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CONVERSION OF SOLVENT REFINED LIGNITE INTO
PREMIUM LIQUID FUELS

Annual Report for the Period January—December 1980

By
Richard J. Baltisberger
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April 1981
Date Published

Work Performed Under Contract No. AB18-78FC02101

University of North Dakota
Grand Forks, North Dakota

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Date Published - April, 1981

PREPARED FOR THE UNITED STATES DEPARTMENT
OF ENERGY

Under Contract No.
(DE-AB18-78FC02101; Task Order 15)

Objectives and Scope of Work

The objectives of this project are:

- (1) To continue the development of analytical separation techniques unique to lignite coal liquids and to apply these techniques to coal liquids produced under different temperature, pressure, or residence time conditions.
- (2) To apply the structural knowledge of solvent refined coals and organic chemical methods for ether cleavage to lignite and other coal samples provided by GFETC to determine structure.
- (3) To determine how carbon monoxide and hydrogen is effective in reducing the scissile (easy to reduce) bonds in lignite and how to optimize the reduction of more difficulty reduced bonds.
- (4) To continue mechanistic studies of the CO-H₂O catalyst reducing medium by observing electron transfer catalysis activity of CO, H₂O, H₂, and/or organics with various minerals present in coal slurries at reactor conditions.

It is anticipated that an understanding of the structural changes of molecular weights fractions obtained under different operating conditions will be gained, general information on ether cleavage reactions will be obtained, information on the role of CO⁺ in the nitrogen removal mechanism, the cleavage of polymers by CO will be learned, and the catalyst activity of various inorganic compounds with CO will be investigated.

Quarterly Report for the Period
January - March, 1980

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Date: April, 1980

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PROJECT TITLE: CONVERSION OF SOLVENT REFINED LIGNITE INTO PREMIUM
LIQUID FUELS (EX-76-C-01-2211)

SUMMARY

Comparison of three preasphaltene samples separated from three lignite derived samples obtained from GFETC prepared at 404, 460 and 480°C shows that increased temperature tends to produce higher molecular weight preasphaltene fractions containing more aromatic carbons with fewer acid (phenolic) sites per molecule. Ether cleavage studies of the model compounds; diphenyl ether, bibenzothiophene, dibenzofuran and anisole, show that partial or complete ether cleavage was obtained with sodium in hexamethylphosphoramide solvent. Thus a careful consideration of acidity before and after cleavage can now give a measure of the diaryl ether content of a mixture. This reaction may be useful in coal liquid analysis. Dentrification of N,N-Dimethylamine without aromatic ring reduction occurs with CO-H₂O and H₂ at 425°C in about 13% conversion. The optimum conditions of 21 conditions gave a 19% conversion occurs at 150 psi H₂S and 750 psi H₂. Thus, H₂S enhances nitrogen removal of this model compound. Using ESR dispersion techniques we have shown the presence of a second CO radical species on MgO, probably CO⁻. As observed by ESR, treatment of carbon monoxide radical species on both CO and MgO with CO₂ or H₂O causes a destruction of one of the radical species at a rate greater than that of the other.

Summary of Progress to Date

During this quarter the following tasks have been undertaken and/or completed:

- (1) Comparison of three preasphaltenes obtained from lignite derived samples (GFETC) prepared at 404, 460 and 480°C shows that the higher temperature tends to produce higher molecular weight material containing more aromatic carbons with fewer acid sites per molecule.
- (2) Ether cleavage of diphenyl ether was effected cleanly with sodium in hexamethyl phosphoramide solvent. Dibenzothiophene, dibenzofuran and anisole were cleaved in lower yields. Therefore, a careful consideration of acidity before and after cleavage can now give a measure of the diaryl ether content of a mixture.
- (3) Denitrification of N,N-Dimethylamine without aromatic ring reduction occurs with CO-H₂O and H₂ at 425°C in about 13% conversion. The optimum condition of 21 conditions gave a 19% conversion occurs at 150 psi H₂S and 750 psi H₂. Thus, H₂S enhances nitrogen removal of this model compound.
- (4) Using ESR dispersion techniques we have shown that the presence of a second CO radical species on MgO, probably CO⁻.
- (5) As observed by ESR, treatment of carbon monoxide radical species on both CO and MgO with CO₂ or H₂O causes a destruction of one of the radical species at a rate greater than that of the other.

Detailed Description of Technical Progress

Task I

Structural Studies of Lignite Derived Asphaltenes and Preasphaltenes

(1) NMR analysis of Three Lignite-Derived Liquefaction Samples

Results:

Three samples of lignite derived liquefaction products selected on the basis of operating temperature were obtained from the Grand Forks Energy Technology Center. The general operating conditions under which the samples were prepared were as follows. The samples were produced in a 5-lb lignite/hr continuous process unit in single pass tests in a continuous-stirred tank reactor (CSTR). The lignite product was derived from a Beulah 2, North Dakota, lignite by hydrogenation with synthesis gas (50:50 H_2 :CO) using an anthracene oil distillate solvent (40% as received coal slurry) at 4000 psi and three different operating temperatures; 400°C (sample 15-4-2), 460°C (15-4-7) and 480°C (15-4-11). The isolation of the preasphaltenes, asphaltenes and the heavy oils was carried out by liquid extraction. Details of the separation were described in our previous quarterly report. The three preasphaltene samples were acetylated and chromatographed by GPC techniques.

Table 1-3 show the distribution of molecular weights for the three GFETC samples. The most apparent properties that change with temperature are as follows: (1) The molecular weight distribution goes to higher weights as the temperature of the liquefaction condition is raised. (2) The acidity maximizes in terms of meq/gm in the middle fractions. However on a per molecule basis, the number of acid sites per molecule is highest at the high molecular weights. The total acidity per molecule

Table 1. GPC Separated Fractions From
Acetylated Preasphaltenes of GFETC Sample
15-Y-2 (404°C)

Fraction	Wt%	Mole Wt ^a	Acidity ^b Meq/gm	H _{aro} , % ^c	H _α , %	H _o , %
1	15.4	582	1.80	32.7	33.3	34
2	26.4	573	1.90	32.8	32.6	34.6
3	17.3	546	1.97	31.8	37.5	30.7
4	7.4	373	2.37	28.9	43.3	27.8
5	7.1	218	2.73	28.2	45.5	26.3
6	7.7	219	2.94	27.6	47.6	26.8
7	4.3	224	2.94	28.1	49.5	22.4
8	6.8	210	2.89	29.6	45.7	25.1
9	3.9		1.92	32.9	39.9	27.2
10	1.9		0.57	41.7	36.9	21.4
11	1.3		0.04	51.6	37.6	10.8
12	0.6		0.005	55.9	36.1	8.0

a Measured by VPO, pyridine solvent

b Measured by C¹⁴ counting

c Measured by proton nmr

Table 2. GPC Separated Fractions From
Acetylated Preasphaltenes of GFETC Sample
15-Y-7 (460°C)

Fraction	Wt%	Mole Wt ^a	Acidity ^b (Meq/gm)	H _{aro} , % ^c	H _a , %	H _o , %
1	8.7	568	1.38	50.5	27.7	21.8
2	24	626	1.48	47.7	29.7	22.6
3	20	429	1.69	51.8	27.5	20.7
4	14	302	2.26	42.6	41.1	16.3
5	8.6	240	3.03	35.0	46.7	18.3
6	8.0	240	3.33	36.9	44.7	18.4
7	6.2		3.22			
8	5.1		1.25			
9	5.1		0.21			

a Measured by VPO, pyridine solvent

b Measured by C¹⁴ counting

c Measured by proton nmr

Table 3. GPC Separated Fractions From
Acetylated Preasphaltenes of GFETC Samples
15-Y-11 (480°C)

Fractions	Wt%	Mole Wt ^a	Acidity ^b (Meq/gm)	H _{aro} , ^c %	H _α ,%	H _o ,%
1	21.7	1165	1.02	54.4	27.7	17.9
2	31.2	831	1.42	51.1	32.0	16.9
3	22.2	607	1.50	51.5	33.7	14.8
4	9.2	463	1.88	49.2	35.8	15.0
5	3.0		0.98			
6	1.9		0.21			

a Measured by VPO, pyridine solvent

b Measured by C¹⁴ counting

c Measured by proton nmr

or per gram decreases as temperature of the reaction is increased. (3)

The nmr analysis shows that the fraction of aromatic hydrogens remains relatively constant per fraction for each individual run. This was observed with f_a for M-11A in the last quarterly report. However, the percent of aromatic hydrogens clearly increases with increased reaction temperature. At the same time the percentage of carbons beta (located more than 1 carbon away from aromatic rings) decreases dramatically with increasing temperature. The 480°C temperature removes many of the external ring aliphatic carbons. This effect is seen in the greatly increased production of gas at 480°C. The real comparison of the nmr must be done after a Brown-Ladner analysis is made and this requires carbon and hydrogen analyses. Samples have been sent out and we expect to be able to report this information in the next quarterly report. During the next quarter oxygen, nitrogen and sulfur analyses will be obtained so that the types of heteroatoms per each fraction can be discussed.

Task II

Ether Linkage Work

Objective:

To develop methods of cleaving ethers in coals and coal derived liquids.

An ether cleavage reaction using trimethyliodosilane (TMSI) on SRL AMAX resulted in no increase in the acidity of the sample on reaction as measured by the silylation technique. At the same time the iodine content of the product increased to 26.7%. The ^1H nmr showed a decrease in aromatic proton content. Of the three reactions possible:

reaction 3 has been shown to be unimportant. Since there is no increase in acidity, reaction 2 must also be unimportant. Reaction 1 could give rise to the increase in iodine with no increase in acidity except that the decrease in aromatic protons suggests that TMSI, iodine or some derivative of TMSI iodinate phenolic rings, perhaps catalyzed by base in the SRC. If this is the case, this reaction will not be useful for further work.

A second procedure to cleave aryl ethers (reaction 4)

has been initiated. Preliminary data has shown that sodium in hexamethylphosphoramide (HMPA) is an excellent reagent for cleavage of diaryl ethers. Diphenyl ether, dibenzylether, benzyl phenyl ether are cleaved quantitatively under mild conditions. Anisole, dibenzofuran and dibenzothiophene are partially cleaved under more forcing conditions. Reduction and cleavage of aliphatic bonds α or β to aryl rings may also take place but this technique has analytical possibilities which look promising.

Task III

Objective:

In the denitrification of N,N-dimethylaniline, the objective was to accomplish the nitrogen removal using a minimum amount of hydrogen.

