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FUNDAMENTAL STUDIES OF RETROGRADE REACTIONS IN DIRECT LIQUEFACTION

TOPICAL REPORT

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ABSTRACT

Most of the proposed processing schemes for improving liquefaction yields involve favoring bond-breaking and radical stabilization reactions over the retrograde reactions. The retrograde reactions are often encountered before liquefaction temperatures are reached. The objective of this program is to elucidate and model the retrograde reaction chemistry in direct coal liquefaction through the application of experimental techniques and theoretical models which have been successfully employed at Advanced Fuel Research (AFR) and SRI International (a subcontractor) to understand and predict coal reaction behavior. The study of retrograde reactions is being done using an integrated approach using extensive characterization of the liquefaction chemistry of three kinds of systems: 1) model polymers; 2) coal; and 3) modified coals.

Three coals from the Argonne sample bank are being used for these studies: Illinois No. 6, Wyodak, and Beulah Zap. For each coal, samples of raw coal, dried coal, ion-exchanged (for removal of alkali metals), methylated (for removal of hydroxyl and/or carboxyl groups), and demineralized coal have been prepared. The coals and modified coals have been characterized by a variety of techniques (TG-FTIR, elemental analysis, SEM/x-ray microanalysis, FIMS, FT-IR, solvent swelling). The coals and modified coals are subjected to liquefaction conditions in a microautoclave reactor system and the products are characterized by their solubility fractions.

The microautoclave reactor system which has been developed allows liquefaction experiments on one gram quantities of coal and enables an analysis of the gas phase to be done. This capability is important since the evolution of certain gases has been associated with retrograde reactions. Experiments with two solvent systems (phenanthrene, naphthalene) are being done at three different degrees of hydrogenation.

The purpose of the liquefaction experiments is to see how these pretreatments affect the liquefaction yields and gain an understanding of the mechanisms of the retrograde reactions. The preliminary conclusions from this study are as follows:

- The extent of retrograde reactions for low rank coals (lignite, subbituminous) is significantly reduced by methylation and demineralization. However, these treatments do not have much impact on bituminous coal.
- Ion-exchange has a modest positive impact for most low rank coals while drying has a modest negative impact. Drying had little impact on the liquefaction yields from the bituminous coal, while the ion-exchange treatment had a modest negative impact.
- In nearly all cases, the changes in the amounts of pyridine solubles by these pretreatments parallel the changes in the amounts of toluene solubles.
- The effects of methylation, demineralization, and ion-exchange on liquefaction yields parallel the effects of these treatments on pyrolysis liquid yields.

A second component of the work has been the preparation and characterization of model polymers in order to study retrograde reactions which are simpler to interpret. The objective of this work is to determine the competing kinetics of bond cleavage and retrogressive reactions for polymers containing chemical bonds relevant to the elements of chemical structure of coals. Under the present contract, we are preparing the following three-atom-bridged polymers of the C-C-C and C-C-O types (I and II) in order to mimic the linkages most commonly invoked in lignin and low-rank coal structures.

Type I $\text{R} = \begin{matrix} \text{H} \\ \text{OCH}_3 \end{matrix}$

Type II $\text{R} = \begin{matrix} \text{H} \\ \text{OCH}_3 \end{matrix}$

These polymer models will then be subjected to various liquefaction conditions and an assessment of the bond cleavage and bond forming reactions will be made by analyzing the resulting products with a variety of analytical methods such as FIMS, NMR, FT-IR and GC-MS.

During the past year, work was completed on preparation of the C-C-O polymers from two starting materials (eugenol and p-allylphenol). Procedures for the reductive demercuration of these polymers were worked out. The polymers were characterized using GPC, NMR, and FIMS. The NMR and FIMS data are consistent with the expected structure of the polymers, although the latter also reveals unexpected behavior.

