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CHEMISTRY OF LIGNITE LIQUEFACTION

Quarterly Report, July—September 1977

By
Virgil I. Stenberg
Richard J. Baltisberger
Kenneth J. Klabunde
Neil F. Woolsey
Donald Severson
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MASTER

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The University of North Dakota
Grand Forks, North Dakota

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PREPARED FOR THE UNITED STATES
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I. Objective Scope of Work

The Fuel Committee was established in 1974, as an interdisciplinary group of chemists and engineers at the University of North Dakota to investigate the chemistry associated with lignite liqucfaction 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, and do catalyst testing and mechanistic studies on the $CO-H_2O-H_2$ and $CO-H_2O$ reducing systems.

II. Summary of Progress to Date

Solvent refined lignite (SRL), obtained by treating lignite with carbon monoxide-hydrogen-water at 1,500-2,500 psi at ca. 400°C, has an average molecular weight of ca. 450 with about 89% carbon, 6% hydrogen, 3% oxygen, 1% nitrogen and 1% sulfur with no inorganic material. Based on nuclear magnetic resonance studies, SRL is highly aromatic with one acid group and 0.1 base groups per average molecule. It is similar to solvent refined coal (SRC's) from bituminous and subbituminous coals in C, H and S elemental analysis, acid content nmr and uv spectra, but lower in nitrogen and base content. The average molecular weights of SRC's and SRL's are dependent upon the conversion conditions. The g and ΔH values as well as the radical concentrations are the same for SRL's and SRC's as determined by electron spin resonance. Ultraviolet spectra of gel permeation fractions show the same aromatic chromophores are present in both larger and smaller molecular weight fractions of SRL with the nmr spectra showing the lower molecular weight fractions to contain methyl type carbons while the larger molecular weight fractions include cyclic aliphatic groups.

Solvent refined lignite can be 90% converted by catalytic hydrogenation into ca. 20% light liquids, 15% light oil, 20% heavy oil and gases (Low et al., 1976). A series of commercially available Ni-Mo, Co-Mo, Ni-W, Pt, and Cr catalysts on Al_2O_3 and SiO_2 supports, and a series of synthesized Ni-Mo/fibrous Al_2O_3, TiO_2 (α or β), ZrO_2 and SiO_2 catalysts have been tested in hydrotreating of SRL into liquids. The temperature (450^{o}) and pressure (3,500 psi) have been optimized. Ni-Mo/Al_2O_3 is the best catalyst overall, but we have determined that on a surface area basis the Ni-Mo/ZrO_2 and Ni-Mo/TiO_2 catalysts are extremely good. Ni-Mo/ZrO_2 is particularly promising, probably due to the dual acid-base character of the ZrO_2 support.

Phenol, ethylbenzene, diphenylether, and carbazole are difficult to reduce under carbon monoxide-water conditions at 425°C in batch autoclaves. These conditions readily convert diphenyl ketone, benzhydrol, quinoline, anthracene and 1,2-diphenylethane into a variety of products. For 1,2-diphenylethane, benzophenone and quinoline, the presence of tetralin had no effect on conversions and it had a negative effect on the conversions of thioanisole and diphenylsulfide. Sodium carbonate aides the conversions of benzophenone and quinoline, has no effect on the reductions of 1,2-diphenylethane and anthracene and had a negative effect on the thioanisole and diphenylsulfide runs. Iron oxide aided the benzophenone and quinoline reductions. Ferrous sulfide favored the thioanisole reduction but it had no effect on the 1,2-diphenylethane run and had a negative effect on the diphenylsulfide one. For all but the quinoline reaction, where hydrogen was superior, a blend of carbon monoxide-water and hydrogen was the optimum set of reducing gases. Carbon monoxide and water outperformed hydrogen for the benzophenone and benzhydrol reductions.

Related to $CO-H_2O$ as a reducing medium, a host of metal oxides (possible in situ catalysts in coal) has been examined by electron spin resonance for activity in electron transfer processes to carbon monoxide forming surface bound $CO^{\overline{\cdot}}$. Only the alkaline earth oxides have shown activity (MgO, CaO, BaO, SrO). Currently, we believe carbon monoxide is adsorbed efficiently on Lewis base sites (two electron donors) and then migrates to one electron reducing sites.

Presentations and Publications

1. V. I. Stenberg, R. J. Baltisberger, N. F. Woolsey and K. J. Klabunde, Chemistry of Lignite Liquefaction, Sept. 15, 1976, Lignite Briefing for Legislators, University of North Dakota.

2. K. J. Klabunde, R. J. Baltisberger, N. F. Woolsey and V. I. Stenberg, Chemical Characterization of Solvent Refined Lignite, Fuels Science, Gordon Research Conference, July 1976, New Hampton, NH.

3. 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.

4. 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).

5. 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), 1976.

6. K. J. Klabunde, D. S. Jones, D. H. Ralston, K. Tanabe, M. Govek, V. I. Stenberg, N. F. Woolsey, and R. J. Baltisberger, Production of Clean Liquid Fuels from Lignite: Catalytic Hydrotreating of Solvent Refined Lignite Employing Low Surface Catalysts and Commercial Catalysts, Lignite Symposium, May 18-19, 1977, Grand Forks, N.D. .