Experimental:

The batch autoclave experiments were done using 2 250-ml Hastelloy C autoclaves heated in a rocking apparatus. The heat-up time was 1.5 hours. N,N-Dimethylaniline (13.5g) was charged under the following conditions cited in Table 4. The results were analyzed by glpc using a Beckman GC-5,

Table 4. The Denitrification of N,N-Dimethylaniline^a

<u>Conditions</u>	<u>Benzene, mole %</u>	<u>Toluene, mole %</u>
1. Ar(1500 psi)	0.8	9.7
2. H ₂ (750 psi), Ar(750 psi)	3.5	9.0
3. CO(750 psi), H ₂ O(8.0 g)	1.8	12.3
4. H ₂ S (~150 psi)	0.0	11.0
5. HCO ₂ H(25 g), Ar(1500 psi)	0.3	4.4
6. HCO ₂ H(5.13 g), Ar(1500 psi)	4.5	8.2
7. HCO ₂ H(2.56 g), Ar(1500 psi)	3.7	8.1
8. HCO ₂ H(25 g), H ₂ (750 psi), Ar(750 psi)	1.5	9.7
9. HCO ₂ H(5.13 g), H ₂ (750 psi), Ar(750 psi)	3.5	11.7
10. HCO ₂ H(2.56 g), H ₂ (750 psi), Ar(750 psi)	5.5	11.9
11. HCO ₂ H(5.13 g), CO(750 psi), H ₂ O(8 g)	1.4	9.9
12. H ₂ S(150 psi), H ₂ (750 psi)	9.2	9.6
13. H ₂ S(150 psi), CO(750 psi), H ₂ O(8 g)	1.7	10.4
14. Na ₂ CO ₃ (3 g), H ₂ (750 psi)	6.9	9.1

a Average two trials with average error of $\pm 0.5\%$ for benzene and $\pm 1.2\%$ for toluene.

The time at reaction temperature was 2 hours.

<u>Conditions</u>	<u>Benzene, mole %</u>	<u>Toluene, mole %</u>
15. Na_2CO_3 (3 g), CO(750 psi), H_2O (8 g)	1.6	6.0
16. FeS_2 (3.35 g), H_2 (750 psi)	2.0	6.7
17. FeS_2 (3.35 g), CO(750 psi), H_2O (8 g)	4.2	11.1
18. S(3.6 g), H_2 (750 psi)	5.3	11.3
19. S(3.6 g), CO(750 psi), H_2O (8 g)	0.6	4.3
20. HCO_2H (5.13 g), H_2 (750 psi), H_2S (150 psi)	5.5	5.5
21. HCO_2H (5.13 g), CO(750 psi), H_2O (8 g), H_2S (150 psi)	1.8	3.5

^a Average two trials with average error of $\pm 0.5\%$ for benzene and $\pm 1.2\%$ for toluene.
The time at reaction temperature was 2 hours.

a 1/8" X 6' column OV-17 and diphenylmethane as the internal standard. The results are in forms of mole percent.

N,N-Dimethylaniline is cleaved under the conditions to benzene and toluene. Hydrogen and CO-H₂O are equally effective in producing benzene and toluene although H₂ favors benzene moreso than CO-H₂O (cf. runs 2 and 3). The optimum condition for the cleavage is the combination of H₂S and H₂. This augments earlier indications that H₂S is a valuable aid to liquefaction (J. G. Gatsis, U.S. Patent 3,503,863, 1970), F. Gowdrain, H. Gierman and J. C. Vluger, J. Inst. Petrol., London, 59 (565) 41, 1973; C.N. Satterfield and M. Model, U.S. NITS, P. B. Rept., 1975, 28101, W. S. Pitts, A. R. Tares, J. A. Guin and J. W. Prather, Preprints, Div. Fuel Chem., American Chemical Society, Vol. 22, No. 2, p. 214, 1977; and M. B. Abdel-Baset and C. T. Ratcliffe, Preprints, Div. Fuel Chem., American Chemical Society, Vol. 25, No. 1, p. 1 (1980)).

Task IV

Electron Transfer Catalysis

Objective

To understand the interactions of CO and CO-H₂O and CO-H₂O-H₂ gaseous mixtures with the surfaces of basic minerals, such as metal oxides, carbonates, etc., that may serve as catalysts in a CO-H₂O in-situ reducing medium for coal.

Introduction

We have found that facile electron transfer processes take place on the surfaces of oxides such as MgO, CaO, SrO, BaO, and ThO₂ (cf. Final Report of our previous DOE contract). For example, we have shown that CO interacts with MgO to form (CO)₂⁻ as well as a series of anionic (CO)_n^{x-} cyclic telomers. Current and future work will elucidate the chemistry of these reactive species on MgO and other basic mineral surfaces.

Results

MgO/SiO₂ Mixture Study

Mixtures of MgO and SiO₂ were prepared and examined for their CO reducing capabilities. As discussed in the previous Quarterly Report, there is some evidence to suggest that the CO reducing site on MgO is a small micropore (this micropore comprises a negligible percentage of the total surface) with the special property to donate one electron. Solid mixture of MgO and SiO₂ are reported in the literature to have the majority of their surface area made up of small micropores.¹ It was hoped that by making up MgO/SiO₂ samples and treating them in a standard fashion, we would produce evidence to support the theory that certain micropores are the active reducing sites. Two facts must be remembered when considering these experiments: 1) SiO₂ by itself will not produce a CO radical anion under the experimental conditions, 2) even though MgO/SiO₂ mixtures will contain very small micropores, there still may need to be a special defect also present to allow the formation of CO radical anions. Therefore, a positive dependence of CO radical anion with micropores would be evidence for reducing site to be some type of micropore. However, if there is no correlation then no conclusion can be drawn due to the fact that a necessary defect is not being formed in the micropores of MgO/SiO₂ mixtures.

The experimental procedure was as follows: a series of samples were prepared by mixing weight percentage of SiO₂ with MgO. Samples made were 0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% and 100% SiO₂ mixed in MgO. Each sample was water washed in boiling water for 4 hours, then dried in a standard oven at 110°C for 2 hours, heat treated in vacuum (10.7 torr) at 800°C for 14 hours, cooled to room temperature and exposed to 150 torr CO.

Results showed no increase in CO radical formation at any concentration of SiO_2 . Also no new types of CO radicals were formed. Therefore, we are unable to make any conclusion about if the CO reducing site is some type of small micropore.

Reaction of CO radical system on MgO and CaO with H_2O , CO_2 and O_2 .

Carbon monoxide radical species on both MgO and CaO were allowed to react with H_2O , CO_2 and O_2 . (Previous work with H_2 has been reported earlier.) No reaction occurred at room temperature and when heated the esr spectrum disappeared. However, reaction with H_2O , CO_2 and O_2 produce new esr spectra. Figures I through IX are esr spectra showing these changes. Table 5 includes the g-values of the new spectra.

Table 5

SYSTEM	g_1	g_2	g_3
$^{12}\text{CO/MgO}$	2.0058	2.0048	2.0023
$^{12}\text{CO/CaO}$	2.0063	2.0048	2.0023
$^{12}\text{CO/MgO} + \text{O}_2$	2.0069	2.0069	2.0024
$^{12}\text{CO/CaO} + \text{O}_2$	2.0059	2.0059	2.0026
$^{12}\text{CO/MgO} + \text{CO}_2$	2.0061	2.0061	2.0024
$^{12}\text{CO/CaO} + \text{CO}_2$	2.0055	2.0055	2.0023
$^{12}\text{CO/MgO} + \text{H}_2\text{O}$	2.0058	2.0058	2.0025
$^{12}\text{CO/CaO} + \text{H}_2\text{O}$	2.0058	2.0058	2.0026

It must be remembered that the g-values reported in Table I are composite values of more than one radical species. Therefore, these g-values may differ slightly from sample to sample due to varying concentration of each type of radical.

1. A. Lecloux, Mem. Soc. Roy. Sci. Leige, 6(1), 169(1971).

The results of these experiments varied with the addition of H_2O , O_2 and CO_2 . When H_2O was added to a CO/MgO system the color turned from peach to yellow. The carbon-12 esr spectra appears to have only been broadened. Addition of H_2O to a carbon-13 broadened the spectra so badly nothing was identifiable. Further experiments will be conducted in an attempt to obtain an informative spectrum.

Addition of H_2O to a CO/CaO system appeared to selectively destroy a radical species without harming the other or others. Upon addition the sample color turned from a bright yellow to yellowish white. The carbon-12 esr spectrum showed a definite change in g values. It appears a radical species exists on CaO with g values of $g_1 = 2.0063$ and $g_2 = 2.0023$. The carbon-13 esr spectra showed the partial destruction of the carbon monoxide dimer anion radical $((CO)_2^{\cdot-})$. However, the spectrum appears to have been broadened. An experiment adding D_2O in place of H_2O will be done to determine if hydrogen splitting is responsible for the broadening.

The addition of O_2 to the CO/MgO resulted in the growth of a new radical. The esr carbon-12 spectra shows a axial g tensor. Addition of oxygen to the carbon-13 MgO system is presently inconclusive; the experiment will be repeated.

Addition of O_2 to the CO/CaO system resulted in the partial destruction of the same radical destroyed by the addition of H_2O .

Addition of CO_2 to MgO and CaO -carbon monoxide radical systems definitely caused selective partial destruction of at least one type of radical species. The low field g value shift for the carbon-12 MgO system clearly shows that the overall line shape is being altered by the loss of one or more radicals. The signal gain of the instrument

had to be increased in order to observe the spectrum. This is the reason why it is assumed that there is radical destruction and not new radical formation. The selective destruction of a radical species is very clearly seen for the carbon-12 CaO system. However, both MgO and CaO systems produce a very complicated carbon-13 esr spectra when reacted with CO₂. Neither spectra have been analyzed completely. MgO spectra C and CaO spectra C have differences but, it is believed that part of the line shapes of both system have things in common. Lines that behaved similarly on the two system have been designated by anions.

Unfortunately, concrete conclusions concerning the results of these experiments cannot be made presently. The CO/MgO system contains probably three different radical species 1) axial $g_{\perp} = 2.0069$, $g_{\parallel} = 2.0024$ 2) Probably axial $g_{\perp} = 2.0023$. Probably radical 3 is the dimer species. The CO/CaO system contains probably two radicals 1) axial $g_{\perp} = 2.0063$, $g_{\parallel} = 2.0023$, 2) $g_{\perp} = 2.0055$, $g_{\parallel} = 2.0023$. Probably radical 1 is the dimer species. The MgO radical 2 and CaO 2 showed similarities but, no positive conclusion can be made. Better resolved ¹³CO spectra must be obtained to analyze the CO radicals on both MgO and CaO.

Future Work

To better understand the radical species present on MgO and CaO the following experiments will be carried out: 1) ¹³CO added to MgO and CaO samples calcined over a range of temperatures. This will be carried out to determine if each type of radical species formed is specific for a certain site. 2) Carbon-13 esr spectra will be obtained for reactions with O₂ and H₂O. 3) esr spectra will be obtained of MgO + CaO ¹³CO radical system reacted with D₂O. 4) Determine the reaction of these systems with NH₃. 5) More computer simulation work to determine the lineshape of a multy-radical system.

