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CHEMISTRY OF LIGNITE LIQUEFACTION

Quarterly Report for the
Period July - September, 1976

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II. Objective and Scope of Work

The Fuel Committee was established in 1974, as a interdisciplinary group of chemists and engineers at the University of North Dakota to investigate the chemistry associated with lignite liquefaction in cooperation with the UND Chemical Engineering Department's efforts on liquefaction and, later, with the Grand Forks Energy Research Center. The ultimate goals of the present work are to develop rapid analytical methods for the structural analysis of SRL and its reduction products, apply the developed analytical methods to these materials, do catalyst testing and mechanistic studies on the $CO-H_2O-H_2$ and $CO-H_2O$ reducing systems. To accomplish these goals, staff members have been hired, and the planned instruments were purchased.

III. Summary of Progress to Date

Studies in the separation of the major groups of SRL are now discontinued due to reaction of the ion exchange resin with the solvent, non-quantitative recovery of the sample from the ion exchange resin and the efforts underway at the Pittsburgh Energy Research Center to find an optimum procedure for this purpose.

One of the two computerized methods of analysis for handling various types of input data has been developed to the point where laboratory uv data is being put into it. Additional more accurate laboratory data has been obtained on the basis set of 20 compounds. The initial inaccuracy occurred because of under-specification performance of the Cary 14 spectrophotometer. The machine was repaired and the data retaken.

The one-liter batch autoclave studies are continuing, using catalysts for the upgrading of solvent refined lignite. Eight new catalysts are being used, which were synthesized during the summer of 1976 under the supervision of Dr. Kozo Tanabe, a distinguished catalyst expert from Hokkaido University on leave at UND for four months (non-ERDA funds). These were tested and the results reported herein are very interesting. They show comparable activity to the best of the commercial catalysts tested thus far, and have less surface area. They hold much promise for future development.

The characteristics of the one-liter batch autoclave are given for temperature _vs._ time (to show the degree of temperature control), pressure _vs._ temperature (to illustrate gas consumption with temperature) and pressure _vs._ time (gas consumption with time).

For the model compound reduction, the results for benzophenone and diphenylmethane are completed and given. For benzophenone, a combination of CO and H_2 is most effective and the CO reaction is promoted by base. Diphenylmethane is difficult to reduce under these conditions.

For electron spin resonance work, the Bruker spectrometer is installed and operating, and a new vacuum line was constructed. The earlier results of the interaction of CO with MgO is being duplicated with some parts of the resultant signal not in agreement with earlier reported results.

Detailed Description of Technical Progress

Task I

1. Separation of Coal Liquids into Fractions

(a) Objectives

The objective of this study is to separate solvent refined lignite (SRL) into well-defined fractions and to analyze these fractions in detail. Conclusions as to the composition of the original sample will then be arrived at by combining the results of the analysis of each fraction. The information will be used for the selection of a set of standard compounds (basis set) to be used in the computer methods of analysis.

(b) Introduction

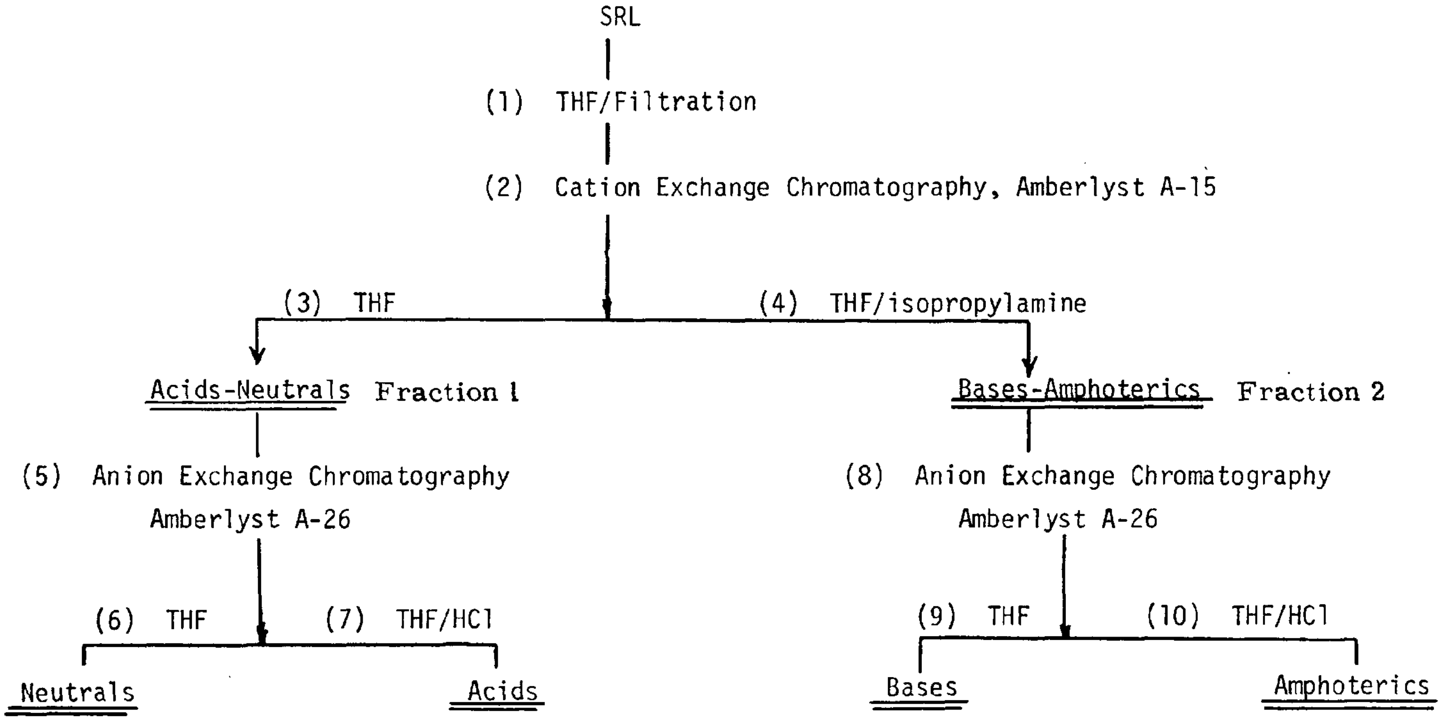
The separation of SRL into acidic, basic, neutral and amphoteric fractions was attempted using ion exchange chromatographic techniques. This approach was considered to be superior to separation by silica gel or alumina chromatography, which would tend to mix the acid and base components. This approach has been used in the analysis of petroleum fractions by several investigators. After initial separation by acidity, the fractions could then be chromatographed by use of silica or alumina for future characterization of the fractions.