Initial liquefaction experiments with the C-C-O linked polymers have revealed a high tendency to coke. This tendency could be a result of the high molecular weight (up to $M_n = 5 \times 10^5$) of the samples thus far studied. The polymers are soluble and believed to be uncrosslinked, but complete characterization is difficult. Further studies will involve the synthesis and study of lower molecular weight samples.

FUNDAMENTAL STUDIES OF RETROGRADE REACTIONS IN DIRECT LIQUEFACTION

CONTRACT NO. DE-AC22-88PC88814

TOPICAL REPORT

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I. INTRODUCTION

Most of the proposed processing schemes for improving liquefaction yields involve overwhelming the retrograde reactions by simply enhancing the bond-breaking reactions. The retrograde reactions are often encountered before liquefaction temperatures are reached. Hence, it is important to focus on the retrograde reactions themselves. The goal of this program is to elucidate and model the retrograde reaction chemistry in direct coal liquefaction through the application of experimental techniques and theoretical models which have been employed at Advanced Fuel Research (AFR) and SRI International (a subcontractor) to understand and predict coal reaction behavior. The program will necessarily include studies of bond-breaking reactions and solvent effects, since these are intimately related to the retrograde reaction chemistry. The results of the experiments in the proposed program are expected to lead to an improved mechanistic understanding of retrograde reaction mechanisms in liquefaction that can be used to explore improved process concepts designed to minimize retrograde reactions and, thus, to improve liquefaction yields.

The research program calls for a study of retrograde reactions by an integrated approach using extensive characterization of the liquefaction chemistry of three kinds of systems: 1) model polymers; 2) coal; and 3) modified coals. Each system has advantages as well as drawbacks; the different systems are expected to provide complementary information. The experience of AFR has primarily been in studying the reaction behavior of coal and model polymers, mainly under pyrolysis conditions, to identify global reactions and transport effects. The experience of SRI has primarily been in studying thermal reactions of model compounds and model polymers from a chemical mechanism perspective, mainly under liquefaction conditions.

II. BACKGROUND

The motivation of the present study comes from work that has been done on the pyrolysis of coals, modified coals, and model compounds. This work has identified several key factors which are important in retrograde reactions which occur under pyrolysis conditions. Solvent swelling^{1,2} has been used as a method for measuring the crosslink density of pyrolysis chars. The amount of tar formation in pyrolysis is another indication of the amount of crosslinking which has occurred.³⁻⁷

Measurements of the solvent swelling ratio for a number of coals pyrolyzed under the same conditions show that the early crosslinking which reduces liquid yields, occurs in low rank coals, as shown in Figure II-1. This result is consistent with the observation that the short time liquefaction yields are lowest for these coals.⁸ Suuberg et al. observed that the low temperature crosslinking associated with low rank coals appeared to correlate with the evolution of CO₂.^{3,4} This correlation was confirmed in recent work done by Solomon and coworkers, as shown in Figure II-2. A similar correlation was found with the loss of H₂O. Based on the assumption that low temperature crosslinking was related to decomposition of carboxyl and/or hydroxyl groups, FT-IR functional group analysis was done on the pyrolysis chars. The results, which are shown in Figure II-3, support the role of both functional groups in crosslinking.

The water content of the coal also appears to play a role in retrograde reaction chemistry. Studies have shown that drying the coal can increase the amount of crosslinking which occurs in pyrolysis⁵ and liquefaction.⁹ Steam pretreatment has been found to have a beneficial effect on pyrolysis¹⁰ and liquefaction yields.^{11,12}

In addition to solvent swelling, an examination of the tar yield and tar molecular weight distribution has been valuable in assessing the degree of crosslinking.^{7,13} Results for Field Ionization Mass Spectrometry (FIMS) analysis of the eight Argonne coals are shown in Figure II-4. It can be seen that the tar molecular weight distribution (MWD) for low rank coals drops off fairly dramatically above 200 AMU. The dramatic cut off is consistent with the occurrence of crosslinking in these coals and the lower tar yields that have been measured. When a low rank coal is methylated, it has been found that the tar yield and the tar MWD begin to resemble a bituminous coal,¹³ as shown in Figure II-5 for a Texas lignite.