FIGURE 1 ESR SPECTRA OF CARBON-12 MONOXIDE RADICALS ON MgO . A) STANDARD ESR SPECTRUM, B) AFTER ADDITION OF 200 M TORR O_2 , C) AFTER ADDITION OF 400 TORR O_2 .

FIGURE 11 ESR SPECTRA OF CARBON-12 MONOXIDE RADICALS ON CaO. A) STANDARD ESR SPECTRUM, B) AFTER ADDITION OF 10 TORR O₂.

FIGURE III ESR SPECTRA OF CARBON-12 MONOXIDE RADICALS ON MgO. A) STANDARD ESR SPECTRUM, B) AFTER ADDITION OF 4 TORR CO₂, C) AFTER ADDITION OF 300 TORR CO₂.

FIGURE IV ESR SPECTRA OF CARBON-13 MONOXIDE RADICALS ON MgO. A) STANDARD ESR SPECTRUM, B) AFTER ADDITION OF 100 TORR CO₂, C) AFTER ADDITION OF 300 TORR CO₂.

FIGURE V ESR SPECTRA OF CARBON-12 MONOXIDE RADICALS ON CaO. A) STANDARD ESR SPECTRUM, B) AFTER ADDITION OR 50 TORR CO₂, C) AFTER ADDITION OF 300 TORR CO₂.

FIGURE VI ESR SPECTRA OF CARBON-13 MONOXIDE RADICALS ON CaO. A) STANDARD ESR SPECTRUM, B) AFTER ADDITION OF 50 TORR CO₂, C) AFTER ADDITION OF 300 TORR CO₂.

FIGURE VII ESR SPECTRA OF CARBON-12 MONOXIDE RADICALS ON MgO . A) STANDARD ESR SPECTRUM, B) AFTER ADDITION OF 25 TORR H_2O .

FIGURE VIII ESR SPECTRA OF CARBON-12 MONOXIDE RADICALS ON CaO . A) STANDARD ESR SPECTRUM, B) AFTER ADDITION OF 25 TORR H_2O .

FIGURE IX ESR SPECTRA OF CARBON-13 MONOXIDE RADICALS ON CaO. A) STANDARD ESR SPECTRUM, B) AFTER ADDITION OF 24 TORR H₂O.

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Quarterly Report for the Period
April - June, 1980

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PROJECT TITLE: CONVERSION OF SOLVENT REFINED LIGNITE INTO
PREMIUM LIQUID FUELS (EX-76-C-01-2211)

SUMMARY

Comparison of three preasphaltene samples separated from three lignite derived samples obtained from GFETC prepared at 404, 460 and 480°C shows that increased temperature produces molecules that contain a higher percentage of aromatic carbons, more condensed aromatic structures, less alkyl substitution on the aromatic edges, less total oxygen and less acid sites per gram. Comparison of the molecular fractions for a given reaction temperature shows that the large molecules tend to be like the higher temperature material described above except for total oxygen. The lower molecular weights are less condensed but contain a larger acid site density. The total oxygen content remains relatively constant for a given temperature set. Ether cleavage studies of model compounds using boron tribromide are nearly completed and this technique appears to be applicable to coal samples. Sodium reaction studies of model compounds in hexamethyl phosphoramide is nearly completed and this technique also appears to be useful in coal ether cleavage reactions. Magnesium oxide serves as an excellent catalyst support for CO methanation, much better than Al_2O_3 . The basic and electron transfer properties of the MgO are apparently very important. Preparation of a number of polymers for model compound studies with $\text{CO-H}_2\text{O}$ for determining the effectiveness of CO and H_2 in reducing scissile bonds has been initiated.

Summary of Progress to Date

During this quarter the following tasks have been undertaken and/or completed:

- (1) Comparison of three preasphaltenes obtained from lignite derived samples (GFETC) prepared at 404, 460 and 480°C show that fraction of aromatic carbons (f_a) increases with reaction temperature and with molecular weight of each temperature set. The degree of condensation increases both with molecular weight and reaction temperature. The acid site density maximizes with the low molecular weights at all temperatures and the higher reaction temperature (480°C) tends to remove some oxygen and acidic sites.
- (2) Comparison of the above data suggest that preasphaltene fractions are composed of two types of molecules. The higher molecular weight fractions contain a sizeable fraction of condensed aromatic molecules with a low acid site density of ca. 1meq/gm material. The lower weight fractions appear in the preasphaltene fraction because of a rather high acid site density (2-3 meq/gm material). The aromaticity of the latter fractions decrease as well as their degree of condensation.
- (3) The optimum temperature condition to minimize residual and preasphaltene product occurs at 460°C. At low temperatures of 404°C insufficient oxygen is removed to reduce the acid site density. At 480°C the acidity is removed but the condensation of the material is greatly enhanced.
- (4) A series of reactions with the MgO reducing site have shown it to be both nucleophilic and very basic.
- (5) We have shown that MgO serves as an excellent catalyst support for CO methanation, much better than Al_2O_3 the basic character and electron transfer properties of MgO are very important.

- (6) Ether cleavage studies of model compounds using boron tribromide or sodium in hexamethylphosphoramide are complete. Both reactions appear to be useful for the analysis of coals or coal derived liquids.
- (7) Two polymers, phenol-formaldehyde and p-polyphenylene, have been prepared as model compounds for studies in determining the mechanism of coal conversion.

Detailed Description of Technical Progress

Task I

Structural Studies of Lignite Derived Asphaltenes and Preasphaltenes

Objective:

To continue the development of analytical separation techniques unique to coal liquids and to apply these techniques to coal liquids produced under different temperatures, pressure and residence time conditions.

Results:

Three samples of lignite derived liquefaction products selected on the basis of operating temperature were obtained from the Grand Forks Energy Technology Center. The general operating conditions under which the samples were prepared were as follows. The samples were produced in a 5-lb lignite/hr continuous process unit in single pass tests in a continuous-stirred tank reactor (CSTR). The lignite product was derived from a Beulah 3, North Dakota, lignite by hydrogenation with synthesis gas (50:50 $H_2:CO$) using an anthracene oil distillate solvent (40% as received coal slurry) at 4000 psi and three different operating temperatures; 400°C (sample 15-Y-2), 460°C (26-Y-7) and 480°C (26-Y-11). The isolation of the preasphaltenes, asphaltenes and the heavy oils was carried out by liquid extraction. Details of the separation were described in our previous quarterly report. The three preasphaltene samples were acetylated and chromatographed by GPC techniques. Work was begun on the application of our acetylation technique to the asphaltene fractions separated from the samples described above.

Work has been completed on the corresponding preasphaltenes from these samples. The samples had been sent out for carbon, hydrogen, nitrogen and sulfur analysis. Oxygen content was then calculated from the difference of these numbers. Table 1-3 report the elemental analyses, the calculated

values of f_a (the fraction of aromatic carbons), σ (the fraction of substituted edge aromatic carbons) and H_{aru}/C_{ar} (the fraction of edge carbons/total aromatic carbon in the sample). The values, f_a , σ and H_{aru}/C_{ar} , were calculated from the C/H ratio using Brown-Ladner analysis assuming $X=Y=2$.

New information that was not reported in the last quarterly report is as follows. The total aromaticity of carbons (f_a) increased both with reaction temperature and molecular weight. The fraction of aromatic carbons that are edge atoms (H_{aru}/C_{ar}) decreased with increasing reaction temperature and with increasing molecular weight. The number average molecular weight of the total preasphaltene sample remained near 450 gm/mol at 404 and 460°C, but the number increased to 690 gm/mol at 480°C. The oxygen content decreased with reaction temperature, but remained relatively constant for different molecular weights at the same reaction temperature. For last quarters report we found the acid site density (meq. acid/gm sample) dropped slightly with increasing temperature but that more predominant effect is that the acid density greatly increases upon going to smaller molecular weights (see figure 1).

The nature of the alkyl substitution changes with reaction temperature. The fraction of aromatic edge atoms that are substituted was calculated two different ways. First aromatic edge atom substitution was calculated as σ in Table 1-3. In this case oxygen was counted as occupying one aromatic edge site. The degree of substitution increased with lower reaction temperature and molecular weight. A more significant number might be the percentage of edge atoms occupied only by alkyl groups. The value of σ was calculated omitting the oxygen contribution and reported as the number in parenthesis in Tables 1-3. It is seen that about 50% of the

substitution on edge aromatic carbons is due to oxygen and that the fraction of alkyl substitution is lower at the higher molecular weights. There was a slight reduction in degree of substitution with temperature of reaction. The amount of alkyl groups attached directly to the rings changes only slightly. A far greater change occurred with loss of other alkyl carbons (beta and gamma to the aromatic rings). The length of the alkyl side chains (C_{ℓ}) decreased with both decreasing molecular weight and increasing reaction temperature. The larger molecules approach C_{ℓ} equal to two which would be consistent with the presence of a number of saturated aliphatic rings in the molecules. The smaller molecules resulting from the break up of bigger molecules contain more methyl type substitution and a lower C_{ℓ} value. The increased reaction temperature tends to remove the aliphatic chains leaving more methyl groups on the resulting product.

The above results are consistent with these preashaltene samples that are composed of two types of molecules. One group contains high molecular weight molecules which have a high degree of aryl condensation (low $H_{\text{aru}}/C_{\text{aro}}$ values) and smaller site density of acid groups (lower meq acid/gm sample). The second groups are molecules with lower molecular weight (200-500 gm/mol), more benzoid in character (high $H_{\text{aru}}/C_{\text{aro}}$), and a large acid site density. The nitrogen content and basicity of the sample remains nearly constant at all times. So in effect the low molecular weight preasphaltenes contain many acid-base sites with which hydrogen bonding can occur and thereby eliminate their solubility in such solvents as benzene or chloroform. The larger molecules lose their solubility because of their large size and their retention of some acid sites.

The major effect of temperature of reaction was to produce higher

molecular weight and more condensed aromatic systems. There was a loss of oxygen during this process and of acid sites but condensation and The molecular weight increase gave rise to a new set of solubility problems. To get some feeling for this condensation and acid removal problem Table 4 shows the distribution of the three samples between the asphaltene, preasphaltene and residual (THF insoluble) fractions. The coal liquid prepared at 404°C apparently was never fully reacted. The 404°C residual percentage was higher than at 460°C and the chemical composition of the preasphaltenes showed a very high oxygen content. The liquid sample prepared at 480°C began to show an increase of residuals probably containing a lot of charred material which is reflected in the highly condensed nature of the preasphaltenes. The 460°C material offered the best of two problems, a minimization of condensation and a maximization of reactivity.

Future Studies:

During the next quarter we plan to study the asphaltenes to determine if similar data is observed as with the preasphaltenes or if there are parameters that are significantly different between the two categories of substances.

Table 1.