7. R. J. Baltisberger, N. F. Woolsey, K. J. Klabunde and V. I. Stenberg, Carbon Monoxide Catalysts and the Reduction of Lignite Model Compounds, COLL. 18, Second Joint Conference, Chemical Institute of Canada and American Chemical Society, (Symposium Speaker), May 31, 1977, Montreal, Quebec, Canada.

8. V. I. Stenberg, (Invited Lecture), Summer Institute in Energy Economics and Mining Ecology for Educators, (high school science teachers), University of North Dakota, Grand Forks, N.D., June 17, 1977. Chemistry of Lignite Liquefaction.

9. 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).

10. James Y. F. Low, K. J. Klabunde, N. F. Woolsey, R. J. Baltisberger, M. Govek, and V. I. Stenberg, Catalytic Hydrogenation of Solvent-Refined Lignite to Liquid Fuels, Energy Sources, 3, 19 (1976).

11. V. I. Stenberg, R. J. Baltisberger, N. F. Woolsey, and K. J. Klabunde, Chemistry of Lignite Liquefaction, 1977 ERDA/NSF/EPRI Principal Investigator's Conference-Coal Research, Pittsburgh, Pennsylvania, August 25, 1977.

12. R. J. Baltisberger, K. J. Klabunde, V. I. Stenberg, N. F. Woolsey, K. Saito and W. Sukalski, Comparison of Solvent Refined Lignites with Solvent Refined Bituminous Coals, ACS Fuel Division Preprints, **22** (5), 84 (1977).

13. V. I. Stenberg, R. J. Baltisberger, N. F. Woolsey and K. J. Klabunde, Chemistry of Lignite Liquefaction, Seminar at North Dakota State University, October 25, 1977.

Detailed Description of Technical Progress

Task I

A. Structural Variation of SRL with Molecular Weight

(a) Objective

To aid in the development of analytical methods to determine average molecular structures of SRC, SRL and their heavy liquids. To compare SRL and SRC structural and chemical differences.

(b) Summary

During this quarter, a number of gel permeation separations were carried out to determine the molecular weight distribution of compounds present in an SRL sample, M-11A. The sample was chosen because large quantities of this sample are available free of ash and, consequently, it is totally soluble in the solvents used in gel separation. The separations were carried out using Bio-Beads and Sephadex gels so that gram quantities of M-11A could be isolated into molecular weight fractions. The large sample sizes allowed one to measure molecular weights (VPO), aromatic/aliphatic proton ratio (nmr) and acid content (basic titration) of the isolated fractions. This information could not be measured when gel separations were run on high pressure chromatographic columns using micro-styragel packings. The major finding of this study was that the average molecular weight of the original SRL was 200 mass units lower than the average calculated from the sum of the nine molecular weight fractions collected during the GPC separation. This could be due to (1) polymerization during separation (2) association of the more homogeneous, separated molecules or (3) insolubility of the high molecular weight fractions, giving a larger than expected molecular weight.

(c) Results

The desired separation was investigated using either Bio-Beads S-X8 or Sephadex LH-20 as the molecular-size separator and tetrahydrofuran (THF) or pyridine as the eluent solvent. Bio-Beads Series S is a series of neutral, porous stryene-divinyl benzene copolymer beads intended for the separation of lipophilic polymers and other solutes using organic solvents. Coleman et al.,have reported the use of this type of gel with SRC samples using THF as the eluent solvent.[1] The value, X8, indicates the degree of cross linkage of the polymer. In case of S-X8 gels the molecular weight exclusion limit is 1,000 gm/mole; Coleman et al., used S-X4 gels in their work which has an exclusion limit of 1,400 gm/mole. Sephadex G series is a bead-formed, dextran gel which is prepared by cross-linking selected dextran fractions with epichlorohydrin. Sephadex LH-20 is a hydroxypropylated derivative of Sephadex G-25 which swells in organic solvents as well as water. The original exclusion limit of G-25 was about 2500 gm/mole in water. The derivative has a slightly lower exclusion limit depending on the extent of swelling by the solvent. THF and pyridine swell the gels to nearly the same extent of about 2.5-3.0 cc/gm of gel. Bio-Beads S-X8 was obtained from Bio-Rad Labs(Richmond, CA) and Sephadex LH-20 was obtained from Pharmacia Chemicals (Piscataway, NJ).

The columns were packed with either a THF or pyridine slurry of the beads into glass columns (10mm X 80cm). The amount of gel packed was chosen to obtain a void volume of about 40-50ml and an elution volume of about 45ml. The column was then washed with 50 ml. of eluent solvent and kept under the solvent so that no air could be absorbed on the column to cause channeling. The samples of SRL were loaded and eluted in two different ways depending on the solvent used. In the case of pyridine it was possible to dissolve one gram of SRL into 5 ml volume. This mixture was then added to the column and eluted with pyridine. The collected fractions were dried under vacuum for weight distribution analysis. In the case of THF, SRL is not completely soluble in 5 ml, so that 40 ml of THF was used to dissolve and load the sample.

Since this loading volume was nearly equal to the column elution volume, a revised collection was used. Approximately 16 five-ml fractions were collected during the initial THF separation. The fractions were combined into sets of two; one and two were combined, three and four were combined, etc. Each combined set was then evaporated to five-ml volumes, passed through a second column and collected in nine 5-ml fractions. The same fraction number for each of the eight fraction sets was then combined so that all molecule weights of the same value were in a single fraction. The final nine fractions were then evaporated to dryness for weight distribution analysis.