The removal of cations from a low rank coal by ion-exchange or demineralization also has a beneficial effect on the tar yield and the extent of crosslinking¹⁴ in pyrolysis studies. The role of cations in direct liquefaction has not been extensively studied.

Figure II-1. Comparison of Solvent Swelling Ratios for Coals of Various Ranks at a Series of Pyrolysis Temperatures.

Figure II-2. Correlation Between Loss of Swelling and Gas Evolution.

Figure II-3. Correlation Between Loss of Swelling and Loss of Functional Groups.

Figure II-4. Tar Molecular Weight Distributions from Pyrolysis-FIMS of the Argonne Premium Coals.

Figure II-5. Comparison of Spectra for Raw and Perdeutero-Methylated Texas Lignite.

The results from these pyrolysis studies, which have shown the importance of oxygen functional groups, water content, and cations on crosslinking, provided much of the motivation for the present study of retrograde reactions in liquefaction using similar analytical techniques.

III. ACCOMPLISHMENTS

III.A. Introduction

The work breakdown structure is given as Figure III-1. The work is divided into four tasks. The polymer synthesis, their characterization by FIMS, GPC and NMR, and the liquefaction experiments with C-C-C polymers are being done primarily at SRI. The coal modifications and the coal liquefaction experiments are being done primarily at AFR.

III.B. Studies with Polymeric Model Compounds

Objective - The objective of this work is to determine the competing kinetics of bond cleavage and retrogressive reactions for polymers containing chemical bonds relevant to the elements of chemical structure of coals. Under the present contract, the plan is to prepare the following three-atom-bridged polymers of the C-C-C and C-C-O types (I and II).

Type I R = $\begin{matrix} \text{H} \\ \text{OCH}_3 \end{matrix}$

Type II R = $\begin{matrix} \text{H} \\ \text{OCH}_3 \end{matrix}$

Polymer Synthesis and Characterization - During the first year, work was completed on the preparation of the C-C-O polymers. The polymers were prepared by the oxymercuration of eugenol (R = OCH₃) and p-allylphenol (R = H).

Figure III-1. Work Breakdown Structure of the Project.

The eugenol was obtained from Aldrich Chemical, Inc. The p-allylphenol was obtained by custom synthesis from Saber Laboratories (Morton Grove, Illinois).

The polymerization was best conducted at 80°C in nitromethane solvent using dry $\text{Hg}(\text{CF}_3\text{CO}_2)_2$ as a catalyst. The growth of the polymer chain was monitored using GPC. However, because a substantial portion of the reaction mixture precipitates out of the solution, the true MW is best determined at the end when the entire product is worked up. The immediate product of direct polymerization contains covalently bonded mercury, which has to be removed by reduction with a borohydride reagent. The polymers were characterized using GPC, NMR, and FIMS. GPC shows that the poly(eugenol) sample has a broad distribution of molecular weights (1×10^5 to 2×10^6 ; $M_n \sim 200,000$). The poly(p-allylphenol) sample, on the other hand, has a narrow MW range with a $M_n \sim 5 \times 10^6$. Light-scattering experiments confirmed the very high molecular weights of poly(eugenol) and poly(p-allylphenol).

An unexpected result was the extremely high molecular weights of the product polymers from eugenol and p-allylphenol that were obtained after demercuration. The polymers were insoluble in most common solvents but were soluble in DMF, indicating that they were not crosslinked. The ^1H -NMR spectra were complicated by peaks due to water and the solvent, even though the DMF used was deuterated. However, the presence of $\text{C}_{\text{ar}}\text{-CH}_3$ methyls and the absence of olefinic protons is consistent with the expected structures. Results of pyrolysis/FIMS of the polymers are depicted in Figures III-2a and III-2b. Major peaks in the spectra are consistent with phenols and their alkylated derivatives. In the case of poly(eugenol), peaks due to dioxygenated benzenes are prominent. The surprising result in the FIMS analysis is that roughly 40% to 50% of the polymer was not devolatilized up to 450°C. These results are consistent with TG-FTIR analysis of the two polymers (30°C/min to 900°C) which showed that 30 to 40% was not volatilized.