(c) Experimentation

A flow diagram for the separation of SRL into four possible fractions is presented in figure 1. In the sequence, SRL was first dissolved in tetrahydrofuran, filtered (84% SRL is soluble in THF) and the resulting filtrate chromatographed through a cation exchange column in the hydrogen form (Amberlyst A-15 from Mallinkrodt Chemical Company). The acidic and neutral compounds passed through the column and were collected in fraction 1 as shown in the diagram. The basic and amphoteric fractions were collected on

Figure 1

SCHEMATIC FOR ISOLATION AND CHARACTERIZATION OF SRL



the column by formation of salts between the pyridine bases in SRL and the sulfonic acid groups of the resin, and then these were removed by displacement elution using a THF -5% isopropylamine mixture . Isopropylamine is a stronger base than any of the basic components of SRL which contain pyridine types as the strongest base component. The stronger base should displace this SRL fraction (2) from the column.

In order to determine the amount of SRL separated into each of the fractions, it is necessary that complete recovery be obtained for both fractions 1 and 2. Recovery was tested in two different ways. First, the collected samples were evaporated to dryness, weighed and compared to the original weight of SRL added to the A-15 column. Secondly, the collected samples were titrated for both acid and base content in order to compare to the original amount of acid or base in the SRL added to the column. Table 1 shows the results of these experiments. The total weight recovered appeared to be good at first glance. When coupled with the acid - base titrations, it was certain that not all the SRL was removed from the ion exchange column. The total base recovery was never more than 90% of the total, and the percentage of base recovered as seen from runs 2, 3 and 4 was proportioned to weight found for those samples. This indicated that some SRL containing basic groups was not eluted by the THF/ isopropylamine mixture. Further evidence that not all the SRL components were being eluted was shown by the balance of the acid recovery being of the order of 67% to 76%. A loss of acid as an amphoteric in fraction 2 would explain the less than 100% recovery of acid. When the weights of fractions 1 and 2 collected for run 3 are added, the total recovery comes to 110%. Run 3 was compared because 88% of the added base was recovered in this separation. The possibility of a weight increase in the chromatographic fraction was checked by carrying out the procedure without SRL. In this case 3 mg. of solid was found in each blank fraction after evaporation of the THF solvent. The residue was analyzed by nmr and appeared to be a compound related to the decomposition of THF. The nmr spectrum showed no aromatic protons, which would have to be the case if the residue were released from the ion exchange resin. The weights reported in table 1 are probably high due to this decomposition of the THF and, therefore, they do not reflect 100% recoveries of the SRL fractions as first appears.

The cation exchange experiments also indicate that not all the basic groups are being absorbed by the A-15 resin, which means a clean separation of the acids and bases was not obtained. This could be due to inadequate length of the column used or interaction between the acid and base groups of the SRL. This problem could have been investigated further, but the experiments indicate quite clearly that not all the SRL is eluted from the column with THF/isopropylamine. This non-quantitative recovery of the acid and base makes the method not useful for consideration at this time. Experimentally, the difficulty in non-quantitative recovery may be that sufficient washing of the column with THF/isopropylamine was not carried out.

Because the non-quantitative recovery of fractions resulted from the cation exchange experiments, it was decided to see if a similar problem would occur with the second step separation on an anion exchange resin, A-26, a stong base resin. The recovery of bases in this case was found to be 68% of the total bases added to a column. Again the data indicate the non-quantitative nature of ion exchange resin under the conditions used in this work.

(d) Work Forecast

During the next quarter, work will be stopped on the chromatographic method development so that the technician can devote his time to the measurement of uv spectra for the development of a computerized method to generate average molecule structures of SRL.

Table I SRL Recovery from Cation Exchange Chromatographs[a]

Analysis	Run Number	Total added	Fraction 1 (Acid-Neutral)	Fraction 2 (Base-Amphoteric)
Gram's SRL	1	0.262	0.159 (61%)	0.103 (39%)
	2	0.345	0.281 (82%)	0.058 (16%)
	3	0.366	0.287 (78%)	0.121 (33%)
	4	0.420	0.403 (96%)	0.009 (2.1%)
	5	0.1330	0.126 (95%)	
gms.	6	no SRL	0.003	.003
Meq. Base	2	0.189	0.014 (7.5%)	0.065 (35%)
	3	0.200	0.065 (31%)	0.115 (57%)
	4	0.231	0.085 (36%)	0.031 (13%)
Meq., Acid	1	0.392	0.197 (50%)	0.101 (26%)
	5	0.200	0.094 (47%)	0.040 (20%)

[a] Cation Exchange Resin, Amberlyst A-15, strong acid type in the sulfuric acid form., Column height 15 and resin, 10 mm diameter.

2. Computerized Methods to Generate Average Molecular Structures

a. Objective

To develop novel, rapid computerized methods to generate average molecular structures for SRL, SRC and their heavy liquids.

b. Introduction

For the past quarter our attention has been given to investigating a reasonable characterization of SRL on the basis of its ultraviolet spectra taken in a suitable solvent. We are using two approaches to adapt the laboratory data for computer analysis: the matrix solution and the vector component solution.

c. Experimentation

The spectra of the aromatic compounds were measured on a Cary 14 Ultraviolet-Visible Spectrophotometer in spectral grade dimethylacetamide. The solvent was able to dissolve 98-99% of KC-SRL. The absorption spectrum was recorded at several concentrations and Beer's Law plots at selected wavelenghts were in general linear and passed through zero, implying little or no significant intermolecular complexation. The data was digitized by recording the molar absorptivity every 5 nm starting at 270 nm (solvent cut off) to the point where the absorptivity was zero at higher wavelengths. In general, two or three different determinations at each wavelength were averaged to give a value of average experimental deviation for each wavelength.

d. Results

Over this quarter the ultraviolet-visible spectra of compounds listed in Table 2 were determined. The spectra of the standard compounds were recorded under the same conditions (solvent, instrument, technique, etc.) as are being used for SRL spectra determinations. This is necessary to accurately assess the effect of experimental error on the overall determination. Furthermore, literature spectra were not consistently run to a value of zero absorptivity at long wavelengths. With these spectra in hand, we have begun to test the calculation procedure. - Quarterly Report April-June

e. Forecast

A few real mixtures will be prepared and their UV spectra recorded. The mixture will then be analyzed by previous computer techniques to assess the error on the real data.

A basis set will be selected by consideration of what compounds have been isolated from coal derived materials. The most likely compounds to be in SRL in the basis set will initially be selected by comparison with mass spectral analyses of coal-derived materials provided by Grand Forks Energy Research Center. SRLs will be analyzed using the computerized approach to see if appropritate (non-negative) solutions can be obtained. When this has been done, the SRLs will be doped with compounds from the basis set to see if the computer analysis can predict the increase in concentration of that material.