Tables I-III summarize the results of three chromatographic separations of SRL, M-11A, for this task. Although more data is to be collected and analyzed in this task, the following conclusions or trends are noted:

1. Sephadex-LH-20 was unsatisfactory for gel permeation separations of SRL in THF. Approximately 30% of the SRL adsorbed on the column irreversibly: (a) Table I shows an elution volume greater than that of the theoretical value of 40 ml. (b) Table I shows a loss of acidity to the column. The reason is that the acid sites of SRL are undergoing adsorption on the column. This must not occur during a proper gel chromatographic separation.

2. Pyridine results in a slightly better total recovery than when THF is used with Bio-Beads SX4 gel.
3. Tables II and III show that both pyridine and THF gave similar separations by molecular weight. Approximately 35% of the SRL has a molecular weight of 1100 to 1800 gm/mole, 20% of the SRL has a value near 680 gm/mole and about 45% of the SRL has a value below 475 gm/mole.
4. The high molecular weight fractions are difficult to re-dissolve in pyridine or just to keep in solution after fractionation. This is consistent with either the low molecular weight fractions being needed to dissolve

the higher weights by association or that some polymerization occurs after separation of the fractions.

5. The average molecular weight measured for M-11A in DMF is 500 gm/mole (VPO). The number average molecular weight calculated from Table III is 780 gm/mole. Again this is indicative of the problem described in 4.

6. Except for fraction 3 the aromatic proton percentage increased as the molecular weight decreased as shown in Table II. Unfortunately, the two highest molecular weight fractions were not completely soluble so this trend cannot be validated.

7. If the aromatic content of the fractions were to increase with lower weights this should be noticeable with an increase in $E^{1\%}$ values. Table II shows overall that at 300 and 280 nm the value $E^{1\%}$ is increasing. However, we are plagued with solubility problems with fractions 2 and 3, which may explain the decrease in $E^{1\%}$. In general, however, there is little change in $E^{1\%}$ which would be consistent with average molecular structures containing the same types of aromatic group at the high and low molecular weights.

8. The acidity (meq./gm) of the SRL fractions reaches a maximum at 680 gm/mole as shown on Table III. A better way to look at this property is that the number of acid sites per molecule is near 1.7 until the molecular weight drops below some middle value (∿ 600 gm/mole) at which point the acid content per molecule drops off rapidly.

9. Nmr data on Table II shows that the fraction of alpha aliphatic hydrogens (H_α) (those aliphatic carbons next to aromatic carbons) increased while the Ho (all other aliphatic hydrogens) decreased as the molecular weight decreased. This is consistent with average structures which tend to have only methyl substitution on the aromatic rings at the low molecular

weights. The increased aliphatic proton content at the high molecular weights do not necessarily mean there is a larger fraction of aliphatic carbons. This also is dependent on the degree of substitution on the aromatic rings. For example, hexamethylbenzene would show no aromatic protons, yet there would be an equal amount of aromatic and aliphatic carbons.

(c) Work Forecast

The gel permeation chromatographic separations will be continued during the next quarter in order to determine if the method will be useful in characterization of the structure of SRL and SRC. The inability of the number average molecular weight to match up with the overall molecular weight as measured by VPO will be studied to determine the reason for this phenomenon.

Table I Gel Permeation Separation of SRL (M-11A) on Sephadex LH-20 Gel with THF as Solvent

				$E^{1\%}_{1cm.}$	
Fraction 5 ml	Wt. mgs.	Meq Acid/gm[a]	Mole. Wt. gm/mole	400 nm	350 nm
1	2.15	2.79	—	—	—
2	32.5	1.88	—	—	—
3	5.4	13.5	—	—	—
4	42.85	1.42	1150± 30	284	503
5	89.59	1.03	610± 90	205	438
6	174.78	0.870	450± 50	159	368
7	147.08	0.748	380± 30	145	303
8	135.09	0.674	407± 2	123	272
9	33.22	1.60	400± 10	166	340
10	23.87	2.68	—	—	—
11	8.54	4.33	—	—	—
Total	695[b]				

(a) A total of 0.854 meq acid collected out of a possible 1.45 meq; 60% recovery.

(b) One gram of SRL added to column, initially.

Table II Gel Permeation Separation of SRL(M-11A) on Bio Beads S-X8 using THF as the Solvent

			$E_{1cm}^{1\%}$							
Fraction 5 ml	Wt. mgs	Mole Wt. gm/mole	400 nm	350 nm	300 nm	280 nm	$\frac{H(aromatic)}{H(total)}$	H_α/H_t	H_o/H_t	H_o/H_α
1	28.36	—	—	—	—	—	—	—	—	—
2	166.22	1619	211	327	451	489	b	b	b	—
3	172.79	1342	238	397	591	660	0.639[b]	0.194	0.165	0.85
4	167.23	673	205	412	706	807	0.589	0.277	0.135	0.48
5	154.68	475	194	395	684	783	0.607	0.292	0.102	0.35
6	125.40	489	194	361	647	901	0.683	0.250	0.068	0.27
7	95.44	—	—	—	—	—	—	—	—	—
8	32.31	—	—	—	—	—	—	—	—	—
9	6.51	—	—	—	—	—	—	—	—	—
Total	948.9[a]									

(a) Original wt. 1190 mg; recovery 85%.