Work was begun on the synthesis of C-C-C polymers using the following reaction sequence:

Figure III-2. FIMS Spectra of C-C-O Polymers.

The α,α' -dibromo-p-xylene (I) was treated with the monoanion of dithiane (II) in THF at -50°C to -30°C . The product (III) was characterized by TLC and NMR and conformed with the anticipated structure. The dianion from III was treated with the dibromide (I) at low temperatures for 3 hours and thereafter at room temperature for 15 hours. The THF-soluble fraction showed a polymer of MW ~ 2500. Desulfurization of the THF-soluble portion was effected using Raney Ni and the product was exhaustively extracted to yield a polymer of MW ~ 1500. Elemental analysis gave C = 83.86% and H = 8.7%, indicating a H/C ratio of 1.24; the expected H/C ratio for the polymer is 1.11.

The final yield of the soluble C-C-C polymer was only about 50 mg. The next step is to prepare additional batches of this polymer and improve the yield.

Liquefaction Experiments - We conducted preliminary liquefaction experiments with both the C-C-O polymers using 100% dihydroanthracene and a 50-50 mixture of anthracene and dihydroanthracene (polymer to solvent 1:5; 400°C , 1h). These experiments were done in microautoclave reactors similar to the type shown in Figure III-3. In all four cases, the product mixtures were not completely soluble in CH_2Cl_2 , implying less than complete conversion. This result is in contrast with that from the "liquefaction" of a bibenzyl polymer, which was completely soluble even in tetralin.¹⁵ ^1H -NMR spectra were recorded of the DMSO-soluble portions of the products from runs with pure dihydroanthracene. These spectra showed peaks due to the anthracene and dihydroanthracene. The products from the "liquefaction" of the C-C-O polymers were also analyzed by FIMS. The majority of the signal was due to anthracene and its hydrogenated derivatives. We did not observe the monomers, dimers, and trimers of eugenol and p-allylphenol to evolve at low temperatures, indicating that during the "liquefaction" these species were not formed. The absence of dimers, trimers, and other oligomers in the Py-FIMS of the polymer suggests that the reactive intermediates rapidly proceed to either monomers or char. This seemingly unlikely scenario is being repeated even during liquefaction, where there is an excess of donor solvent to stabilize the intermediate.

III.C. Experiments with Coal and Modified Coals

Objective - Study retrogressive reactions in coals and modified coals under coal liquefaction conditions.

Coal Modifications - Three coals from the Argonne sample bank are being used (Illinois No. 6, Wyodak, and Beulah Zap). Coal samples have been prepared so that for each coal there is a supply of raw coal, dried coal, acid-demineralized coal, ion-exchanged coal for the removal of exchanged metal cations (Ca, Na, K) and methylated coal for the blocking of hydroxyl and/or

1. Bomb Reactor
2. High Temperature Valve
3. High Temperature Adapter (High Pressure Equipment Corp. #20-12LF4-HT) with Teflon Packing
4. Short (1") Connection Between Reactor and Valve (1/4" O.D. x 1/16 I.D.)
5. Base Plate to Hold Reactor
6. Thermal Insulation
7. Electrically Heated Fluidized Sand Bath

Figure III-3. Schematic of AFR Microautoclave Reactor System.

carboxyl groups. All of the coal modifications have been done at AFR, except for the methylation work which is being done at SRI. The starting samples have been characterized by the following procedures: TG-FTIR to determine proximate analysis, condensable product yield, gas yields, etc.; elemental analysis to determine C,H,N,O, and S, mineral analysis and spatial distribution by the contractor's SEM x-ray microanalyzer; quantitative FT-IR analysis of minerals and functional groups; FIMS analysis of molecular weight distributions of condensable products; and solvent swelling to determine the crosslink density.