TABLE 2

1. Phenanthrene
2. Anthracene
3. Naphthalene
4. 9-Methylanthracene
5. Biphenyl
6. 9 10-Diphenylanthracene
7. Pyrene
8. Acenaphthene
9. 1-Methylphenanthrene
10. Coronene
11. Dibenz (a,c) anthracene
12. Chrysene
13. Perylene
14. Fluoranthene
15. Benzo (g,h,i) Perylene
16. Indole
17. Bipyridine
18. Carbazole
19. Dibenzofurane
20. Dibenzothiophene

Task II

1. Catalyst Selection for SRL Reductions

(a) Objective

To select 6-10 catalysts for more detailed study for SRL Reduction.

(b) Introduction

This task incorporates the selection of 6-10 industrial heterogeneous catalysts and testing these catalysts in SRL hydrogenations. Activity and selectivity for formation of light liquids are the important criteria in this study. Also important are investigations of the products from these hydrogenations so that some conclusions about how each catalyst operates can be made. As reported in Quarterly Report II, the catalysts have been selected, statistical experimental design porameters planned, and the first series of experiments carried out, along with detailed MS-computer analysis of liquid fractions.

(c) Experimentation, Results and Discussion

During this reporting period further experiments were carried out with our "best catalyst" (as reported in J. Y. F. Low, K. J. Klabunde, N. Woolsey, R. Baltisberger, V. Stenberg and M. Govek, Energy Sources, in press and reference 5) the Harshaw $NiO-MoO_3/Al_2O_3$HT-100, and results are summarized in Tables 3 and 4. These data are compared with results obtained from a simultaneous investigation of SRL hydrogenation, employing new-novel catalysts synthesized in our laboratory.

The synthesis of our new catalysts was done under the direction of Professor Kozo Tanabe, our Distinguished Visiting Foreign Scientist (May - August 1976) a world renowned catalysis expert. This program was entirely NSF supported (no ERDA funds involved). However, the results are so meaningful to Task II of our ERDA contract that they are reported here. The results indicate that we have discovered a series of very active low surface area SRL hydrogenation catalysts.

A series of NiO-MoO_3 catalysts on various supports was prepared.

Supports

(1) $TiO_2(\alpha)$: this material is known to have high reducing ability (single electron donor ability) and can serve to activate the MoO_3 by partial reduction.[1]

(2) TiO_2-$SiO_2(\beta)$: this it is known to show a pronounced denitrogenation activity at low reaction temperatures with NiO-MoO_3.[2]

(3) TiO_2-SiO_2 : this mixed oxide is known to have extremely high acid strength (Ho $\leqq -8.2$)[3].

(4) ZrO_2: this oxide has both basic and acidic properties[4].

(5) Special Al_2O_3 samples: high surface area fibers with low bulk densities were used .

Surface areas of the prepared impregnated catlaysts (NiO-MoO_3/support) were measured by Brunner-Emmett-Teller methods employing low temperature nitrogen. Acid amounts in these catalysts were determined by measuring the change in the concentrations of methyl red (pKa= +4.8) in benzene before and after a catalyst was suspended. Acid strength distribution was obtained from Differential Scanning Calorimeter diagrams of the catalysts on which pyridine was absorbed at room temperature.

Hydrogenations of SRL with these catalysts were carried out in a 1-liter Hastelloy C-Magne-Drive autoclave. The autoclave was charged with 75 g SRL and 18.75 g catalyst, purged and pressurized to 2500psi with hydrogen. Then, with stirring, the reactor was heated to 450°C for two hours, cooled to 150°C and depressurized through acid traps, cold traps and to a 200 liter gas bag. Ammonia was determined by back titration, gas density by volumetric weighing and gas volume by a wet test meter. (Reactor characteristics-graphs 1-3).

The reactor contents were distilled to 200°C. The remaining material was extracted in a Soxlet with THF, the THF stripped off, and the residue vacuum distilled. The following fractions were collected: at 0.4 torr: IBP-70°C, 70-110, 110-180, 180-250°C. Residue left was considered to be unconverted SRL which determined the overall conversion. Table 3 summarizes the distillation data. A MoO_3-NiO-Al_2O_3 (FF) catalyst showed the highest activity among the prepared catalysts. The % conversion over the catalyst was 92%, the same value as that over MoO_3-NiO-Al_2O_3(HT-100E), a best catalyst among the commercial available catalysts^5. The activities of the other catalysts were in the range of 85-90%. Since, however, the specific surface areas of MoO_3-NiO-TiO_2(α) and MoO_3-NiO-TiO_2(β) are about 30% of that of a standard catalyst, MoO_3-NiO-Al_2O_3 (HT-100 E), the activities per unit surface area of the catalysts containing TiO_2 are much higher than that of the standard catalyst. It should be also noted that the molybdenum contents of all the prepared catalyst are less than that of the standard catalyst (see Table 4).

The largest amount (59.4 %) of total distillation fraction was found for MoO_3-NiO-Al_2O_3(FF) while the smallest amount (51.8%) for MoO_3-NiO-Al_2O_3(FE). The amount of the fraction Atm was largest (10.5%) for MoO_3NiO-Al_2O_3(FF) and smallest (4.8%) for MoO_3-NiO-ZrO_2 and the amount of the fraction 180-230°C was largest (7.9%) for MoO_3-NiO-TiO_2(β) and smallest (2.8%) for MoO_3-NiO-Al_2O_3 (FE). For the other fractions, the smallest amounts were in the range of 65-75% of the largest amounts. The volume of gas evolved, plus unconverted hydrogen and the amount of ammonia, were largest for MoO_3-NiO-ZrO_2 and smallest for MoO_3NiO-Al_2O_3(FF). A MoO_3-NiO-Al_2O_3(FF) catalyst gave smaller amount of gas and larger amount of liquid than MoO_3-NiO-Al_2O_3(HT-100E).

No correlation was found between catalytic activity and acid amount at an acid strength of $Ho \leq 4.8$. The DSC diagrams of MoO_3-NiO-Al_2O_3(HT-100E) and MoO_3-NiO-TiO_2(α) showed broad peaks of heat absorption due to the desorption of pyridine in a wide range of desorption temperatures indicating a large acid strength distribution. In the case of $MoO_3NiO-TiO_2-SiO_2$, a relatively sharp peak was observed at a high temperature (440°C), indicating the existence of highly strong acid sites. However, the catalyst did not show any characteristic behavior of a strong acid catalyst for the hydrocracking of SRL. Though acid sites are considered to act as active sites for cracking of SRL, acid sites alone do not seem to relate directly to hydrocracking activity, but would play an important role in cooperation with active sites for hydrogenation.