(b) Material was only partially soluble in d-pyridine. Not enough sample was soluble to obtain an nmr for fraction.
2. Fraction 3 gave an nmr signal, but only 60% of the sample would dissolve.

Table III Gel Permeation Separation of SRL(M-11A) on Bio Beads S-X8 Gel using Pyridine as the Solvent

Fraction	Wt. gm	Mole wt. gm/mole	Meq acid/gm[a]	Acid sites per molecule
1	123.8	1855 ± 35	0.9 ± 0.2	1.76
2	164.9	1124 ± 48	1.65 ± .05	1.90
3	179.3	683 ± 12	2.05 ± .05	1.40
4	140.1	421 ± 11	1.35 ± .15	0.57
5	107.5	344 ± 13	0.6 ± 0.1	0.21
6	89.6	341 ± 7	0.24 ± 0.07	0.08
7	73.4	295 ± 6	——	
8	23.1	——	——	
9	0.6	——	——	
Total	902[b]			

a. Total acid added to column = 0.945 meq (corrected for 90% recovery), recovery 0.951, 0.795 meq for two different separations. In both separations maximum acid content occurred at 683 mole wt. fraction.

b. One gram of SRL loaded on the column.

B. SRL and SRC Comparison Studies

(a) To compare SRL and SRC as to their structural and chemical differences.

(b) Summary and Results

We have concluded our comparison of SRL with SRC's from bituminous coals, based on gross properties of the materials. This paper was reported at the Chicago ACS meeting in August. A preprint of our paper to be submitted to "Fuel" is included in this section.

Comparison of Solvent Refined Lignite With Solvent Refined Bituminous Coals

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Abstract

Comparison of laboratory deashed samples of solvent refined lignite, subbituminous and bituminous coals on the basis of gross combustion analysis, acid and basic titers, molecular weight, nuclear magnetic resonance, ultraviolet and electron spin resonance spectra including various derived parameters indicated that there is relatively little difference between the range of values for lignite and bituminous coal derived solvent refined products. The probability that coal nitrogen content is reflected in the solvent refined product was noted.

Solvent refining of coals has a promising future for the preparation of clean burning fuels.[1] Solvent refining has advanced to the pilot plant scale for bituminous and subbituminous coals.[2] Lignite has also more recently been solvent refined on a 23 kg/hr process development unit.[3]

Solvent refining, in general, involves treating finely ground coal with hydrogen and a hydrogen transfer solvent (coal derived) at elevated temperature and pressure (typically 400^{o} and 207 MPa). For lignite, with its inherent water content, a 1:1 gas ratio of $CO:H_2$ with the solvent is advantageous.[4] In either case, the coal is solublized in the solvent, apparently by reductive depolymerization although evidence is being accumulated that supports hydrogen rearrangement and partial aromatization during this process also.[5]

Our interest in solvent refined lignite (SRL), stemming from our close association with the process development unit producing SRL,[3] has led to a detailed comparison of SRL with other solvent refined coals (SRC), both bituminous and subbituminous, in order to ascertain if there is any significant difference between SRL and SRC's. If SRL and SRC are essentially the same, the technology for further hydrotreating of SRC could be used without modification on SRL. If SRL and SRC are different, further investigation of second stage hydrotreating would be in order.

The samples used in this study are summarized in Table 1.[6] Note that as received, only three samples were maf, i.e., M11A (SRL), Amax and Tacoma II (both SRC's). Of five other samples obtained all contained unreacted coal and ash. Because the latter samples gave inconsistent oxygen analyses when determined by difference from combustion analysis and by neutron activation analysis, Table 2, no accurate comparison could be made with samples containing ash. Thus, a standard deashing procedure was developed to obtain the pyridine soluble portion of all eight samples, cf. Experimental. Hence, material soluble in pyridine which passed through a 5 μ filter was defined as solvent refined product for all eight samples. Table 2 summarized initial ash content, the amount of material remaining in the Soxhlet extraction thimble and that removed by 5 μ filtration. The variable amounts of material going through the Soxhlet filter from sample to sample make the 5 μ filtration imperative if accurate comparisons are to be made. The maf samples were over 94% soluble in pyridine. The procedure to remove pyridine (cf. Experimental) was checked by nmr spectroscopy of the resulting SRL or SRC in hexamethyl phosphoramide and, in a few cases, by mass spectroscopy. Less than 0.5% of pyridine could have been detected but none was found.

The maf samples were carried through the deashing procedure in order to check for changes during deashing, cf. Table 3. The changes were not large. The molecular weight increase for Tacoma II may not be significant because the precision limit on the molecular weight determination before deashing (a commercial, one point analysis) was quite large (±40). Table 4 shows molecular weights and acidic and basic titer data for all the deashed samples. A summary of the combustion analysis data of deashed samples is given in Table 5. The oxygen reported was determined by neutron activation analysis and in all but one case (M5C) the sum of the composite elements is within 1.5% of 100%. This precision is reasonable for this type of material. There were some small changes in nmr spectra of the maf samples during deashing, but the aromatic to aliphatic ratios remained relatively constant.

