exploit such chemistry might be practical.

Demethylation of the $\text{---[C}_6\text{H}_3(\text{o-Me})\text{-O-CH}_2\text{CH}_2\text{]}_n\text{---}$ Polymer

The complete lack of crosslinking observed under Py-FIMS conditions for this polymer, if anything, increases the relevance comparing its behavior with that of the analog containing free -OH rather than -OMe groups. Four different reactions for effecting the selective cleavage of the ArO-Me bond in the presence of the ArO-CH₂ bond were studied. The first reaction is the method of Harrison, (15) which involves heating of the polymer with Lil in collidine at 185°C for about 10 h. During the reaction the sample darkened considerably, although after aqueous work up, the solid isolated was only light brown, and was partially soluble in CDCl₃. The ¹H NMR of the CDCl₃ solution was essentially identical to that of the starting material, except that the peak due to the methoxy group now had the same area as that due to the O-CH₂ peak. Also, there was a small broad peak at 5.5 ppm, most likely due to free phenolic. These data are consistent with cleavage of about a third of the methyls in the starting polymer.

The second reaction was a variation on the first one. It involved heating the polymer with NaCN in DMSO at 185°C. (16) Unfortunately, the product from this reaction was only slightly soluble in DMSO. The soluble portion was found to be the unconverted starting material. The rest of the product was dark and intractable. We also tried the method of McKervery (17) using lithium aluminum hydride in benzene. However, this procedure was not successful with our polymer.

Finally, we attempted the reaction with iodotrimethylsilane. This reagent is potent enough to cleave the ArO-CH₂ linkages as well, and we hoped that by carefully controlling the conditions, we might achieve the desired selectivity. Tests in small scale experiments in NMR tube showed that the cleavage of O-CH₃ was about three times faster than that of the O-CH₂ linkage. We are encouraged by these early results and will pursue this reaction in the next quarter.

V. TASK 4 - DATA INTEGRATION AND REPORTING

Work was completed on the ACS Denver paper, titled "The Effects of Moisture and Cations on liquefaction of Low Rank Coals." A copy is included as Appendix A. The conclusions from this paper are as follows:

- The tar yields and liquefaction yields are reduced for all three cations tested (K^+ , Ca^{++} , Ba^{++}) and are lower for the fully exchanged coals. The ability of cations to act as initial crosslinks is an important aspect of their role in retrogressive reactions.
- The previously observed correlation between pyrolysis tar and liquefaction yields for coals and modified coals appears to hold for the vacuum-dried cation-exchanged coals, but not always for the re-moisturized coals.
- The total evolution of CO_2 and CO from pyrolysis is changed significantly by cation-exchange. However, only in the case of CO does the evolution profile change significantly.
- After careful demineralization, a calcium form Zap or Wyodak coal can be prepared at $pH=8$, which is similar to the raw coal with regard to pyrolysis and liquefaction behavior.
- At $pH=8$, cations are most likely to be coordinating multiple oxygen functionalities around themselves through electrostatic type interactions, which diminishes the importance of valency.
- Some of the moisture in a coal is associated with the cations. The moisture content has a larger role in liquefaction than in pyrolysis because it is present for a longer period of time.

In addition, three abstracts were prepared for the International Conference on Coal Science (Banff, Alberta, CANADA, September 12-17, 1993) based on the work done under this project. The first is titled "The Role of Cations in Retrogressive Reactions During Pyrolysis and Liquefaction," which concerns the work done on coals and modified coals. The second is titled "Application of a Spectral Deconvolution Technique to Coal FT-IR Spectra," which concerns the use of FT-IR methods for measurement of carboxyl and hydroxyl functions. The third paper is titled "Pyrolysis Pathways and Kinetics of Polymeric Models for Low-Rank Coals" which focuses on the thermal decomposition chemistry of the β -ether-linked lignin model polymers. Copies of the three abstracts are included in Appendix B.

VI. PLANS FOR EIGHTH QUARTER

Task 2. Studies with Coals and Modified Coals

The demineralized and methylated Zap lignite sample have been prepared and sent to Advanced Fuel Research for liquefaction and TG-FTIR studies. SRI has retained a portion (4 grams out of 14.2 grams), and it is still possible that they will subject this portion to partial dealkylation. However, even though the objective here would be for example to hydrolyze the methyl esters without cleaving the methyl ethers, the subtleties involved in cleaving one type of O-Me linkage without cleaving another (see Task 3), together with limitations in the remaining time and funds, could prevent us from producing a partially methylated Zap sample whose liquefaction behavior could be reliably interpreted.

Work will be completed on the use of the FT-IR methods for measuring carboxyl and phenolic functions.

Task 3 - Studies with Polymeric Model Systems

Small portions of the $\text{—[C}_6\text{H}_3(\text{o-OMe})\text{CH}_2\text{CH}_2\text{O-]}_n\text{—}$ polymer will be subjected to further variations of ether cleavage conditions to see if partial (or complete) de-methylation can be accomplished with only very little cleavage of the -C-C-O- linkage. This would then provide two (or more) polymer samples of the same or similar molecular weight with varying percentages of "protected" hydroxy groups, whose crosslinking behavior could then be directly compared. We do not yet know how successful this attempt will be, since we are trying to find conditions under which one alkyl-aryl ether (ArO-Me) is cleaved, while another ($\text{ArO-CH}_2\text{CH}_2\text{-}$) is essentially untouched, in order that varying molecular weight distributions between the methylated and de-methylated polymers will not grossly distort the results.

Task 4 - Data Integration and Reporting

Work will be completed on the use of the FG-DVC liquefaction model to simulate results for modified coals.

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