GPC Separated Fractions from Acetylated Preasphaltenes of GFETC Sample 15-Y-2 (404°C)

Fraction	Mol Wt ^a	C, % ^b	H, %	H/C ^c	N, %	S, %	O, % ^d	f _a ^e	σ ^f	H _{aru} /C _{ar} ^g	c _L
1.	582	78.83	4.94	.75	1.48	0.52	14.23	.75	.52(.22) ^h	.67	2.01
2.	573	78.79	4.78	.73	1.30	0.57	14.56	.76	.52	.65	2.06
3.	546	—	—	—	—	—	—	—	—	—	1.82
4.	373	77.96	5.11	.79	0.89	0.48	15.56	.72	.59	.75	1.64
5.	218	76.28	5.44	.86	0.85	0.47	16.96	.70	.60(.33)	.86	1.57
6.	219	75.84	5.68	.90	0.86	0.45	17.17	.68	.61	.93	1.56
7.	224	75.73	5.87	.93	0.89	0.52	16.99	.67	.61	.98	1.45
8.	210	77.14	6.10	.95	1.00	0.88	14.88	.67	.57	.95	1.54

a. measured by VPO, pyridine solvent

b. single point elemental analyses reported as weight per cents

c. mole ratio

d. obtained by difference

e. fraction of aromatic carbons, Brown-Ladner Method, X=Y=2

f. fraction edge aromatic carbons that are substituted

g. fraction of edge carbons/total aromatic carbons

h. Fraction of aromatic carbons substituted only with alkyl groups

Table 2 GPC Separated Fractions from Acetylated Preasphaltenes of GFETC Sample 26-Y-7 (460°C)

Fraction	Mol Wt ^a	C,% ^b	H,%	H/C ^c	N,%	S,%	O,% ^d	f _a ^e	σ ^f	H _{aru} /C _{ar} ^g	c ₂
1.	562	82.40	4.74	.69	1.90	0.51	10.45	.83	.35 (.17) ^h	0.65	1.78
2.	626	83.66	4.67	.57	1.63	0.75	9.29	.83	.36	0.60	1.76
3.	429	82.13	4.74	.59	1.37	0.54	11.22	.83	.36	0.66	1.75
4.	302	80.58	5.00	.74	1.24	0.67	12.51	.79	.46	0.74	1.40
5.	240	79.80	5.38	.81	1.14	0.49	13.19	.74	.53 (.32)	0.80	1.39
6.	240	78.62	5.62	.85	1.05	0.59	14.12	.73	.51	0.87	1.40
7.	—	80.78	5.83	.87	0.96	0.63	11.75	.73	.48	0.53	—

a. measured by VPO, pyridine solvent.

b. single point elemental analyses reported as weight per cents

c. mole ratio

d. obtained by difference

e. fraction of aromatic carbons, Brown-Ladner Method, X=Y=2

f. fraction edge aromatic carbons that are substituted

g. fraction of edge carbons/total aromatic carbons

h. fraction of aromatic carbons substituted only with alkyl groups

Table 3 GPC Separated Fractions from Acetylated Preasphaltenes of GFETC Sample 26-Y-11 (480°C)

Fraction	Mol Wt ^a	C, % ^b	H, %	H/C ^c	N, %	S, %	O, % ^d	f _a ^e	σ ^f	H _{aru} /C _{ar} ^g	C ₂
1.	1165	84.61	4.62	.66	1.43	0.46	8.88	.85	.32(.14) ^h	0.61	1.64
2.	831	84.44	4.73	.67	1.26	0.47	9.10	.84	.36	0.63	1.52
3.	607	83.98	4.79	.68	1.27	0.46	9.50	.85	.36(.20)	0.57	1.43
4.	463	82.85	4.82	.70	1.22	0.64	10.47	.82	.39	0.68	1.41
5.	—	86.24	5.35	.74	1.09	1.10	6.22	—	—	—	—

a. measured by VPO, pyridine solvent

b. single point elemental analyses reported as weight per cents

c. mole ratio

d. obtained by difference

e. fraction of aromatic carbons, Brown-Ladner Method, X=Y=2

f. fraction edge aromatic carbons that are substituted

g. fraction of edge carbons/total aromatic carbons

h. fraction of aromatic carbons substituted only with alkyl groups

Table 4

Distribution of GFETC Samples into Asphaltenes, Preasphaltenes and Residuals^a

Sample	Reaction Temp, °C	Initial wt. sample, gm	Asphaltene Wt, gm	Preasphaltene Wt, gm	Residual Wt, gm	Residual % of three fractions
15-Y-2	404	395	37 (9%) ^b	38 (9.5%)	52 (13%)	40% ^c
26-Y-7	460	450	35 (7.8%)	29 (6.4%)	35 (7.8%)	35%
26-Y-11	480	300	25 (8.3%)	16 (5.3%)	42 (14%)	50%

a. Asphaltenes determined by difference between hexane insoluble and toluene insoluble weights, preasphaltenes determined by difference between toluene and THF insoluble weights. Residue equals the THF insoluble weight.

b. Percent of total starting material.

c. Since total starting material may contain some recycle solvent this percentage was calculated from the weight of residuals divided by the total weight of asphaltenes, preasphaltenes and residual weight.

Task II

Ether Linkage Work

Objective:

To develop methods of cleaving ethers in coals and coal derived liquids.

A. Sodium Cleavage

After the initial success in cleaving aryl ethers with sodium in various solvents our current work has focused on a) developing the quantitative aspects of the cleavage and b) assessing interferences which possibly could take place in coal reactions. While neither of these studies is complete we have roughed out the scope of the reaction. Diaryl, dibenzyl and benzyl aryl ethers cleave most readily with sodium/HMPA in 100% over 5-20 hr at room temperature. Anisole and dibenzofuran cleave less readily in 50-60% yield over 24 hr the former at room temperature, the latter at reflux in THF. Dibenzopyran cleaves to only 15-23% in 24 hrs.

Sodium cleavage of diphenyl ether in HMPA/THF was shown to follow both one (reaction 1) and two (reaction 2) electron reaction paths.

Control of these reaction paths may be possible and is important for quantitative purposes.

Several possible secondary reactions of functionalities present in coal and coal derivatives were examined for their susceptibility to ether

cleavage conditions. Thus, dibenzothiophene is cleaved in 70-80% yield, benzofuran and benzothiophene reacted to some extent. Styrene polymerizes and stilbene is reduced under these conditions. A series of reactions to determine the importance of the recently reported carbon bond cleavage of bibenzyl to ether cleavage under sodium/HMPA conditions was carried out. While bibenzyl is cleaved by sodium/HMPA in yields up to 80%, this reaction seems to be quite solvent sensitive (DME 9%, THF variable from 0 to 80%, ether 68%) and may well be sensitive to trace impurities. When one equivalent of sodium was added to a 1:1 mixture of ether (benzyl phenyl or dibenzyl ether) and bibenzyl, the ether was cleaved nearly completely. These results show carbon carbon bond rupture to be less likely than ether cleavage and may allow quantitative application of this technique to coals.

B. Boron tribromide cleavages

Since boron tribromide has been used in the literature to cleave mainly methoxyl ethers, the scope of this reaction was investigated first. A 130% equivalent excess of boron tribromide in methylene chloride was added at ⁰-70 C to the ether and then allowed to warm to room temperature. The following results were obtained:

Compounds Reacting (% Cleavage)

Anisole (100%)
 dibenzyl ether (100%)
 Benzylphenyl ether (100%)
 dioctyl ether (60%)
 1-naphthyl acetate (93%)
 methyl p-anisoate (p-methoxyl cleaved)
 benzofuran, benzothiophene, indole (all form polymers)

Compounds not Reacting

diphenyl ether
 dibenzofuran
 dibenzothiophene
 methyl benzoate
 p-anisic acid
 methyl phenyl sulfide

Studies directed toward determining interferences have shown: a) pyridine base present in 1:1 molar ratio with boron tribromide inhibits ether cleavage but addition of an excess of BBr_3 overcomes this effect. b) 1-naphthol in a 1:1 molar ratio inhibits ether cleavage (by ester formation?) but addition of an excess of boron tribromide overcomes this effect.

Work Forecast

In this quarter limited studies on the mechanism of sodium reactions will be conducted and some further model compound work with boron tribromide will be carried out.

A solvent refined coal will be treated with trimethyliodosilane, boron tribromide and sodium/HMPA. The extent of ether cleavage will be followed by acetylation before and after reaction with labeled acetic anhydride. Preliminary attempts to react a coal (lignite) under the above conditions will be initiated also. The latter will involve further development work with the acetylation technique on coal.

Task III

Model Compound Reductions with $\text{Co-H}_2\text{O}$ Objective:

Coal has a very complex structure consisting of a variety of C-C, C-N, C-O and C-S bonds. We have chosen p-cresol-formaldehyde polymer, lignin and p-polyphenylene (p-sexiphenyl) for our studies as model compounds mimicking different types of C-C bonds in coal.

Results:

Para-cresol-formaldehyde polymer was synthesized from p-cresol and formaldehyde using HCl as a catalyst. Guidelines for the preparation was taken from the methods of Koebner [Angew. Chem., 46, 251 (1933)] and Yoshimura *et al.* [Japan Patent, 7590695 (1975); Chem. Abstr. 83, 180286p (1975)]. The structure was analysed by IR, NMR, average molecular weight determination and elemental analyses. The product was found to be a mixture of mainly two polymers by HPLC. The molecular weights of the two main polymers were found to be 1848 and 972 which corresponded to 15 and 8 units polymers, respectively. These polymers will be separated by gel permeation chromatography.

The p-polyphenylene was prepared from biphenyl in the presence of anhydrous AlCl_3 and anhydrous CuCl_2 following the method of Kovacic *et al.* [J. Org. Chem., 2416 (1964)]. The structure of p-sexiphenyl is being confirmed.

These polymers will be studied for their cleavage by carbon monoxide and water both in presence and absence of a catalyst. The reduction with $\text{CO-H}_2\text{O}$ will be compared with H_2 . The effect of added hydrogen donor solvents (tetralin and other less volatile solvents) will be tested for the conversion of the polymers to products.

Task IV

Electron Transfer Catalysis

Objective:

To understand the interactions of CO and $\text{CO-H}_2\text{O}$ and $\text{CO-H}_2\text{O-H}_2$ gaseous mixtures with the surfaces of basic minerals, such as metal oxides, carbonates, etc., that may serve as catalysts in a $\text{CO-H}_2\text{O}$ in-situ reducing medium for coal.

Introduction:

We have found that facile electron transfer processes take place on the surfaces of oxides such as MgO , CaO , SrO , BaO , and ThO_2 (cf. Final Report of our previous DOE contract). For example, we have shown that CO interacts with MgO to form $(\text{CO})_2^-$ as well as a series of anionic $(\text{CO})_n^{x-}$ cyclic telomers. Current and future work will elucidate the chemistry of these reactive species on MgO and other basic mineral surfaces.