Initial experiments on the methylation of coals using Liotta's¹⁶ procedure were conducted with PSOC 1098, an Illinois No. 6 coal. Subsequent experiments were conducted with the Argonne Wyodak coal and the Argonne Beulah Zap Lignite.

Several techniques were used to assess the degree of alkylation. In contrast to literature reports, it was found that the titrimetric estimation of active hydrogens was very difficult because of the absence of clear end points. Infrared analysis (KBr Pellet, transmission mode) showed a distinct decrease in the % transmission in the OH region. However, the OH band was not eliminated. A more quantitative determination will be attempted using an FT-IR instrument. Elemental analysis of the methylated Illinois No. 6 coal showed that about 5 additional carbons were added for every 100 carbons. This result suggests that nearly all the hydroxyls were methylated.

Methylated Wyodak coal showed a very substantial decrease in the OH intensity, although the peak was not completely eliminated. The elemental analysis of the starting coal (dried) and the once methylated derivative gave the following compositions, assuming constant oxygen:

Starting Coal:	$C_{100}H_{72}O_{25}N_{1.4}$
Once Methylated:	$C_{116}H_{102}O_{25}N_{1.6}$

Every OH group that is methylated should result in an increase of one carbon and two hydrogen atoms. The observed increase in hydrogen (30) matches closely with that in carbon (16). If the slight increase in nitrogen is to be ascribed to remaining tetrabutylammonium ions, the number of O-methyls introduced reduces from 16 to 12.

Methylation of the Argonne Zap lignite was also attempted. The IR spectrum of the product showed a much larger amount of residual OH intensity as compared with the Wyodak. Elemental analysis also showed a disproportionately large increase in carbon and nitrogen. We suspect that not all of the tetrabutylammonium ion was removed during the aqueous wash and

perhaps more than one methylation step may be necessary for lignites. We subjected the product to a second methylation and also methylated another batch of Zap lignite using a longer alkylation period and a more extensive wash to remove excess alkylammonium salt.

Ion-exchanged samples of the three coals were prepared using a procedure similar to that used by Hengel and Walker.¹⁷ In this procedure, the alkali metal cations are removed by treatment with ammonium acetate solution. The coals were demineralized using the procedure of Bishop and Ward.¹⁸

Coal Characterizations - Thus far, each of these three coals has been characterized by SEM/x-ray and TG-FTIR. Both instruments were developed at AFR. The SEM/x-ray system is based on a method originally described by Solomon and Manzione.¹⁹ It consists of an ISI model SX-30 scanning electron microscope with a Princeton Gamma Tech System model 4 x-ray analyzer. The analyzer has the capability of measuring elements heavier than sodium.

The results of the x-ray analysis of the ion-exchanged and demineralized samples confirmed that the concentrations of ion-exchangeable metal cations (Ca, Mg, Na, K) were significantly reduced as shown in Table III-1. It is evident that the Zap and the Wyodak coals have higher concentrations of Ca and Mg which are often ion-exchanged on carboxyl groups in high oxygen coals. It is not clear why the Ca content of the demineralized Zap lignite was higher than for the ion-exchanged Zap lignite. This measurement will be repeated.

The results of TG-FTIR analysis of the raw, ion-exchanged, demineralized and methylated Zap lignite are shown in Figures III-4 and III-5. Each figure shows differential and integral plots for the major volatile species. An integral plot for the overall weight loss is included as the first plot in each figure, along with the time-temperature profile. The main differences are seen in the yields of tar and CO₂, which have been identified previously (see Section II) as key indicators of the extent of crosslinking. The CO₂ yields were lower for the ion-exchanged, demineralized, and methylated Zap lignite when compared to the raw coal. The corresponding tar yields are higher. From these results, one can infer that the amount of crosslinking increases in the order methylated < demineralized < ion-exchanged < raw. The results for the Wyodak coal were very similar. However, the results for the Illinois coal were not significantly different for the various pretreatments when compared to the raw coal.