Table 3

Composition of Catalyst

Catalyst	% Composition of Catalyst		
	MoO_3	NiO	Support
MoO_3-NiO-TiO_2(α)	11.4	3.4	85.2
MoO_3-NiO-TiO_2(β)	10.1	3.0	86.9
MoO_3-NiO-TiO_2-SiO_2	10.0	3.0	87.0
MoO_3-NiO-ZrO_2	10.0	3.0	87.0
MoO_3-NiO-Al_2O_3(FE)	10.1	2.9	87.0
MoO_3-NiO-Al_2O_3(FF)	10.0	3.0	87.0
MoO_3-NiO-Al_2O_3(H)	10.0	3.1	86.9
MoO_3-NiO-Al_2O_3(HT-100E)	16.8	3.8	79.4

Table 4

Hydrocracking of Solvent Refined Lignite over Various Mixed Oxide Catalysts

Catalysts	Gas			Distillation of Fractions Wt. % of SRL							Total Conv. (%)	Acid Amount (m mol/g)	Surface area (m^2/g)
	Volume (ℓ)	Density (g/ℓ)	NH_3 (g)	Atm.	18-70	70-110	110-180	180-230	Vac. Btm.	Total Frac.			
MoO_3-NiO-TiO_2(α)	98	0.21	0.88	6.0	8.6	13.6	21.1	6.2	12.6	55.5	87	0.0162	56
MoO_3-NiO-TiO_2(β)	100	0.22	0.84	5.9	9.7	9.7	24.0	7.9	11.1	57.2	89	0.0193	54
MoO_3-NiO-TiO_2SiO_2	97	0.29	0.86	8.4	7.3	11.0	24.1	7.5	14.7	58.3	85	0.0168	83
MoO_3-NiO-ZrO_2	101	0.26	0.94	4.8	7.7	10.0	26.4	7.4	10-12	57.9	88-90	0.0189	
MoO_3-NiO-Al_2O_3(FE)	96	0.27	0.77	7.6	9.3	9.5	22.6	2.8	13.3	51.8	87	0.0300	130
MoO_3-NiO-Al_2O_3(FF)	92	0.27	0.83	10.5	10.1	12.5	21.6	4.7	8.4	59.4	92	0.0360	183
MoO_3-NiO-Al_2O_3(H)	94	0.27	0.84	7.9	10.9	11.8	19.8	5.9	11.3	56.0	89	0.0238	144
MoO_3-NiO-Al_2O_3(HT 100)	94	0.27	0.89	8.4	9.2	11.3	23.0	5.0	8.3	56.9	92	0.0285	196

Amount of SRL = 75.0 g

Amount of Catalysts = 18.75 g

Reaction Temp. = 450°C

Reaction time = 2 hr.

Hydrogen pressure = 2500psi (initial), 4700 ~ 4950 (maximum)

IB-70 = initial boiling point

Vac. Btm. = Vacuum bottom

References

(1) H. Hattori, M. Itoh, and K. Tanabe, J. Catalysis, 38, 172 (1975).

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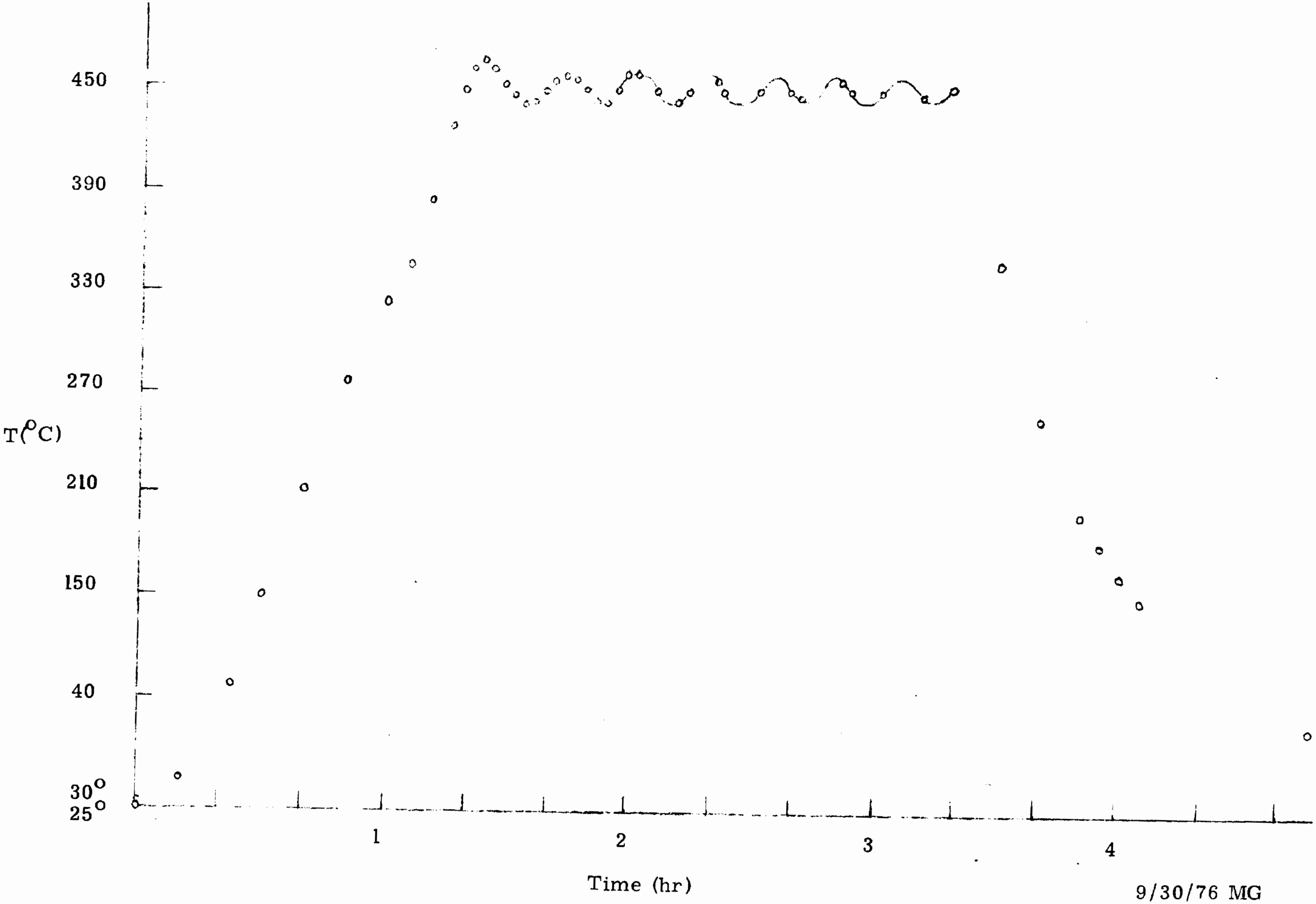
(3) K. Tanabe, M. Itoh, and M. Sato, ibid., 676 (1973).

(4) T. Yamajuchi, H. Sasaki, and K. Tanabe, Chem. Lett., 1017 (1973).