Results:

I. MgO Reducing Site Reactivity

To determine the chemical nature of the MgO reducing site, a series of reactions have been performed. The reagents used so far are CO_2 , O_2 , H_2O , pentane, H_2 , NH_3 and $\text{N}(\text{CH}_3)_3$. The procedure was to heat treat about 100 mg MgO in vacuum (10^{-6} torr) for about 15 hours, cool to room temperature, allow contact with a single reagent for 15 minutes, pump the reagent away (10^{-5} torr), and add 150 torr CO. The purpose of these experiments was to determine what type of molecules will either block or not interfere with the reducing site.

The results indicate that the reducing site is nucleophilic and very basic. Reagents O_2 , pentane, H_2 and $\text{N}(\text{CH}_3)_3$ didn't block the site. However, CO_2 , H_2O and NH_3 completely destroyed the electron transfer properties of the site. Carbon dioxide is electrophilic indicating that the reducing site is a high electron density site. The reason H_2O and NH_3 blocked the site can be explained by acid-base reaction basicity. Trimethylamine didn't block the site, therefore nonbonded lone electron pairs cannot be held responsible for blocking the site. In the case of H_2O , the ionization will produce a proton, and being a electrophile, will block the site. In the case of NH_3 , its ionization can react in a similar manner. It is concluded that this reaction must be occurring to block the site since it is the only reaction $\text{N}(\text{CH}_3)_3$ is unable to perform. Therefore the site is both nucleophilic and very basic.

II. MgO/[CO] Reactivity

To determine the chemical nature of the MgO/[CO] a series of reactions with a series of small molecules has been proposed. The procedure is to prepare a MgO/ ^{12}CO sample by standard means. After the sample is at least 30 days old it will be exposed to one of the series of reagents. The esr spectrum will be recorded at room temperature and then followed by a heat study. Reactions that appear controllable will be repeated using a MgO/ ^{13}CO sample. This will develop a better understanding of the ^{13}CO hyperfine splitting spectrum. Fifteen samples have been prepared and as of the time this report was written the samples have aged the minimum required time. The results of these reactions will be in the next report.

III. MgO as a Catalyst Support

There is evidence that the combination of MgO and CO yields an excellent medium for the reduction of metal oxides to zero valent active metal catalysts. It is possible that transition metal oxides and sulfides could be reduced under a CO-H₂O atmosphere in the presence of basic minerals to yield active hydrogenation-hydrogenolysis and/or methanation catalysts.

Recently we have shown that MgO does indeed serve as an excellent catalyst support for Ni metal, and an extremely active methanation catalyst resulted. In fact, MgO is much superior to Al₂O₃ in this regard. Further work is in progress regarding the unusual effects of MgO on zero valent metal catalysts.

Quarterly Report for the Period

July - September, 1980

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PROJECT TITLE: CONVERSION OF SOLVENT REFINED LIGNITE INTO
PREMIUM LIQUID FUELS (EX-76-C-01-221)

SUMMARY

Structural data for three lignite preasphaltenes were used to develop average molecules. All of the models have a structural pattern of aromatic centers linked by furan or etheral oxygens. Each average molecule contains one phenolic hydroxyl group. Preasphaltenes formed at high temperature contain the most condensed aromatic groups. Reductive conditions have been studied on the polymers; sexiphenyl and lignin, as models for lignite liquefaction. Carbon monoxide, water and hydrogen sulfide give the best conversion of lignin and with sexiphenyl in the presence of a cobalt molybdeum catalyst. ESR work with the CO/MgO system has indicated that there are two different radicals present. Ether cleavage of diphenyl ether using sodium hexamethylphosphoramide was shown to be a one electron process. Cleavage in liquid ammonia may allow selectivity between ether types at low temperature. Preliminary application of this and other techniques to coal samples look encouraging.

Detailed Description of Technical Progress

Task I

Structural Studies of Lignite Derived Asphaltenes and Preasphaltenes

Objective:

To study coal liquids produced under different temperatures, pressures and residence time conditions.

Results:

Three samples of lignite derived liquefaction products selected on the basis of operating temperature were obtained from the Grand Forks Energy Technology Center. The general operating conditions under which the samples were prepared were as follows. The samples were produced in a 5-lb lignite/hr continuous process unit in single pass tests in a continuous-stirred tank reactor (CSTR). The lignite product was derived from a Beulah 3, North Dakota, lignite by hydrogenation with synthesis gas (50:50 H_2 :CO) using an anthracene oil distillate solvent (40% as received coal slurry) at 4000 psi and three different operating temperatures; 400°C (sample 15-Y-2), 460°C (26-Y-7) and 480°C (26-Y-11). The isolation of the preasphaltenes, asphaltenes and the heavy oils was carried out by liquid extraction. Details of the separation were described in our previous quarterly report. The three preasphaltene samples were acetylated and chromatographed by GPC techniques. Work was begun on the application of our acetylation technique to the asphaltene fractions separated from the samples described above.

The nature of the preasphaltene isolated from the above three fractions are illustrated in Table I, which shows that the nitrogen and sulfur content of the coal derived samples are nearly independent of operating temperature and molecular weight of the preasphaltene. This would be consistent with the nitrogen and sulfur being contained in aromatic ring structures such as quinolines, carbazoles and

thiophenes which are not removed from the preasphaltenes at these reaction temperatures.

The oxygen functionality shows a repeating pattern as illustrated in Table two and figure one. Table two shows that the total oxygen concentration in millimoles of oxygen per gram of SRL preasphaltene is nearly constant for a given reaction temperature. There is a slight increase in phenolic (acidic) oxygen concentration with decreasing molecular weight. The phenolic oxygen content was measured by an acetylation procedure previously described in a quarterly report. The remainder of the oxygen concentration is constant on a per gram basis. Figure one shows a smooth curve relationship between acidity and number average molecular weight. The M_n value was measured by VPO using pyridine as the solvent. Further examination of Table two shows that the numbers of phenolic hydroxyl groups on a per mole basis stays near 1 phenolic site per molecule except for the very low molecular fractions formed at 400°C. Models of the preasphaltene structure that would be consistent with the above data would be a type of repeating polymer composed of benzene and naphthalene aromatic moieties connected by furan linkages. This assumes that the remainder of the non-phenolic oxygen are aromatic ethers or furans. Figures 2-4 show this type of repeating structure that would be consistent with the elemental analyses, NMR and titration data. Each average structure contains one phenolic site per molecule. The small amount of nitrogen and sulfur present could be explained by the substitution of a basic nitrogen for an aromatic carbon with every fifth average molecule and a carbazole nitrogen for an furan oxygen site for every fifth or sixth molecule. Likewise the sulfur would appear as a dibenzothiophene for every tenth average molecule.

The actual phenolic oxygen content is given in the empirical formula for each figure. The fraction of aromatic carbons was calculated from proton NMR data using the Brown-Ladner approach and assuming $x=y=2$. The fraction of edge aromatic

carbons, $H_{\text{aro}}/C_{\text{aro}}$, was calculated from the formula:

$$\frac{H_{\text{aro}}}{C_{\text{aro}}} = \frac{H_{\text{ar}}^* + \frac{H_{\alpha}^*}{2} + n \left[\frac{O}{H} \right] + \frac{OH}{H}}{f_a \left(\frac{C}{H} \right)} \quad (1)$$

For the calculation of $H_{\text{aro}}/C_{\text{aro}}$ one uses the number of edge aromatic carbons per furan or ether linkage for n . A furan linkage has 4 edge atoms that are not counted in proton NMR while an aryl ether has 2 edge atoms that are not counted. The value of $H_{\text{aro}}/C_{\text{aro}}$ was then calculated by the value of n obtained from the model. There is good agreement between the value of $H_{\text{aro}}/C_{\text{aro}}$ measured from the model and the value measured from equation (1) using proton NMR data, a selected n value and elemental analysis data. The ratio O/H or OH/H are mole ratios of obtained from elemental analysis. The H^* values are integrated areas obtained from NMR. Likewise a similar treatment was used to calculate sigma, σ , the fraction of edge carbons that have an alkyl group attached.

$$\sigma = \frac{\frac{H_{\alpha}^*}{2} + n \left[\frac{O}{H} \right] + \frac{OH}{O}}{\frac{H_{\text{ar}}^*}{2} + \frac{H_{\alpha}^*}{2} + \left[\frac{O}{H} \right] + \frac{OH}{H}}$$

The nature of the polymeric structure changes as one goes from 400° to 480°C. At 400°C figure 2 shows a large portion of benzene rings ($H_{\text{aro}}/C_{\text{aro}} = 1.0$) and the ratio of total aromatic carbon to furan oxygen is $29/4.2 = 5.6$. As the temperature is raised to 460°C the preasphaltene has a C_{aro}/O ratio of 10.3 and an $H_{\text{aro}}/C_{\text{aro}}$ value of 0.85. There are more naphthalene rings in this preasphaltene. At 480°C the C_{aro}/O ratio is 12.2 and $H_{\text{aro}}/C_{\text{aro}}$ approaches 0.75 which would only occur with the presence of three-four ring aromatic moieties in the molecules.

The effect of increasing reaction temperature is the formation of very condensed preasphaltenes at low temperature (400°C) which contain mostly benzene and furan linkages. As the temperature of the reaction is increased furans or ethers are removed which lead to more condensed systems in the preasphaltene.

Future work

The critical part of the generation of the above average structures is that of exact knowledge of the structure of all the oxygen in the preasphaltenes. This, of course, is the major emphasis of task II and our efforts in that area are described there.

Table 1 Distribution of Nitrogen and Sulfur
Preasphaltene Samples

<u>Sample</u>	<u>wt. % N</u>	<u>wt. % S</u>	<u>M_n</u>
Y-15-2 (400°C)	1.48	0.52	582
	1.30	0.57	573
	0.89	0.48	373
	0.85	0.47	218
	0.86	0.45	219
	0.89	0.52	224
26-Y-7 (460°C)	1.90	0.51	568
	1.63	0.75	626
	1.37	0.54	429
	1.24	0.67	302
	1.14	0.49	240
	1.05	0.59	240
26-Y-11 (480°C)	1.43	0.46	1165
	1.26	0.47	831
	1.27	0.46	607
	1.22	0.64	463
Beulah 3	.80	3.03	---

Table 2 DISTRIBUTION OF ETHERAL AND ACID OXYGEN IN GFETC
PREASPHALTENE SAMPLES

Sample	Mole wt gm/mole	Total O ₂ mmol/gm ²	mmol/gm	OH mol/mol	mmol/gm	Etheral O ₂ mol/mol
15-Y-2 (400°C, 26MPa)	582	8.9	1.8	1.0	7.1	4.1
	573	9.1	1.9	1.1	7.2	4.1
	373	9.7	2.4	0.9	7.3	2.7
	218	10.6	2.7	0.6	7.9	1.7
	219	10.8	2.9	0.6	7.9	1.7
	224	10.6	2.9	0.6	7.7	1.7
26-Y-7 (460°C, 26MPa)	568	6.5	1.4	0.8	5.1	2.9
	626	5.8	1.5	0.8	4.3	2.7
	429	7.0	1.7	0.7	5.3	2.3
	302	7.6	2.3	0.7	5.3	1.6
	240	8.2	3.0	0.7	5.2	1.3
	240	8.8	3.3	0.8	5.5	1.3
26-Y-11 (480°C, 26MPa)	1155	5.6	1.0	1.2	4.6	5.4
	831	5.7	1.4	1.2	4.3	3.6
	607	5.9	1.5	0.9	4.4	2.7
	463	6.5	1.9	0.9	4.6	2.1