FIMS analyses were done of the raw coals and modified coals. The spectra of the demineralized and methylated low rank coals more closely resemble the spectra of bituminous coals, which is consistent with a reduction in low temperature crosslinking, as discussed in Section II. The FIMS results will be presented in the Fifth Quarterly Report.

TABLE III-1 - MINERAL COMPONENTS OBTAINED FROM SEM X-RAY
MICROANALYSIS OF RAW AND ION-EXCHANGED COALS

	Illinois #6				Beulah Zap				Wyodak			
	<u>Raw</u>	<u>Ion- Exchanged</u>	<u>Demin.</u>	<u>Raw</u>	<u>Ion- Exchanged</u>	<u>Demin.</u>	<u>Raw</u>	<u>Ion- Exchanged</u>	<u>Demin.</u>	<u>Raw</u>	<u>Ion- Exchanged</u>	<u>Demin.</u>
Na	0.04	0.00	0.00	0.32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.07	0.00	0.02	0.35	0.05	0.11	0.23	0.01	0.03	0.23	0.01	0.03
Al	1.23	0.71	0.34	0.33	0.39	0.19	0.55	0.50	0.05	0.55	0.50	0.05
Si	2.60	1.83	0.00	0.38	0.40	0.02	0.66	0.63	0.05	0.66	0.63	0.05
K	0.18	0.11	0.03	0.02	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.00
Ca	0.63	0.05	0.04	1.09	0.06	0.37	1.09	0.11	0.04	1.09	0.11	0.04
Ti	0.08	0.04	0.03	0.03	0.02	0.00	0.07	0.07	0.00	0.07	0.07	0.00
S(o)	1.48	1.36	1.57	0.30	0.28	0.33	0.36	0.38	0.35	0.36	0.38	0.35
S(m)	1.54	1.65	0.86	0.39	0.37	0.12	0.19	0.08	0.13	0.19	0.08	0.13
Fe*	0.47	0.30	0.22	0.17	0.14	0.07	0.20	0.20	0.01	0.20	0.20	0.01
Ash	13.17	8.06	1.12	6.86	2.50	1.80	6.44	3.11	0.30	6.44	3.11	0.30

*Non-Pyritic Iron

Figure III-4. TG-FTIR Analysis of Zap Lignite.

Figure III-5. TG-FTIR Analysis of Zap Lignite.

Liquefaction Experiments - After the samples were characterized, experiments were done under coal liquefaction conditions in microautoclave reactors. A schematic of the experimental system is shown in Figure III-3. Two liquefaction solvents are being used (naphthalene and phenanthrene) with three degrees of hydrogenation. The yields of toluene solubles, pyridine solubles, residue, and gas are being routinely determined. For selected experiments, the gas, liquids, and the solid products are being subjected to more detailed characterization by the same techniques used for the starting materials.

After leak testing of the reactor containing the coal and solvent, it is purged (pressurized - depressurized) with N_2 and the valve on the reactor is closed. The reactor is then immersed into a 400°C fluidized sandbath for the required time (30 min), lifted out and quenched with water. The reactor is subsequently pressurized to 1000 psig and is equilibrated into an 870 cc evacuated gas sample tank. The entire volume is taken to be 900 cc. The gases are measured chromatographically from the sample tank.