(5) J. Y. F. Low, K. J. Klabunde, D. E. Severson, N. F. Woolsey, R. J. Baltisberger, M. Govek, M. J. Wolf, J. Rice, St. Switzer, M. L. Mannering, and V. I. Stenberg, Batch Autoclave Hydrogenation of Solvent Refined Lignite, ACS Fuel Division Preprints, 20(1), 122 (1975).

(e) Work Forecast

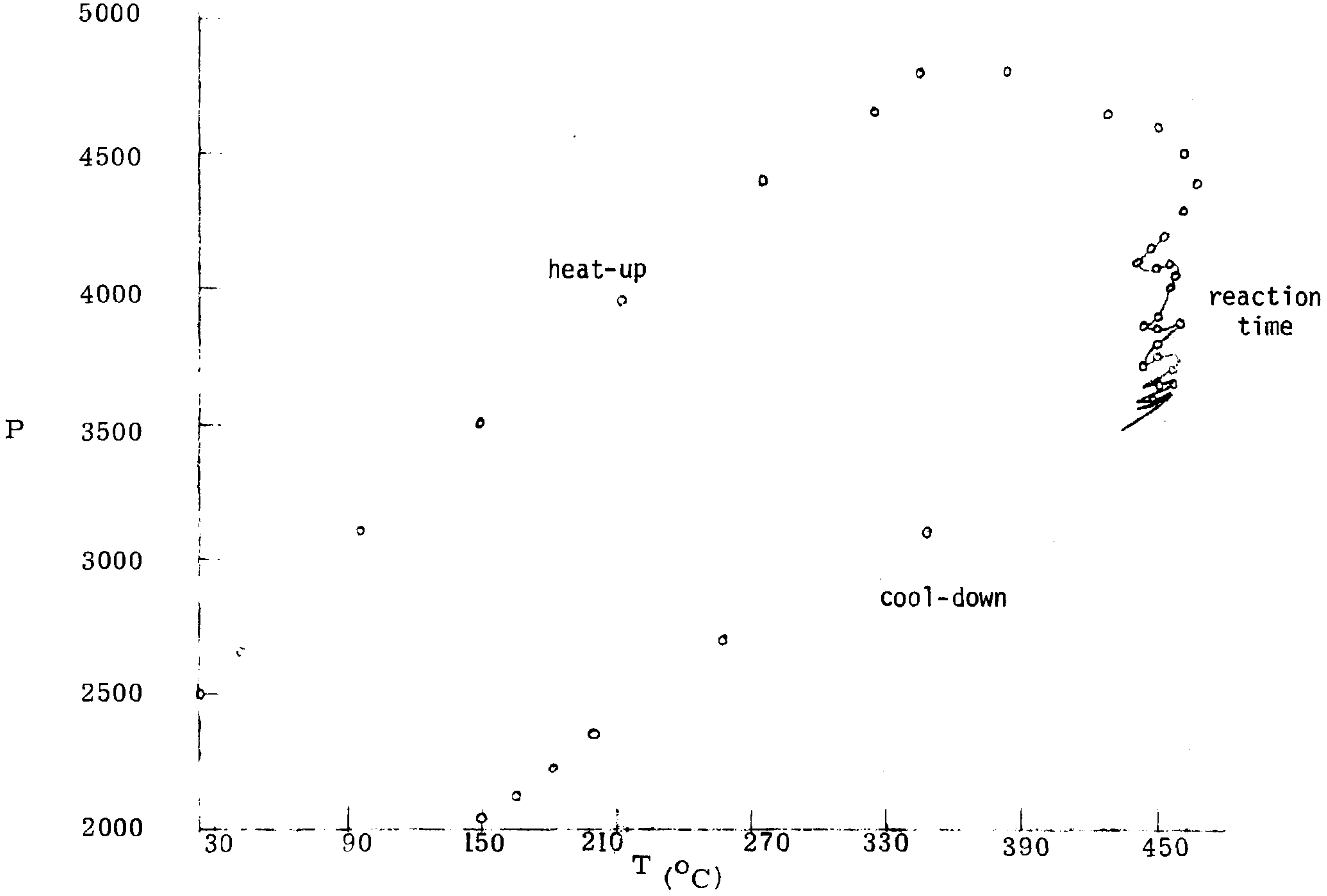
We will continue with the catalyst testing and are searching for technician time to get Mr. Jones working more on this Task and less on Task III. We are hiring part-time people to help with the gas chromotographic analyses of Task IV.



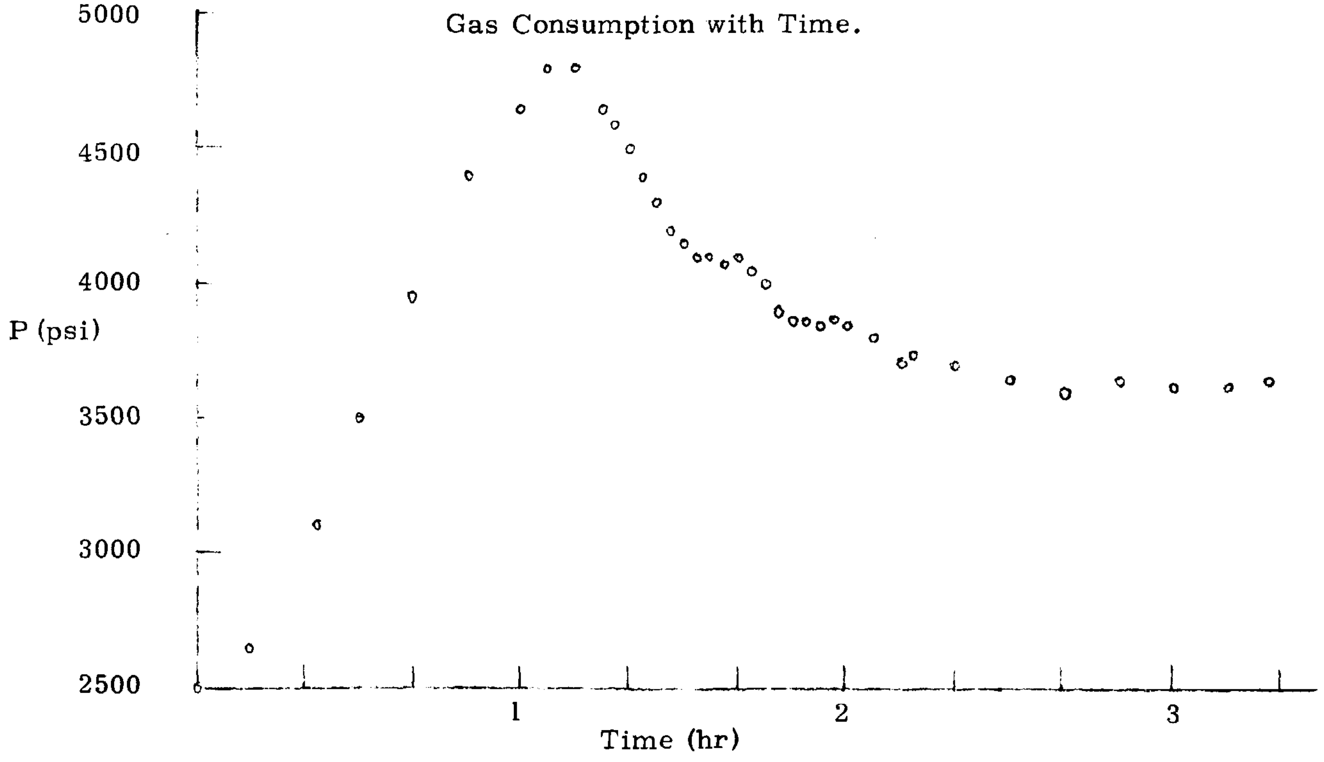
9/30/76 MG

Graph 1. Temperature vs. Time Plot to Illustrate the Degree of Temperature Control.