The changes in the maf samples during deashing are within the range of values found for SRL's and SRC's examined. Hence, these changes, even if systematic, allow a meaningful comparison of the samples.

Using the raw data of Tables 3, 4 and 5, the average molecular compositions of the eight SRL's and SRC's were calculated, cf. Table 6. The range of compositions (atoms per average molecule) for carbon, hydrogen, oxygen and sulfur are the same for SRL's and SRC's. While the range of the percentage of nitrogen overlap for SRL's and SRC's, the number of nitrogen atoms per average molecule run higher for SRC's than for SRL's. The basic and acidic titers per average molecule are summarized in Table 7, which show that the range of basicity is higher for SRC's than for SRL's. The ratio of basic to nonbasic nitrogen of approximately one, however, is the same for SRL's and SRC's.

A similar relationship for the acidity and oxygen content does not hold directly because the conditions for nonaqueous acid titration have been shown to titrate carbazole N-H as well as phenol.[7] The lack of carbonyl in the ir and carbon-13 nmr spectra indicate that acidic carboxyl oxygen is absent. By assuming all nonbasic nitrogen is carbazole like (and thus titratable), the acidic SRL oxygen is calculated to be 57% and SRC, 52%. These values are the same within the precision of the measurements and considering the assumptions made. Thus, it appears the ratio of acidic to total oxygen is the same for SRL and SRC. Furthermore, the total amount of oxygen in each is essentially the same for SRL and SRC despite the great variation of oxygen in starting coal (see below).

In Table 8, the electron spin resonance data of the SRL's and SRC's are shown to be virtually the same. The range of g values is very narrow. Further, the range of line widths, ΔH, for SRL's and SRC's is consistent with the relationship derived for vitrain coals between ΔH and the percentage of hydrogen in the vitrain coal.[8] The uniformity of ΔH simply reflects the similarity of the amounts of hydrogen in the SRL and SRC samples. Additionally, the concentration of radicals in both SRL and SRC samples are quite similar.

Table 9 shows a summary of values calculated by a Brown and Ladner analysis of the proton nmr data.[9] It should be noted here that carbon-13 nmr of some samples gave the same f_a value as that found by proton analysis. This does not necessarily validate the assumptions made in the Brown and Ladner approach because the precision errors of pulsed carbon-13 nmr can be fairly high when a strongly absorbing solvent e.g., d_5-pyridine or dioxane, is used. Note that for all values calculated, the ranges for SRL's and SRC's have significant overlap such that little distinction between the samples can be made on this basis.

The ultraviolet spectra between 270 and 400 nm of three samples are reproduced in values of $E^{1\%}$ in Figure 1. Note the featureless nature and the quantitative similarity of the spectra. The uv spectra of the other five samples lie within the range of those shown. Detailed mathematical analyses.

indicate that within 5% precision limits, these spectra are indistinguishable. The reduced fractions J-1-11-87 and COSteam are given in Table 9 and Figure 1 to compare with SRL's and SRC's.

The molecular weight data shown in Table 4 indicates the possible tendency of SRC's to be slightly higher in molecular weight (except for one sample) than SRL's. Whether further comparisons will bear this out or not must be determined.

Summary

Comparison of the SRL's and SRC's herein described indicates little difference between the samples. The range of properties within the SRL samples and within the SRC samples in general is greater than the difference between SRL's and SRC's. Thus, the properties observed seem to be more a function of reaction and treatment conditions than of starting coal.

The possibility that SRC's may have higher molecular weights than SRL's has been observed. Perhaps the largest possible distinguishing factor between SRL's and SRC's, however, is in the nitrogen content. The wide variation of starting coal composition for these samples is shown in Table 10. Note the rather smooth increase in nitrogen content from lignite, to subbituminous, to bituminous coal. Compare this trend to the average nitrogen content of the derived SRL and SRC's, _cf._ Table 5. There seems to be a relationship between starting coal nitrogen content and solvent refined product nitrogen content. This might be of some interest for further hydrotreating of these materials.