Lignite, Beulah 3 - 19.57% O₂ (MAF); 10.6 meq/gm $\approx$ 15% O₂

Figure 1 Acidity of all Preasphaltene Fractions as a Function of Molecular Weight.

$$C_{38.2}H_{28.8}O_{5.2}N_{0.6}S_{0.1}$$

$$M_n = 582$$

$$C_{38.2}H_{27.8(OH)}O_{1.0}N_{4.2}S_{0.6}$$

$$f_a = 0.79 ; 0.76 \text{ (NMR)}$$

$$\frac{H_{aro}}{C_{aro}} = 1.00 ; 1.03 \text{ (NMR)}$$

$$\sigma = 0.105 ; 0.161 \text{ (NMR)}$$

Figure 2 Average Structure of First Fraction of Y-15-2 (404°C).

$$C_{29.4}H_{19.3}(OH)_{0.72}O_{2.38}N_{0.4}S_{0.07}$$

$$M_{\bar{n}} = 429$$

$$f_a = 0.86 ; 0.83 \text{ (NMR)}$$

$$\frac{H_{\text{aro}}}{C_{\text{aro}}} = 0.85 ; 0.91 \text{ (NMR)}$$

$$\sigma = 0.143 ; 0.114 \text{ (NMR)}$$

Figure 3 Average Structure of Third Fractions of 26-Y-7 (460°C).

$$M_n = 1165$$

$$f_a = 0.86 ; 0.85 \text{ (NMR)}$$

$$\frac{H_{aro}}{C_{aro}} = 0.75 ; 0.79 \text{ (NMR)}$$

$$\sigma = 0.150 ; 0.126$$

Figure 4 Average Structure of First Fraction of 26-Y-11 (480°C).

Task II Ether Linkage Work

Objective: To develop methods of cleaving ethers in coals and coal derived liquids.

A. Sodium Cleavage.

With the scope of the reaction outlined in previous reports in hand we have initiated studies designed to investigate the quantitative application of the sodium/HMPA conditions to coal derived materials. In particular it is necessary to know the nature of the products of ether cleavage before quenching the reaction with water. Thus, diphenyl ether cleavage could result in phenoxide ion and benzene formation via a one (path a) or two (path b) electron process:

Preliminary stoichiometric results reported last time suggested both paths were operative. Further investigation has indicated what now appears to be exclusively a one electron (path a) process. Details of this study are presented in a communication to be submitted for publication shortly (Appendix 1). In the course of this study a new radical attack on silicon was observed. Siloxane I was used as solvent for the cleavage.

I

Phenyl radical attack on silicon resulted in formation of trimethylphenylsilane and isopropoxy radical which decomposed by disproportionation or was reduced to isopropoxide ion. This reaction merits further study but not under this contract. Some exploratory runs with sodium in liquid ammonia, similar to literature reactions, have indicated the possibility of controlling the type of aryl ethers cleaved by controlling the temperature of the reaction. Thus, at -78° in liquid ammonia sodium cleaves diphenyl ether quantitatively to benzene and phenol. Anisole, however, is 98% unreactive at -78°C but reacts to give 63% phenol at -33°C . Preliminary application of this technique has been started on lignite but no results are currently available.

B. Boron tribromide cleavages.

A short paper for publication has been prepared on the synthetic application of boron tribromide cleavage to polyfunctional ethers of interest as coal models. This is attached as Appendix 2.

Both this technique and trimethyliodosilane have been applied to an SRC and to lignite. Preliminary analytical data showed low uptake of halogen. Acetylation studies are in progress.

Work Forecast

The preliminary application of the sodium/HMPA, the boron tribromide and the trimethyliodosilane ether cleavage techniques to an SRC and lignite will be completed. Further application to coal samples will be initiated. Application of the acetylation technique to lignite will be studied further also.

Task III

Objective:

In the modeling of coal, polymers offer a limited but useful role. This report describes the carbon monoxide-water reduction of sexiphenyl and lignin.

Experimental and Results

Lignin is used as a model compound for coal conversion and the results are given in Table 3. The best conversions are obtained in the presence of sulfur and the best to date with carbon monoxide, water and hydrogen sulfide (run 9).

Sexiphenyl, a linear polymer of six phenyl groups, was used as the second model for coal conversion. The results are listed in Table 4. The compound is difficult to reduce to simpler molecules. Run 12 describes the best results to date and illustrates again the superior character of hydrogen sulfide addition to the carbon monoxide-water reduction solution when the cobalt molybdenum catalyst is used.

These results are interpreted in terms of hydrogen sulfide as a gaseous shift catalyst (reaction 1-3)

Table 3. The Conversion of Lignin

Run No.	Gases	Catalyst	Conversion, %
1	H ₂	None	0 ^a
	CO-H ₂ O	None	38.7
2	CO-H ₂ O-H ₂	None	43.0
3	CO-H ₂ O	CoOMoO ₃	35.1
4	CO-H ₂ O	FeS	39.1
5	CO-H ₂ O	CaCO ₃	45.2
6	CO-H ₂ O	Pyrite	46.7
7	CO-H ₂ O	Marcasite	49.8
8	CO-H ₂ O	S	59.2
9	CO-H ₂ O-H ₂ S	None	75.1

The lignin was supplied by Westvaco Corporation, North Charleston, SC 29406.

The weight of lignin used was 3.0 grams.

The catalyst weight is 10 weight percent of the lignin used.

The conditions were 425°C, a 250 ml Hastelloy C reactor on a rocking heated mount for 2 hours.

^aCharred

The conversions were calculated on the basis of the amount of oil extracted into ether.

The pressure of CO was 750 psi, the H₂S was 150 psi and H₂ was 750 psi. the weight of water used was 10.8 g. the initial pressure was kept at 1500 psi total by the addition of argon.

Table 4.

The Conversion of Sexiphenyl^{a,b}

Run No.	Gases	Catalyst	Sexiphenyl Moles	Benzene Percent	Toluene Percent	Phenol/Thiophenol, %	Biphenyl Percent	Others
1	CO-H ₂ O	None	9 X 10 ⁻⁴	T	T	-	< 1	None
2	CO-H ₂ O	CoO·MoO ₃	9 X 10 ⁻⁴	2.5	1.2	-	1.5	1.5
3	CO-H ₂ O	CoO·MoO ₃ ^c	9 X 10 ⁻⁴	4.5	1.5	-	1.9	1.6
4	CO-H ₂ O	Fes	9 X 10 ⁻⁴	T	T	-	< 1	None
5	CO-H ₂ O	Pyrite	9 X 10 ⁻⁴	1.9	0.6	T	0.9	1.2
6	CO-H ₂ O	Na ₂ CO ₃	9 X 10 ⁻⁴	-	-	-	< 1	None
7	CO-H ₂ O	S	9 X 10 ⁻⁴	< 1	< 1	1.2	1.1	1
8	CO-H ₂ O	None	6 X 10 ⁻⁴	2.8	0.7	T	2.2	2.5
9	CO-H ₂ S-H ₂	None	9 X 10 ⁻⁴	6.5	2.8	2.5	7.3	6.2
10	CO-H ₂ O	S	9 X 10 ⁻⁴	1.9	0.6	7.8	1.1	1.1
11	CO-H ₂ S-H ₂ O	None	9 X 10 ⁻⁴	4.3	1.2	T	3.4	4.0
12	CO-H ₂ S-H ₂ O	CoO·MoO ₃	8 X 10 ⁻⁴	15.2	4.0	-	10.0	10.5
13	CO-H ₂ S-H ₂ O	CoO·MoO ₃ ^c	9 X 10 ⁻⁴	3.5	1.6	-	1.8	3.8
14	HCO ₂ H	None	9 X 10 ⁻⁴	T	T	T	1.2	-
15	HCO ₂ H	S	8 X 10 ⁻⁴	2.9	1.1	T	1.5	1.0

^a The reactions were done at 450°C in 12-ml 316 ss reactors at 350 psi CO, 150 psi H₂S, and 0.22 g H₂O for 2 hr.

^b Absolute mole percent.

^c Presulfided by pretreatment with H₂S at 425°C for 2 hrs.

Catalyst mass is 10% of the sexiphenyl weight.

Task IV

Electron Transfer Catalysis

Objective

To understand the interactions of CO and CO-H₂O and CO-H₂O-H₂ gaseous mixtures with the surfaces of basic minerals, such as metal oxides, carbonates, etc., that may serve as catalysts in a CO-H₂O in situ reducing medium for coal.

Introduction

We have found that facile electron transfer processes take place on the surfaces of oxides such as MgO, CaO, SrO, BaO, and ThO₂ (cf. Final Report of our previous DOE contract). For example, we have shown that CO interacts with MgO to form (CO)₂⁻ as well as a series of anionic (CO)_n^{x-} cyclic telomers. Current and future work will elucidate the chemistry of these reactive species on MgO and other basic mineral surfaces.

ResultsI. Site Chemistry

Heat treated MgO was exposed to a series of chemicals of varying properties, the chemicals removed under vacuum, and then the MgO samples exposed to CO. The purpose of the experiments was to determine what chemicals poison the active site.

<u>Chemical Added</u>	<u>Active toward CO?</u>
H ₂	Radical growth
CO ₂	No radical growth
H ₂ O	No radical growth
toluene	Radical growth
1-pentene	Radical growth
NH ₃	No radical growth
N(CH ₃) ₃	Radical growth
O ₂	Radical growth

1-butane

Radical growth

propene

Radical growth

Conclusion

The active site is very basic. It can be poisoned by weak acids and even by bases possessing removable protons (ie. NH_3).

II. $(\text{CO})_n^- / \text{MgO}$ Reactivity (Experiments performed at UND)

A series of $(\text{CO})_n^- / \text{MgO}$ samples were prepared, aged for three weeks, and brought to UND for study on the ESR system. They were exposed to a series of reagents:

1. If a reagent was added and the MgO turned from red to yellow a low field line became of major importance. The $^{13}\text{CO}/\text{MgO}$ sample always changed from the typical center line spectrum to a new spectrum with no center line.
2. If a reagent was added and the MgO turned from red to yellow then little or no signal was observed.
3. In all cases if a reagent was added and no color change was observed, there was no change in the ESR spectrum. Therefore, it is concluded that there are two different radicals present. This was proven by comparing a MgO sample heat treated at 500°C to a sample heat treated at 800°C . ^{13}CO was added. The 500°C sample was yellow and contained no center line. The 800°C sample was red and contained a center line. From now on the 500°C radical will be labeled as Rad I and 800°C as Rad II. In conclusion Rad I is only dominant when the sample is an intense yellow and is gone when white, so Radical I is associated with yellow color. The spectrum has no center line and therefore is believed to be an odd carbon system. The g values are approx. 2.0063, 2.0048 and 2.0023. Rad II is associated with a red color, has a center line (hence an even carbon system) and g values of 2.0058, 2.0048 and 2.0023.