Graph 2. Pressure vs. Temperature Graph to Illustrate Gas Consumption with Temperature.



Graph 3. Pressure vs. Time Graph to Illustrate Gas Consumption with Time.



Task III

1. The Reduction of Model Compounds under the COSTEAM Conditions

(a) Objectives

To determine both the function of the hydrogen-donor solvent and the role of mineral matter in lignite as a catalyst in the formation of SRL using CO-H_2-H_2O or CO-H_2O.

(b) Introduction

The carbon monoxide experiments of this task were begun during the second quarter to determine the function of the hydrogen donor solvent and the role of mineral matter in lignite as catalysts for the reduction. This task is defined to use model compounds.

On designing the experiments for the suggested twelve (12) compounds listed in the contract with the conditions cited, it was evident that a minimum of 96 reductions would have to be done. Further, the publishable data would have to be duplicated, which adds to the number of experiments. Since the 1-liter, magnetically-stirred autoclave can only be run 3 times a week under optimum conditions, it was necessary to employ the two 300-ml Hastelloy batch autoclaves, purchased under this contract, to accomplish the objective of this task. Our initial planning took this into account.

(c) Experimentation

The reductions are done in a pair of 300-ml rocking Hastelloy C autoclaves, described in Quarterly Report II. The temperature is maintained at 425°C for two hours. The heat up time is a slightly more than an hour, and the cool-down time is about the same. Initially the autoclaves are charged with 750 psi of reducing gases and 750 psi of argon (1500 psi total). At 425°C, the reactions will achieve a total pressure of about 4,000 psi. After cool-down, the gases are vented and the products removed by decanting.

The water layer is separated from the organic layer by a separatory funnel and filtered through a sintered glass funnel. A 3-ml aliquot of the resultant solution is combined with 2 ml of 1-bromonaphthalene (internal standard) and analyzed by gas-liquid chromotography. The results were obtained on a Varian Aerograph 90-P instrument (cf. Quarterly Report II).

(d) Results and Conclusions

The work on the model compounds with the various reducing gases and catalysts is continuing. The benzophenone reduction series is complete, all the results duplicated, and are summarized in Table I . All data was obtained using a set of 300-ml Hastelloy C rocking autoclaves. The conclusions for the benzophenone reduction are as follows:

1. Benzophenone is reduced by CO-Ar-H_2O to diphenylcarbinol (benzhydrol), diphenylmethane, benzene and toluene.
2. Diphenylcarbinol is the precursor to diphenylmethane.

It can be seen from Table 4, as the reaction temperature is lowered, the percentage of diphenylcarbinol present increases as the percentage of diphenylmethane decreases. Likewise, when the reaction temperature in increased, the percentage of diphenylcarbinol present decreases as the percentage of diphenylmethane increases.

3. The increasing order of effectiveness of reducing gases for conversion are: H_2-H_2O, CO-H_2O and CO-H_2-H_2O.
4. The effect of tetralin in the CO-Ar-H_2O system with Na_2CO_3 as a catalyst favors the conversion of diphenylcarbinol to diphenylmethane without influencing the overall conversion.
5. The effect of tetralin on the H_2-Ar-H_2O reduction of benzophenone is to lower the overall conversion and the yield of each of the products.
6. The effect of tetralin in the CO-H_2-H_2O reduction of benzophenone is negligible.

7. During the benzophenone reduction with various gas mixtures, tetralin is converted in low yields to naphthalene.

8. The mole percent yield of benzene is 3-20 times that of toluene in the benzophenone reduction solutions.

The results of the diphenylmethane reductions obtained similarly are given in Table 5. We will not be doing further work on diphenylmethane because of its low conversions and lack of reactivity under these conditions. Experimentally, it is difficult to differentiate the runs because the experimental error is near that of the observed differences.

The preliminary results on the reduction of 1, 2-diphenylethane are given in Table 6. Much of the work remains to be duplicated. Hence, conclusions are hazardous at this point. Conversions are in an excellent range for differentiation in results of the different reduction conditions.

(e) Work Forecast

The 1,2-diphenylethane runs are midway to being completed, and, though not quite as far, the reductions of benzhydrol are being done. In roughly a month's time these will be done. We then plan to proceed with naphthalene and diphenylether. We are encountering no problems which are not normal to laboratory operations and which are not solvable by well-known methods.

Table 5
Reduction of Benzophenone

Run	Temperature	Reducing gas[1]	Solvent[2]	Catalyst[3]	$C_{10}H_{12}$,%	$C_{10}H_{16}$,%	Ph_2COH,%	Ph_2CH_2%	PhH,%	$PhCH_3$,%	Conversion,%[4]
1.	400	CO	None	Na_2CO_3	---	---	32.1	6.4	0.5	---	38.9
2.	425	CO	None	Na_2CO_3	---	---	22.4	19.2	0.7	0.03	42.3
3.	450	CO	None	Na_2CO_3	---	---	6.3	42.3	4.6	0.8	54.0
4.	475	CO	None	Na_2CO_3	---	---	3.9	45.0	19.3	1.8	60
5.	425	CO	None	Na_2CO_3	---	---	22.4	19.0	0.65	0.03	42.3
6.	425	H_2	None	Na_2CO_3	---	---	25.4	6.2	1.2	0.03	32.8
7.	425	CO,H_2	None	Na_2CO_3	---	---	9.5	47.0	2.5	0.6	59.6
8.	425	CO,H_2[5]	None	Na_2CO_3	---	---	2.88	52.4	1.12	0.3	51.6
9.	425	CO	None	Na_2CO_3	---	---	22.4	19.2	0.65	0.03	42.2
10.	425	CO	$C_{10}H_{12}$	Na_2CO_3	93.6	6.4	3.7	33.6	0.75	0.27	38.4
11.	425	CO,H_2	None	Na_2CO_3	---	---	9.6	47.0	2.5	0.60	59.6
12.	425	CO,H_2	$C_{10}H_{12}$	Na_2CO_3	92.9	7.1	13.5	42.2	4.4	0.62	58.7
13.	425	H_2	None	Na_2CO_3	---	---	25.4	6.2	1.2	0.03	32.8
14.	425	H_2	$C_{10}H_{12}$	Na_2CO_3	95.2	4.8	21.1	11.8	1.7	trace	35.0
15.	425	CO	None	None	---	---	0.0	6.8	0.2	0.3	7.2
16.	425	CO	None	FeS	---	---	trace	31.9	0.9	0.3	33.0
17.	425	CO	None	$NaCHO_2$	---	---	12.9	31.6	1.3	0.3	45.9
18.	425	CO	None	NaOH	---	---	11.2	31.9	2.2	0.3	45.4