Products are dissolved and washed out of the reactor with toluene. The insoluble products are filtered into a paper thimble and put into a Soxhlet extractor for 24 hour extraction with toluene, and into the vacuum oven for drying. The drying process was monitored by a high pressure, high temperature continuous extractor system with an FT-IR monitor. Hexane was used for the elution of toluene out of the coal because hexane can easily be evaporated afterwards. It was found that eight hours at 100°C in the vacuum oven was enough time to remove the toluene from the coal residue (solvent refined coal - SRC).

The toluene solubles (solvents + oils + asphaltenes) were concentrated in a rotary vacuum evaporator and measured by weight in aluminum foil dishes. A stable weight was usually reached after drying them at room temperature for 24 hours and at 80°C for 2 hours. The residue from the toluene extraction was subsequently extracted with pyridine to allow determination of the pyridine solubles and insolubles.

The results of liquefaction experiments with the coals and modified coals are given in Tables III-2 and III-3 for the liquid and gas products, respectively, and summarized in Figures III-6 to III-8. The results show that the decrease in crosslinking, as implied by the reduction in CO_2 yield, roughly correlates with the increased liquefaction yields based on the toluene solubles. The trends in CO_2 yield and toluene solubles from liquefaction parallel the results for CO_2 yield and tar yield, respectively, determined from pyrolysis in the TG-FTIR analysis.

The extent of retrograde reactions for low rank coals (lignite, subbituminous) is significantly reduced by methylation and demineralization. However, these treatments do not

TABLE III-2 - SOLUBLE AND INSOLUBLE PRODUCT YIELDS FROM LIQUEFACTION EXPERIMENTS
(DAF WT.%)

Exp #	Coal (Type/Preparation)	Toluene Solubles Total	Oils	Toluene Insolubles	Pyridine Solubles	Pyridine Insolubles	Gas	V.S.R. of Coal	DAF% Pyridine Extract of Coal
North Dakota Lignite									
24	fresh	26	12	69	38	57	5.0	2.0	15
26	vacuum dry	15	4	78	29	64	7.2	2.7	5
15	ion-exchanged	46	26	48	80	14	6.0	2.3	7
18	demineralized	52	23	46	88	9	2.1	3.0	10
21	methylated	54	30	42	76	21	3.5	2.4	40
Wyodak									
25	fresh	39	13	56	48	46	5.2	—	7
28	vacuum dry	33	11	62	45	50	4.7	2.7	11
17	ion-exchanged	25	8	75	47	53	0.4	2.5	9
20	demineralized	56	23	43	97	2	1.5	3.1	18
23	methylated	62	27	32	89	4	6.5	1.6	53
Illinois #6									
6,8,13	fresh	47	17	52	98	1	0.9	—	27
27	vacuum dry	56	5	41	96	1	2.1	2.5	36
16	ion-exchanged	22	5	77	82	17	1.0	2.5	19
19	demineralized	53	12	46	91	8	0.9	3.0	22
22	methylated*	67	33	30	100	0	3.0	1.7	48

Notes:

Experimental conditions: 400°C, 30 min., 100% dihydrophenanthrene (DPH)

* PSOC 1098

TABLE III-3 - GAS PRODUCT YIELDS FROM LIQUEFACTION EXPERIMENTS
(DAF WT.% X 10³)

Exp #	Coal (Type/Preparation)	H ₂	CO ₂	CO	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂	H ₂ S	CS ₂	Yield %
North Dakota Lignite											
24	fresh	—	430	24	25	21	2.5	—	—	—	5.0
26	vacuum dry	—	641	31	30	20	6.2	—	—	—	7.3
15	ion-exchanged	7.4	491	43	28	52	2.8	—	—	—	6.2
18	demineralized	3.6	120	24	24	34	7.9	—	—	—	2.1
21	methylated	2.2	185	31	115	17	3.1	—	—	—	3.5
Wyodak											
25	fresh	2.1	409	34	31	36	8.4	—	—	—	5.2
28	vacuum dry	8.7	332	31	20	27	6.2	—	3.7	40	4.7
17	ion-exchanged	7.4	—	24	7	4	1.8	—	—	—	0.4
20	demineralized	5.6	97	19	6	20	5.4	—	—	—	1.5
23	methylated	112.6	219	39	247	29	6.0	—	—	—	6.5
Illinois #6											
6,8,13	fresh	3.9	35	2	16	31	4.6	—	—	—	0.9
27	vacuum dry	19.6	44	11	22	30	3.5	—	—	76	2.1
16	ion-exchanged	4.6	73	6	5	13	2.1	—	—	—	1.0
19	demineralized	9.9	28	8	9	33	5.1	—	—	—	0.9
22	methylated	36.5	47	13	153	32	3.3	3.1	4.0	7	3.0