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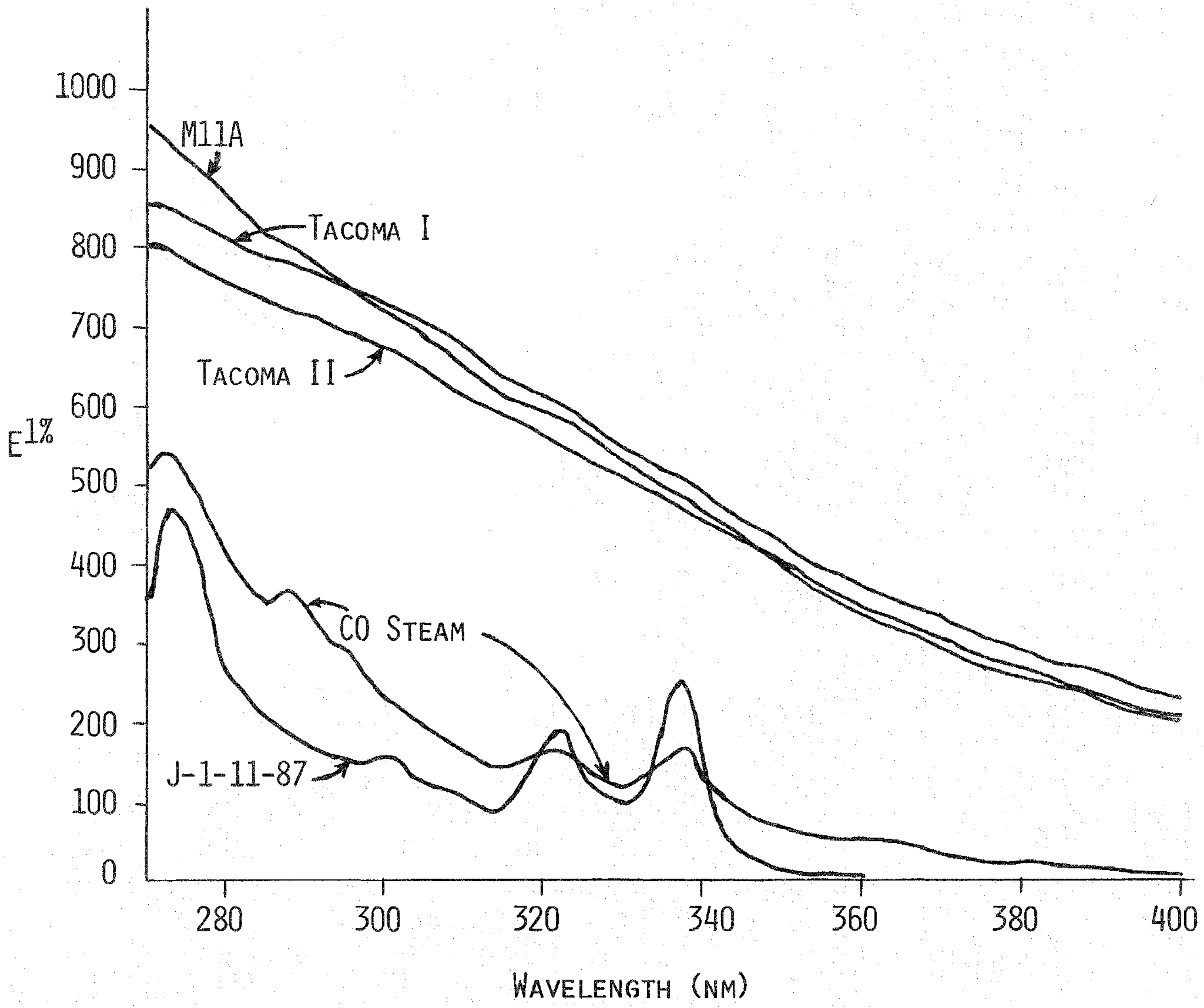


Figure 1 Comparison of the ultraviolet spectra of SRL (M11A), SRC's (Tacoma I and II) and reduction products (J-1-11-87 and COSteam).

TABLE 1 COMPARISON OF PERCENTAGE OXYGEN BY DIFFERENCE TO NEUTRON ACTIVATION ANALYSIS

SAMPLE	ASH, %	OXYGEN, % DIFFERENCE	OXYGEN, % NEUTRON ACTIVATION
SRL			
M5C	9.56	3.88	7.31
M11A (MAF)	0	2.92	2.35
M13A	8.00	2.91	5.37
M21A	8.92	7.04	5.57
SRC			
AMAX (MAF)	0.21	12.36	3.37
TACOMA II (MAF)	0.27	3.81	3.22
TACOMA I	19.1	10.7	6.53
WILLSONVILLE	16.5	8.49	7.71

Table 2 Summary of Results Using the Standard Deashing Procedure

Sample	Initial ash,%	Material remaining in thimble,%	Material remaining on filter,%	Material dissolved,%
SRI				
M5C	9.56	12.52	3.17	84.31
M11A(maf)	0	2.93	0.27	96.80
M13A	8.00	20.84	1.60	77.56
M21A	8.92	26.11	5.88	68.01
SRC				
Amax(maf)	0.21	4.79	1.10	94.11
Tacoma II(maf)	0.27	4.53	0.09	95.38
Tacoma I	19.1	29.22	1.17	69.61
Wilsonville	16.5	29.50	11.18	59.32

TABLE 3 PROPERTY CHANGES OF THREE SAMPLES USING THE STANDARD DEASHING PROCEDURE

	M11A	AMAX	TACOMA II
ACID TITER (MEQ/G)			
BEFORE	1.58	2.22	1.63
AFTER	1.40	2.06	2.07
BASIC TITER (MEQ/G)			
BEFORE	0.30	0.55	0.84
AFTER	0.29	0.69	0.94
MOLECULAR WEIGHT			
BEFORE	450	597	495
AFTER	497	585	590
NMR AROMATIC/ALIPHATIC			
BEFORE	1.07	1.00	0.826
AFTER	1.32	1.11	0.897

Table 4 Properties of Samples Deashed by the Standard Deashing Procedure

SRL	MW	Acid titer, meq/g	Basic titer, meq/g
M5C	581	2.18	0.61
M11A	497	1.40	0.29
M13A	513	1.80	0.32
M21A	463	1.73	0.30
SRC			
Amax	585	2.06	0.69
Tacoma II	590	2.07	0.94
Tacoma I	660	1.42	0.68
Wilsonville	460	1.91	0.47