1. Each gas at initial partial pressure of 750 psi
2. 0.014 moles
3. 0.015 moles
4. Based on recovered benzophenone
5. 375 psi CO and 375 psi CO

Table 6

Reduction of Diphenylmethane

Run	Reducing gas	Solvent	Catalyst	$C_{10}H_{12}$, %	$C_{10}H_{16}$, %	PhH, %	$PhCH_3$, %	Conversion, %
1.[a]	CO	none	none	-	-	0.5	0.7	1.2
2.	CO	none	Na_2CO_3	-	-	1.2	1.5	2.7
3.[a, b]	CO, H_2	none	Na_2CO_3	-	-	1.2	1.5	2.6
4.	H_2	none	Na_2CO_3	-	-	0.9	0.9	2.3
5.[a]	H_2	tetralin	Na_2CO_3	2.7	97.2	0.5	0.7	1.2
6.[a]	CO	tetralin	Na_2CO_3	4.0	97.0	0.5	0.7	1.2
7.	CO, H_2	none	Na_2CO_3	-	-	1.0	1.1	2.1

Conditions: 0.6 moles water, 425°C, 750 psi argon, 0.015 mole Na_2CO_3 (when used), 750 total psi of reducing gases, 0.015 moles tetralin (when used),

[a] Not duplicated.

[b] 750 psi CO and 750 psi of H_2 with no argon.

Table 7

Reduction of 1,2-Diphenylethane

Run	Reducing gas	Solvent	Catalyst	$C_{10}H_{12}$, %	$C_{10}H_{16}$, %	PhH, %	$PhCH_3$%	PhC_2H_5, %	Conversion, %
1.[a]	CO	none	none	-	-	9.0	83.7	7.3	73.6
2.	CO	none	Na_2CO_3	-	-	13.4	74.1	12.4	70.6
3.[a]	H_2	none	Na_2CO_3	-	-	26.8	54.5	18.8	77.7
4.[a]	CO	none	NaOH	-	-	13.4	72.6	14.0	73.0
5.[a]	none	none	NaOH	-	-	9.0	83.7	7.3	73.6
6.[a]	CO	none	Na_2OOCH	-	-	16.5	72.0	11.7	75.4

Conditions: 0.6 moles of water, 425°C, 750 psi Ar., 0.015 mole Na_2CO_3 (when used), 750 psi reducing gases.

[a] Not duplicated.

Task IV

1. Mechanism of the CO Reducing System

(a) Objective

To investigate the mechanism of solvent-refining or its related processes under the system of $CO-H_2O$ or $CO-H_2-H_2O$ in the presence of constituents present in the mineral matter of lignite.

(b) Introduction

This task deals with possible modes of activation of carbon monoxide and carbon monoxide-water over minerals present in lignite and possibly acting as catalysts in the $CO-H_2O-H_2$ solvent refining or COSTEAM process. Since the $CO-H_2O$ system is very effective in liquefaction of lignite (moreso than H_2 alone), we sought unusual activation mechanisms. One such mechanism is the initiation of radical processes when CO adsorbs on metal oxide.

For example, a very interesting phenomenon occurs when CO is allowed to adsorb on a surface of magnesium oxide (MgO). Part of the CO is adsorbed in such a way that paramagnetic species are produced (CO adsorbed with an electron pair split or CO^+ formed). We are attempting to clarify this process and find out if it is an important step in activation of CO and $CO-H_2O$ for reaction with organics in lignite. We are studying these processes by electron spin resonance (ESR). Magnesium oxide was chosen for initial studies because there is some prior literature concerning this phenomenon[1]. This prior literature reports one radical species in the CO-MgO system, but, in fact, we are finding a much more complex and interesting reaction mode, as described below.

(c) Experimentation

The primary instrument for this task, the electron spin resonance spectrometer (Bruker ER-420) is installed, checked out and in excellent operating condition. Dr. R. Kaba has been operating the machine on a regular basis and has been desinging and constructing a vacuum line apparatus to remove oxygen from the samples. He had been using a vacuum line already in existence in the Chemistry Department, but because of apparent contamination, the new line was constructed.

(d) Results and Discussion

The MgO sample normally used had a reported purity of 99.9% and was supplied by ROC/RIC Corporation. The sample was first boiled in distilled water for several hours, filtered and air dried at 65°. Pellets of the material (prepared manually) were degassed by heating under vacuum at temperarues in the 440-850° range. An epr spectra was recorded at this time and, the MgO sample generally had a very strong background signal.[3] Lunsford[1] did not report a background signal. This difference was only the first of many differences in the present work and that reported by Lundsford. For the sake of brevity, these differences are summarized in tabular form for two samples from this present work: K-I-17 (Background present) and K-I-20 (Background absent).

It is evident from Table 7 that there are marked differences between the observations in our laboratory and Lunsford's results. It should be emphasized that the radical or radicals in sample K-I-17 and K-I-20 (where there was <u>no</u> background signal) are quite different from the CO derived radical reported by Lunsford. Indeed, the temperature study of sample K-I-17 suggests that there are three or more different radical species present at one time or another. This is in marked contrast to the single radical species reported by Lunsford. At first it was thought that the differences were due to use of a "dirty" vacuum line for calcinations of MgO. The vacuum line (with an obtainable vacuum of <u>ca</u>. $5X10^{-4}$ torr) used in the inital work was also used for general organic reactions. A new vacuum line (which will only be used for epr sample preparations) was recently completed.

Although the new vacuum line has only been in operation for a short time, preliminary results indicate that differences between the present work and that of Lunsford cannot be ascribed to the use of a "dirty" vacuum system or to the poorer vacuum obtainable. A MgO sample (H_2O washed as described) prepared on the new vacuum line had the same background signal as MgO calcined on the old vacuum system. Heating an unwashed MgO sample (99.9% purity from ROC/RIC) at 580° for 20 hr., however, gave epr spectra considerably different from the H_2O washed material. In addition to very intense Mn^{2+} and Cr^{3+} signals, this sample gave a background signal. This new background signal differs from the original background signal in the following manner: it is (1) very weak and (2) anisotropic. This background signal appears to have uniaxial anisotropy of the g-factor ($g_{\parallel} \cong 2.01$, $g_{\perp} \cong 2.00$). However, because of the low intensity and overlapping lines of Mn^{2+} and Cr^{3+}, it is not possible to rule out a unsymmetric g-tensor for this species.