Notes:

Experimental conditions: 400°C, 30 min., 100% dihydrophenanthrene (DPH)

* PSOC 1098

Figure III-6. Liquefaction Results for North Dakota Lignite.

Figure III-7. Liquefaction Results for Wyodak Subbituminous Coal.

Figure III-8. Liquefaction Results for Illinois No. 6 Bituminous Coal.

have much impact on bituminous coal. Ion-exchange has a modest positive impact for most low rank coals while drying has a modest negative impact. Drying had little impact on the liquefaction yields from the bituminous coal, while the ion-exchange procedure had a modest negative impact. In nearly all cases, the changes in the amounts of pyridine solubles by these pretreatments parallel the changes in the amounts of toluene solubles.

III.D. Data Evaluation and Reporting

The approach will be to explain the results qualitatively in terms of chemical mechanisms and quantitatively in terms of a liquefaction model. The mechanisms will be developed considering previous experimental results and mechanistic explanations from the literature. The results from the experiments with the model polymer systems will be interpreted in terms of actual coal liquefaction systems. Particular attention will be paid to the role of the solvent system and its impact on retrogressive reactions, in light of previous work done on this subject at SRI.

The effect of the various chemical modifications on crosslinking reactions and liquefaction yields will also receive close attention, in light of work done previously on this subject at AFR. In addition, an attempt will be made to incorporate the mechanistic information developed in this program into AFR's FG-DVC model⁷ which has been modified for liquefaction systems.²⁰ These modifications will be continued under the current program, if necessary, and the mechanistic understanding developed under the current program will be added.

In both the qualitative and quantitative modeling work, an effort will be made to relate the results to real liquefaction systems. This would include, for example, a discussion of the role of a hydrogenation catalyst and a different set of process conditions. A discussion will be included of possible process improvements that may be suggested by the results and recommendations will be made for further research.

Work on this task has not yet begun, except for some preliminary work on assessing the application of a network model which can predict coal fluidity²¹ (recently developed at AFR under separate funding) to the modeling of coal liquefaction.

IV. CONCLUSIONS

The preliminary conclusions from this study are as follows:

- The extent of retrograde reactions for low rank coals (lignite, subbituminous) is significantly reduced by methylation and demineralization. However, these treatments do not have much impact on bituminous coal.
- Ion-exchange has a modest positive impact for most low rank coals while drying has a modest negative impact. Drying had little impact on the liquefaction yields from the bituminous coal, while the ion-exchange treatment had a modest negative impact.
- In nearly all cases, the changes in the amounts of pyridine solubles by these pretreatments parallel the changes in the amounts of toluene solubles.
- The results from pyrolysis studies of crosslinking in coals and coals modified by methylation, demineralization, or ion-exchange are relevant in liquefaction.

V. PLANS

The plans for the next year are as follows:

- Complete verification of C-C-O polymer structure and liquefaction experiments. Time and funds permitting, we will compare these results with those for lignin samples.
- Complete synthesis and characterization of C-C-C polymers and liquefaction experiments.
- Complete partial methylation and characterization of all three coals.
- Complete liquefaction experiments on coals and modified coals.
- Explain the results qualitatively in terms of chemical mechanisms and quantitatively in terms of a liquefaction model.

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