The following is a list of reagents and results with interaction with MgO.

MgO	$\xrightarrow[1 \times 10^{-6} \text{ torr}]{800^\circ\text{C}}$	$\xrightarrow[\text{CO}]{150 \text{ torr}}$	$\xrightarrow[\text{out}]{\text{pumped}}$	$\xrightarrow{\text{cont'd}}$
<u>Reagent</u>		<u>esr ^{13}C</u>	<u>color</u>	<u>Radical type</u>
no reagent		center line	red	Rad II
pumped out RT		center line	red	Rad II
BF_3 100 torr		no center	yellow	Rad I
CO_2 100 torr		no center	yellow	Rad I
O_2 1 torr		no center	yellow	Rad I
Cl_2 100 torr		_____	brownish	Rad doesn't contain carbon
HCl 100 torr		no center	yellow	Rad I
NH_3 100 torr		no center	yellow	Rad I
$\text{CH}_2=\text{CH}_2$ 100 torr		center line	red	Rad II
$\text{HSn}(\text{t-Bu})_3$		no center	yellow	Rad I
vapor press				

III. Trapping and/or Externally Generating $(\text{CO})_x^-$

Attempts to trap and remove the reactive $(\text{CO})_x^-$ species from the surface are underway. Trapping with CH_2Cl solutions of $\text{Cl-N}(\text{P}\phi_3)_2$ are being studied and will be reported next time. Electrochemical generation of solution $(\text{CO})_x^-$ species is also be attempted.

IV. Spectroscopic Investigation

Solid state ^{13}C NMR on the $(\text{CO})_x^-/\text{MgO}$ species are underway. Laser-Raman studies are also underway.

V. CaO Studies

A series of $^{13}\text{CO}/\text{CaO}$ samples have been prepared and are being aged.

VI. New Equipment

Another high vacuum line has been assembled and an improved IR cell has been built for Co/CaO studies.

VII. MgO as a Catalyst Support

Further work on supporting Ni on MgO has shown the resultant catalysts to be extremely active in methanation, arene hydrogenation, and alkane hydrogenolysis. Studies of particle size are underway.

This work indicates that MgO served as an excellent support of zero-valent metals. These metals could be formed by reduction of coal minerals in a CO-H₂O atmosphere.

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Quarterly Report for the Period
October - December, 1980

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Date: January, 1981

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PROJECT TITLE: CONVERSION OF SOLVENT REFINED LIGNITE INTO
PREMIUM LIQUID FUELS (EX-76-C-01-221)

SUMMARY

Analyses of three asphaltene samples of SRL prepared at 400, 460 and 480°C has been completed except for the elemental analysis. Comparison of the number average molecular weight (VPO, pyridine) shows the asphaltene to be smaller molecules than the preasphaltenes obtained at the same temperature; 516 vs. 330 (400°C), 520 vs. 430 (460°C) and 680 vs 310 (480°C). (Preasphaltenes are listed first) Comparison of acid titer show both types of materials have similar phenol contents: 2.08 vs 1.85 meg/gm (400°C), 1.85 vs. 1.24 meg/gm (460°C) and 1.22 vs. 1.21 meg/gm (460°C). The aromaticity of the asphaltene decreased with increasing molecular weight while the preasphaltene trend is in opposite direction. Ether cleavage of three preasphaltene samples (listed above) by the boron tribromide, trimethylsilyliodide and sodium-HMPA techniques has been completed. All ether cleavage methods give the same increase in hydroxyl content for the same sample. This leads to the tentative and surprising conclusion that only aryl alkyl mixed ethers are being cleaved. This result requires further testing of the cleavage methods. Hydrogen sulfide in combination with hydrogen gas or carbon monoxide-water and in the absence of heterogeneous catalysts has proven to be beneficial to the conversion of lignin, sexiphenyl and lignite (Beulah number 3, ND) in the absence of added solvents. Sulfur can be substituted for hydrogen sulfide without much change in the conversions presumably because of its in situ conversion to hydrogen sulfide in a reducing atmosphere. Hydrogen sulfide is about the same in effectiveness as nine heterogeneous catalysts examined. The lignin conversion results parallel the conversion results of the lignite.

Detailed Description of Technical Progress

Task I

Structural Studies of Lignite Derived Asphaltenes and Preasphaltenes

Objectives:

To study coal liquids produced under different temperatures, pressures and residence time conditions.

Results:

Three samples of lignite derived liquefaction products selected on the basis of operating temperature were obtained from the Grand Forks Energy Technology Center. The general operating conditions under which the samples were prepared were as follows. The samples were produced in a 5-lb lignite/hr continuous process unit in single pass tests in a continuous-stirred tank reactor (CSTR). The lignite product was derived from a Beulah 3, North Dakota, lignite by hydrogenation with synthesis gas (50:50 H_2 :CO) using an anthracene oil distillate solvent (40% as received coal slurry) at 4000 psi and three different operating temperatures; 400°C (sample 15-Y-2), 460°C (26-Y-7) and 480°C (26-Y-11). The isolation of the preasphaltenes, asphaltenes and the heavy oils was carried out by liquid extraction. Details of the separation were described in our previous quarterly report. The three preasphaltene samples were acetylated and chromatographed by GPC techniques previously described in earlier reports. The asphaltene fractions were then analyzed for molecular weight, acid content, and elemental content. In addition, proton nmr analyses were carried out to determine the aromatic nature of each fraction.

The nature of the asphaltenes are illustrated in Table 1, which shows the molecular weight distribution and acid density of each fraction collected. The molecular weights were measured by VPO techniques using pyridine as the solvent. The phenol content (acidity) was measured by the acetylation procedure using C^{14} labeled acetic anhydride. Both techniques have been described in earlier reports.

Table 1. Molecular Weight and Acid (Phenol) Content of the GFETC Asphaltene Fractions

<u>Sample</u>	<u>M_n^a</u>	<u>Wt %^b</u>	<u>Acidity, mmol/gm</u>
15-Y-2 (400°C)	612	7.66	1.96
	520	8.14	1.98
	450	8.28	2.10
	420	9.28	2.35
	310	13.20	2.74
	310	18.19	2.23
	240	19.06	1.12
	250	9.40	0.41
	260	2.38	0.17
		<u>95.7</u>	
26-Y-7 (460°C)	763	5.33	1.23
	638	5.37	1.24
	510	8.52	1.28
	442	12.58	1.41
	343	15.02	1.76
	295	20.94	1.49
	250	13.83	0.62
	260	4.35	0.18
	360	1.05	0.11
		<u>87.00</u>	
26-Y-11 (480°C)	825	2.96	1.28
	725	3.27	1.28
	600	6.07	1.34
	550	11.00	1.44
	390	15.00	1.83
	340	30.70	1.60
	250	14.79	0.38
	270	22.32	0.09
	270	8.65	0.03
		<u>114%</u>	

^a Measured by VPO, pyridine

^b Based on amount of asphaltene added to the column

In comparison to total preasphaltenes the average molecular weights of the total asphaltenes were considerably lower. Table 2 shows the difference between the average molecular weights and the largest wt% fraction at each reaction temperature. So the first major difference between the two classes is the higher molecular weight of the preasphaltenes. The acidity of the preasphaltenes and asphaltenes at 400°C were very similar (2.74 mmol acid/gm at 310 M_n versus 2.4 mmol acid/gm 373 M_n for the preasphaltene). However at the higher temperatures, 460° and 480°C, there was a definite removal of OH groups at all molecular weights for both categories.

The nmr analyses have been collected but the fraction of aromaticity, f_a , can not be determined because the elemental analyses have not been completed. Preliminary nmr data, however, does show a marked change in the trend of aromaticity. The high molecular weight asphaltenes have about the same percent aromatic protons as the preasphaltenes. The low molecular weight asphaltenes contain a much higher percent of aromatic protons. The asphaltenes at the low M_n values are thus very aromatic, which would tend to explain why they fall into the asphaltene category. It should be noted these fraction contain few acid sites as shown in Table 1.

A critical question that remains to be answered is how the other oxygen (ethers) content changes with the asphaltenes. This we can not answer until the asphaltene elemental analyses are completed.

Table 2. Comparison of M_n for GFETC Preasphaltenes andⁿAsphaltenes

Reaction Temp. (Sample)	Preasphaltene		Asphaltene	
	Total	Fraction ^a	Total	Fraction ^a
400°C (15-Y-2)	516	573 (26%)	330	310 (20%)
460°C (26-Y-7)	419	626 (23%)	430	295 (26%)
480°C (26-Y-11)	680	830 (31%)	310	340 (30%)

^a Number in parenthesis indicated Wt% of fraction collected, which was the largest fraction.

Task II

Objectives:

To develop methods of cleaving ethers in coals and coal derived liquids. Application of sodium/HMPA, trimethyl silyliodide (TMSI) and boron tribromide (BTB) ether cleavage techniques to some preasphaltene samples.

Results:

Using techniques described in previous reports the reagents above were used to cleave three preasphaltene samples. The acidity before and after treatment are reported in Table 3.

Table 3

<u>Sample</u> <u>Preasphaltenes</u>	Acidity Before Treatment (meq/g)	Acidity After Treatment with		
		<u>Na/HMPA</u>	<u>TMSI</u>	<u>BTB</u>
15-Y-2	2.08	2.98	2.87	2.82
26-Y-7	1.85	2.24	2.35	2.23
26-Y-11	1.21	1.99	2.07	1.84
<u>Asphaltenes</u>				
15-Y-2	1.85	—	1.89	—
26-Y-7	1.24	—	1.19	—
26-Y-11	1.22	—	1.43	—
<u>Coal</u>				
Ruelah #3 (demineralized)	2.86	—	2.60	—

Remarkably, all preasphaltene samples increased in acidity about the same amount independent of the ether cleavage reagent. This result requires further verification. The only type of ether which all reagents cleave is aryl alkyl ethers. It seems unusual that this would be the only type of ether present. Alternately, partial cleavage of various ether types could simply fortuitously have given this

result. The percentage of ether oxygen cleaved is 11-22% for the three preasphaltenes samples (based on combustion analysis before cleavage - other data is currently unavailable). This indicates most of the oxygen present as ethers is not cleaved by any of the reagents. The only type ether fitting this classification based on model compound work carried out previously is dibenzofuran ethers. This result fits the structural postulates concerning the rigidity of preasphaltene molecules in our last report.

The preliminary TMSI cleavage results (Table 3) of asphaltenes indicates very little change in ether content during this treatment. Without combustion data (not currently available) the importance of this result cannot be assessed. The single coal sample (Table 3) indicating no change during TMSI treatment, could simply reflect difficulty in applying this technique to coals. Further modification for coal samples seem necessary.