Another MgO sample (99.99% from ROC/RIC) was also calcined at 580° for 20 hr. without any pre-treatment (H_2O wash). The epr spectra of this MgO sample showed very intense lines only from Mn^{2+}, but neither background Cr^{3+} was evident. A sample of this new MgO sample is now being prepared with a H_2O wash before calcination. The results of this last experiment should be very interesting, as it should be possible to tell if the background signal is a result of either the initial H_2O treatment or a property of the original MgO sample (99.9%) used in this investigation.

(e) Work Forecast

Once the problems with the background signal in MgO are solved and it is determined that Lunsford's work can be reproduced (or we become confident the work cannot be reproduced) it is proposed that a rapid survey of interesting catalysts (for example, MgO, CaO, Na_2CO_3, NaOH, FeS, etc., which may be present in lignite minerals or ash) be undertaken to determine which catalysts have the greatest propensity for forming a radical species when exposed to a CO atmosphere. Then more extensive studies will be undertaken with the most promising catalysts.

Table 8

Comparison of Experimental Conditions and Results for CO Adsorbed on Various MgO Surfaces

	Lunsford[a]	K-I-17[b]	K-I-20[c]
Pre-H_2O wash	yes	yes	yes
Calcination	800° for 16 hr.	450° for 20 hr.[d]	450° for 20 hr.
Background signal	no	yes	no
CO addition	~150 Torr	~150 Torr	~300 Torr[e]
Color after CO addition	peach	peach (light cream)	light peach
EPR signal	yes; uniaxial anisotropy of g-factor	yes; complex[f]	yes; complex[f]
EPR signal growth	yes[g]	yes[g]	yes[g]
EPR signal saturation	yes; at powers greater than _ca._ 1mw	not readily noticeable except for power above _ca._ 50 mw	-
Desorption of CO	90% removed at 400°	90% removed at ~350°[h] (Background remained)	-
Readsorption of CO	-	Added ~150 torr of CO. Addition epr lines were visible, but not similar to original CO species.	-

Footnotes for Table 7

a. J. H. Lunsford and J. P. Jayne. *J. Chem. Phys.*, **44**, 1492 (1966).

b. Present work; prepared from 99.9% MgO from ROC/RIC; background signal present.

c. Present work; prepared from 99.9% MgO from ROC/RIC; no background signal present.

d. Similar results were obtained with calcination temperatures up to 850°.

e. First added 150 Torr of CO, but this produced only a very weak signal from CO derived radicals. Upon doubling the amount of CO, the signal was increased significantly. However, at no time was the signal intensity of the sample greater than or equal to that of K-I-17.

f. These epr signals were too complex to be ascribed to a signal radical species. This was confirmed by temperature studies, see later. There were differences in the epr signals of K-I-17 and K-I-20; however, they were at the same time similar.

g. All samples reach a steady-start concentration of radical species in 14-20 days.

h. At *ca.* 300° the spectra was dramatically changed with new lines becoming visible. Lunsford did not report any such changes with increasing temperature, implying that the process was a simple desorption of radical species.

Footnotes and References:

1. J. H. Lunsford and J. P. Jayne, *J. Chem. Phys.*, **44**, 1492 (1966).
2. On one occasion the background signal was not present (sample K-I-20). The procedures used for this sample were not noticeably different from the procedures used when the background was present. The reasons for the lack of background signal in this sample are not known.
3. The background signal was isotropic, centered at a g-value of *ca.* 2.00, with a line width of *ca.* 3G peak to peak. The background signal is indeed a

problem, as it occurs at the same approximate field as the absorbances of the CO derived radicals on MgO. Also, normally the six lines from Mn^{2+} were visible. However, these lines were of very weak intensity. A signal from Cr^{3+} was not visible.

Publications

* J. Y. F. Low, K. J. Klabunde, D. E. Severson, N. F. Woolsey, R. J. Baltisberger, M. Govek, M. J. Wolf, J. Rice, S. Switzer, M. L. Mannering and V. I. Stenberg, Batch Autoclave Hydrogenation of Solvent Refined Lignite, ACS Fuel Division Preprints, 20 (1), 122 (1975).

* V. I. Stenberg, R. J. Baltisberger, K. J. Klabunde, N. F. Woolsey, D. Severson, M. Souby, Chemistry of Lignite Liquefaction, Quarterly Report 1, March 1, 1976, prepared for the Energy Research and Development Administration and Distributed through the National Technical Information Service.

* V. I. Stenberg, R. J. Baltisberger, K. J. Klabunde, N. F. Woolsey, D. Severson, M. Souby, Chemistry of Lignite Liquefaction, Quarterly Report 2, July 1, 1976, prepared for the Energy Research and Development Administration and distributed through the National Technical Information Service.

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J. Y. F. Low, K. J. Klabunde, N. F. Woolsey, R. J. Baltisberger, M. Govek, and V. I. Stenberg, Catalytic Hydrogenation of Solvent Refined Lignite, Energy Sources, in press.

V. I. Stenberg, R. J. Baltisberger, N. F. Woolsey, K. J. Klabunde, Chemistry of Lignite Liquefaction, 1976 ERDA/NSF/EPRI Principal Investigator's Conference - Coal Research, Golden, Colorado, September 3-4, 1976.

N. F. Woolsey, K. J. Klabunde, R. J. Baltisberger, V. I. Stenberg and R. Kaba, Characterization of Solvent Refined Lignite and Solvent Refined Coal. Computerized Methodology Development, ACS Fuel Division Preprints, 21, 33 (1976). (Storch Award Invitation Lecture given by K. J. Klabunde).

N. F. Woolsey, R. J. Baltisberger, K. J. Klabunde, V. I. Stenberg and E. J. O'Reilly, Approaches to the Analytical Analysis of Solvent Refined Lignite, Coal Chemistry Workshop, Stanford Research Institute, August 26-27, Menlo Park, CA (lecture given by N. F. Woolsey).

* Reported previously.

Visitors during the quarter

1. Fabrizio Bargellini INTEC/CURFO
   Santiago, Chile
2. Guillerno Norieca INTEC/CORFO
   Santiago, Chile
3. Dr. Bjornbon, Stockholm Sweden

Related Professional Activities of the Chemists of the Fuel Committee

1. Participated in a lignite seminar every second week (participants are from: Grand Forks Energy Research Center, UND Chemical Engineering Department and UND Chemistry Department).
2. The chemists held weekly seminars with the postdoctoral research associates and technicians of the project.