TABLE 5 ELEMENTAL ANALYSIS OF THE STANDARD DEASHED SAMPLES

SAMPLE	%C	H	N	S	O	TOTAL
SRL						
M5C	85.61	5.44	1.42	0.80	5.00	98.27
M11A	89.19	5.08	1.14	1.42	2.85	99.68
M13A	88.56	5.60	0.96	1.42	4.07	100.61
M21A	87.19	5.91	0.76	1.24	3.59	98.69
SRC						
AMAX	87.23	5.42	1.93	0	3.89	98.47
TACOMA II	87.15	5.56	2.24	1.71	3.42	100.08
TACOMA I	87.71	5.62	2.25	0.77	2.47	98.82
WILSONVILLE	87.32	5.31	1.62	1.16	3.69	99.10

TABLE 6 AVERAGE MOLECULAR FORMULA OF THE STANDARD DEASHED SAMPLES

SAMPLE	C	H	N	S	O
SRL					
M5C	41.4	31.4	0.59	0.15	1.82
M11A	36.9	25.0	0.40	0.22	0.89
M13A	37.8	28.5	0.35	0.23	1.30
M21A	33.6	27.1	0.25	0.18	1.04
SRC					
AMAX	42.5	31.5	0.81	0	1.42
TACOMA II	42.8	32.5	0.94	0.31	1.26
TACOMA I	48.2	36.8	1.06	0.16	1.02
WILSONVILLE	33.4	24.2	0.53	0.17	1.06
J-1-11-87	16.6	19.7	--	--	--

TABLE 7 ACID AND BASE PROPERTIES OF THE STANDARD DEASHED SAMPLES

SAMPLE	ACID (EQ/MOLE)	BASE (EQ/MOLE)
SRL		
M5C	1.27	0.35
M11A	0.70	0.14
M13A	0.92	0.16
M21A	0.80	0.14
SRC		
AMAX	1.21	0.40
TACOMA II	1.22	0.55
TACOMA I	0.94	0.45
WILSONVILLE	0.88	0.22

Table 8 Electron Spin Resonance Data on the Standard Deashed Samples

Sample	G-value		ΔH		Radical concentration, spins/g X 10^{-18}
SRL	20°C	-196°C	20°C	-196°C	
M5C	2.0027	2.0028	5.6	6.2	2.8
M11A	2.0029	2.0030	6.3	6.7	1.2
M13A	2.0028	2.0030	6.2	6.6	1.7
M21A	2.0028	2.0029	5.7	7.0	1.9
SRC					
Amax	2.0027	2.0030	5.6	6.3	1.9
Tacoma II	2.0028	2.0028	6.7	7.0	2.7
Tacoma I	2.0028	2.0030	6.7	6.1	1.6
Wilsonville	2.0030	2.0030	6.2	6.3	1.8

Table 9 Proton NMR Data on the Standard Deashed Samples

Sample	Haro/Halip	Fa	σ	Hara/Car	C_L	Ra	Car	Haru
SRL								
M5C	0.713	0.779	0.339	0.611	1.60	7.28	32.2	19.7
M11A	1.32	0.854	0.284	0.662	1.38	6.33	31.5	20.9
M13A	0.945	0.806	0.337	0.684	1.41	5.82	30.4	20.8
M21A	0.819	0.778	0.363	0.733	1.49	4.49	26.1	19.1
SRC								
Amax	1.11	0.833	0.296	0.693	1.54	6.43	35.4	24.5
Tacoma II	0.897	0.797	0.368	0.722	1.45	5.68	33.7	24.3
Tacoma I	1.18	0.825	0.300	0.716	1.40	6.65	39.7	28.4
Wilsonville	1.18	0.834	0.230	0.610	1.41	6.44	27.9	17.0
J-1-11-87	0.349	0.565	0.316	0.785	3.13	2.01	9.41	7.38
CO Steam	0.511	0.634	0.283	0.822	2.56	--		

TABLE 10 ULTIMATE ANALYSIS* OF STARTING COALS [2,3]

	%C	H	N	S	ASH.	O(DIFF)
LIGNITE (DRY)	67.46	4.26	0.96	0.64	8.36	18.32
SUB BITUMINOUS	67.95	4.94	1.06	0.62	7.77	17.65
BITUMINOUS	72.69	4.97	1.67	3.09	9.21	8.37

* Moisture free samples

Experimental

Analysis were preformed by Spang Micro-analytical Laboratory and Chemanalytics. Commercial molecular weights were by single point VPO determination in DMF by Spang Microanalytical Laboratories. Neutron activation analyses for oxygen were performed by InterconTelRad of San Diego. Ultraviolet spectra were determined on a Cary-Model 14 spectrometer in dimethyl acetamide solvent and reported as $E^{1\%}$.

The deashing procedure was carried out by Soxhlet extraction with pyridine followed by filtration through a 5 µ Teflon filter (Milipore Corp., Bedford Mass.) and vacuum drying as previously described.[12]

Pmr were measured on a Varian EM 390 nmr spectrometer. Samples were dissolved in d_5-pyridine containing a calibrated amount of octamethylcyclotetrasiloxane as standard. Correction for pyridine was based on a standard vs. residual pyridine integration. Generally six integrations at three different Rf powers were run and averaged. Analysis of the data was carried out via the Brown and Ladner procedure.[9, 11] Molecular weights were determined with a Wescan VPO in DMF at 73°. Three different concentrations were extrapolated to infinite delution. Little association in this solvent was noted.