Work Forecast

Methods to cleave dibenzofurans completely will be investigated with model compounds and these applied to the preasphaltene samples of Table 3. Acetylation and ether cleavage in coal using modifications of current techniques will be applied to coal samples. Analytical data to complete analysis of the samples in Table 3 will be sought.

Task III

Objectives:

To cleave polymers using carbon monoxide and water.

Introduction:

The planned experiments using p-cresol-formaldehyde are temporarily held up awaiting a hplc column on order. The reductions of a substitute polymer p-sexiphenyl ($C_6H_5-C_6H_4-C_6H_4-C_6H_4-C_6H_4-C_6H_5$) and lignin have been completed and compared to one sample of lignite. We gratefully acknowledge that the data on volatility has been obtained with the aid of the Grand Forks Energy Technology Center.

Experimental:

The batch autoclave experiments were done in a 250-ml Hastelloy C reactor on a rocking mount. The heat-up time was 1.5 hours and the reactions were kept at the reaction temperature of 425°C for two hours. The initial pressure was 1500 psi in each case with variations done with argon make-up gas. Conversions were based upon solubility: diethyl ether solubility for lignin, tetrahydrofuran solubility gpc analyses for sexiphenyl and tetrahydrofuran solubility for lignite. The reactor was cleaned in between each reaction by soaking the reactor with concentrated nitric acid for one-half hour, and subsequently washing with water, saturated sodium bicarbonate, water, detergent solution and water.

Results:

The data is illustrated for lignin in Table 1, for sexiphenyl in Table 2 and lignite in Table 3.

Table 1. The Conversion of Lignin

Run No.	Gases	Catalyst	Conversion, %
1	H ₂	none	0 ^a
2	H ₂ -H ₂ O	none	12.5
3	H ₂ -H ₂ O	CoO·MoO ₃	45.9
4	CO-H ₂ O	none	38.7
5	CO-H ₂ O	CoO·MoO ₃	35.1
6	CO-H ₂ O	Ferrous sulfide	39.1
7	CO-H ₂ O	Ferric benzoate	43.0
8	CO-H ₂ O	Sodium benzoate	43.5
9	CO-H ₂ O	Pyrite	46.7
10	CO-H ₂ O	Ferrous benzoate	49.1
11	CO-H ₂ O	Marcasite	49.8
12	CO-H ₂ O	Calcium benzoate	52.0
13	CO-H ₂ O	Sulfur	59.2
14	CO-H ₂ S	none	31
15	CO-H ₂ O-H ₂ S	none	75.1
16	CO-H ₂ O-H ₂ S	CoO·MoO ₃	90
17	CO-H ₂ O-H ₂	none	43.0

The lignin was supplied by Westvaco Corporation, North Charleston, SC 29406. the weight of lignin used was 3.0 grams and the catalyst weight is 10 weight percent of the lignin used.

The conditions were 425°C, a 250 ml Hastelloy C reactor on a rocking heated mount for 2 hours at temperature with a 1.5 hour heat-up time. The conversions were calculated on the basis of the amount of oil extracted into ether. The initial pressure of CO was 750 psi, the H₂S was 150 psi and H₂ was 750 psi. The weight of water used was 10.8 g. The initial pressure was kept at 1500 psi total by the addition of argon.

^aCharred

Table 2.

The Conversion of Sexiphenyl¹

Run No.	Gases	Catalyst	Sexiphenyl, ² moles	Benzene, %	Toluene, %	Phenol/ Thiophenol, %	Biphenyl, %	Others
1	CO-H ₂ O	None	9 X 10 ⁻⁴	T	T	-	< 1	None
2	CO-H ₂ O	Na ₂ CO ₃	9 X 10 ⁻⁴	-	-	-	< 1	None
3	CO-H ₂ O	FeS	9 X 10 ⁻⁴	T	T	-	< 1	None
4	CO-H ₂ O	S	9 X 10 ⁻⁴	< 1	< 1	1.2	1.1	1
5	CO-H ₂ O	Pyrite	9 X 10 ⁻⁴	1.9	0.6	T	0.9	1.2
6	CO-H ₂ O	CoO·MoO ₃ ³	9 X 10 ⁻⁴	2.5	1.2	-	1.5	1.5
7	CO-H ₂ O	CoO·MoO ₃ ³	9 X 10 ⁻⁴	4.5	1.5	-	1.9	1.6
8	CO-H ₂ S	None	6 X 10 ⁻⁴	2.8	0.7	T	2.2	2.5
9	CO-H ₂ S	S	9 X 10 ⁻⁴	1.9	0.6	7.8	1.1	1.1
10	CO-H ₂ S-H ₂ O	None	9 X 10 ⁻⁴	4.3	1.2	T	3.4	4.0
10 11	CO-H ₂ S-H ₂	None	9 X 10 ⁻⁴	6.5	2.8	2.5	7.3	6.2
12	CO-H ₂ S-H ₂ O	CoO·MoO ₃ ³	9 X 10 ⁻⁴	3.5	1.6	-	1.8	3.8
13	CO-H ₂ S-H ₂ O	CoO·MoO ₃ ³	8 X 10 ⁻⁴	15.2	4.0	-	10.0	10.5
14	HCO ₂ H	None	9 X 10 ⁻⁴	T	T	T	1.2	-
15	HCO ₂ H	S	8 X 10 ⁻⁴	2.9	1.1	T	1.5	1.0

¹The reactions were done at 450°C in 12-ml 316 SS reactors at an initial charge 350 psi H₂S, and 0.22 g H₂O for 2 hours at temperature with a 1.5 hour heat-up time. The percent yields are in absolute mole percent. The catalyst mass is 10% of the sexiphenyl weight.

²The initial amount of sexiphenyl employed.

³Presulfided by pretreatment with H₂S at 425°C for 12 hours.

Table 3. The Conversion of Lignite¹

Run No.	Gases	Catalyst	Conversion, %
1	CO-H ₂ O	None	61
2	CO-H ₂ O	CoO·MoO ₃	68
3	CO-H ₂ O-H ₂	None	73.8
4	CO-H ₂ O-H ₂ S	None	89
5	CO-H ₂ O-H ₂ S	CoO·MoO ₃	89.5
6	CO-H ₂ O-H ₂	S	90
7	CO-H ₂ O	S	80
8	H ₂ -H ₂ O	None	74
9	H ₂ -H ₂ O	CoO·MoO ₃	80
10	H ₂ S-H ₂ O	None	20
11	CO-H ₂ O	CaCO ₃	65
12	CO-H ₂ O	FeS	75
13	CO-H ₂ O	Pyrite	80
14	CO-H ₂ O	Pyrrrolite	80
15	CO-H ₂ O	Marcasite	86
16	CO-H ₂ O	Calcium benzoate	75
17	CO-H ₂ O	Sodium benzoate	80
18	CO-H ₂ O	Ferrous benzoate	77

¹The weight of lignite used in every reaction was 3.0 grams. The catalyst weight is 10 weight percent of lignite used. The conditions were at 425°C in a 250 ml Hostelloy C reactor on a rocking heater mount for 2 hours at room temperature. The heat-up time is 1.5 hours. The conversions were calculated on the basis of MAF coal and unconverted solid recovered after reaction. The pressure of CO was 750 psi, the H₂S was 150 psi and H₂ was 350 psi. The weight of water used was 10.8 g. The initial pressure was kept at 1500 psi total by the addition of argon.

Task IV

Electron Transfer Catalysis

Objectives:

To understand the interactions of CO and CO-H₂O and CO-H₂O-H₂ gaseous mixtures with the surfaces of basic minerals, such as metal oxides, carbonates, etc., that may serve as catalysts in a CO-H₂O in-situ reducing medium for coal.

Introduction:

We have found that facile electron transfer processes take place on the surfaces of oxides such as MgO, CaO, SrO, BaO, and ThO₂ (cf. Final Report of our previous DOE contract). For example, we have shown that CO interacts with MgO to form (CO)₂[•] as well as a series of anionic (CO)_n^{x-} cyclic telomers. Current and future work will elucidate the chemistry of these reactive species on MgO and other basic mineral surfaces.

Results:

I. Recall that two (CO)_n radicals have been identified on MgO. Rad I on 500°C treated MgO and Rad II on 800°C treated MgO. Several types of experiments have been carried out attempting to gain further information about the structures and chemical properties of these species:

- (1) Heat treatments have shown that the color associated with Rad II is not due to Rad II, but to other adsorbed non-radical (CO)_n species.
- (2) ESR computer simulations support Rad II as possessing an even number of carbons, with C₆O₆⁻³ being the most likely species. This is particularly supported by the g value observed and compared with electrochemical results of E.V. Patton and R. West, J. Phys. Chem., **77**, 2652 (1973). Their solution generation of C₆O₆⁻³ yields a g value almost identical to the average value we obtain for Rad II.

	gx	gx	gz
Rad II	2.0058	2.0048	2.0023

gave = 2.0043

- (3) ^{13}C NMR solid state studies at Colorado State University on the $^{13}\text{CO}/\text{MgO}$ sample we sent were not useful. They could observe no ^{13}C bands. The reason is not known, but could be due to: (1) radical interference, (2) too low concentration, or (3) solid state broadening.
- (4) Attempted trapping and removal of $(\text{CO})_n$ radicals from MgO with $\text{Cl} - \text{N}(\text{P}\phi_3)_2$ dissolved in CH_2Cl_2 was not successful.
- (5) Electrochemical experiments were carried out to determine if, in solution, we could generate $\text{C}_5\text{O}_5^{\cdot-3}$, were not successful. We found that the $\text{C}_5\text{O}_5^{\cdot-2} \rightarrow \text{C}_5\text{O}_5^{\cdot-4}$ reaction is very facile without the intermediate $\text{C}_5\text{O}_5^{\cdot-3}$ species being observed. Thus, we still do not know if our Rad I is $\text{C}_5\text{O}_5^{\cdot-3}$ on the MgO surface. If our Rad I is $\text{C}_5\text{O}_5^{\cdot-3}$, this tells us that this unstable species is formed and stabilized on the MgO surface. Or perhaps the reducing site on MgO is only capable of giving up 3 electrons.

II. We have carried out several experiments with CaO .

(1) CO on CaO forms two radicals (Unknown radical and Rad II) as on MgO . The major species is Rad II which we now believe is $\text{C}_6\text{O}_6^{\cdot-3}$ Rad I (from MgO work) will not form on CaO .

(2) IR studies of CO/CaO show a series of broad bands at 1670(m), 1635(s), 1610(m), 1390(m), 1295(w), 1060(w) and 965(w). Temperature and oxygen treatments are underway.

III. We have continued our catalyst work with MgO . We have spent most of our effort on trying to understand the unusual effects of MgO on Ni , Co , and Fe metal catalysts. IR studies of CO adsorption on Ni/MgO show that extremely high Ni dispersion is possible on MgO .