Titrations were carried out as previously described.[11]

EPR Techniques. Spectra were recorded on a Bruker ER-420 EPR Spectrometer operating in the X-band microwave region. The ER-400-X-DR double cavity was used in this study. The g-valves were determined by direct comparison with aqueous potassium peroxylamine disulfonate (g-value of 2.0055). The frequency was determined to three significant figures from the frequency dial on the microwave bridge. The low temperature g-values were determined using a quartz liquid nitrogen dewar (Scanlon Co., S-816), after correcting for the slight differences in field experienced by the two cavities.

The g-values were calculated by standard procedures.[13]

The estimated uncertainty in the g-values is ± 0.0001. Radical concentrations at room temperature were determined relative to 1,1-diphenyl-2-picrylhydrazl, DPPH,[14] a 5 mg sample of *ca*. 0.6% by weight in KCl being used. The area under the first derivative curves was estimated by a numerical double integration.[15] The power was kept below 2mW to avoid saturation. The sample and standard were interchanged in the cavity to correct for possible differences in sample position. The samples were prepared as follows: For g-value and linewidth determinations the SRL or SRC samples, *ca*. 4% by weight, were ground in KCl. For the radical concentration experiments the sample content was increased to *ca*. 10% and only *ca*. 20 mg of the sample was used. All samples were degassed (*ca*. 0.7 - 0.07 Pa, 1 hr) in quartz epr tubes before sealing.

References

1. P. C. White and M. B. Neuworth, "Coal Liquefaction", Quarterly Report, October-December, 1976, Energy Research and Development Administration, Washington, D.C. 20545; pg. 1-2.

2. Two such operations are (1) a bituminous coal solvent refining PDU at Fort Lewis, WA operated by Pittsburgh and Midway Coal Co. and (2) a solvent refining PDU at Wilsonville, AL operated by Catalytic, Inc.

3. Operated by Project Lignite of the University of North Dakota, Grand Forks, ND.

4. D. Jones, R. J. Baltisberger, K. J. Klabunde, N. F. Woolsey and V. I. Stenberg, *J. Org. Chem.*, in press; H. R. Apell, I. Wender and R. D. Miller, Div. Fuel Chemistry Preprints, *Am. Chem. Soc.* **13** (4), 39-44 (1969).

5. M. Farcasiu, T. O. Mitchell and D. D. Whitehurst, "Preprints of the 1976 Coal Chemistry Workshop" at Stanford Research Institute, Menlo Park, CA 94025, pg. 101-124.

6. The samples were obtained as follows: M5C (undeashed) prepared by the University of North Dakota Engineering Department under Project Lignite, from North Dakota lignite. Conditions: 2500 psi of 1:1 $CO:H_2$ at 455°C (max). M11-A (deashed) as for M5C except 479°C (max). M13A-(partly deashed) as for M5C. M21A-(undeashed) as for M5C except at 2000 psi of 1:3 $CO:H_2$ at 439°C (max). Tacoma I (undeashed) prepared by Pittsburgh and Midway Coal Co. in their Fort Lewis PDU from a blend of Kentucky no. 9 and no. 14 bituminous coals from the Colonial Mine. Conditions: 1500 psi of hydrogen (85% minimum at 450°C (maximum) using recycle solvent; product not filtered and stored in the open. Tacoma II (deashed) as for Tacoma I except the product was filtered before the solvent was distilled and was stored in closed container. Amax (deashed) Catalytic Inc., Wilsonville, Alabama from Amax subbituminous coal from the Bel Ayr Mine in Wyoming. Conditions: 2500 psi of H_2 and recycle gases at 460° (max) using recycle solvent heavy in phenols and 1,2 and 3 ring aromatics. Wilsonville (undeashed) as for Amax except not filtered. J-1-11-87, a hydrocracking fraction from an SRL. Conditions:[10] batch autoclave, 4500 psi (max) of H_2 at 450° for 2 hr. using presulfided HT-100 (Ni-Mo) catalyst. Bp 110-180°C (0.4 mm) followed by removal of solid which precipitated on standing in freezer for *ca.* one month. COSteam Pittsburgh Energy Research Center (an ERDA Laboratory). North Dakota lignite treated in a tubular reactor with synthesis gas under COSteam conditions (4000 psi of $CO:H_2$). The whole product was chromatographed on alumina. This fraction was eluted with toluene (aromatics fraction).

7. Private communication from B. Farnum of the Grand Forks Energy Research Center. We have confirmed this result under the conditions for our titration.

8. H. L. Retcofsky, G. P. Thompson, R. Raymond and R. A. Friedel, *Fuel*, **54**, 126 (1975).

9. J. K. Brown and W. R. Ladner, *Fuel*, **39**, 87 (1960); *cf.* G. A. Haley, *Anal. Chem.*, **43**, 371 (1971) and D. R. Clutter, L. Petrakis, R. L. Stenger, Jr. and R. K. Jensen, *ibid.*, **44**, 1395 (1972).

10. *cf.* J. Y. F. Low, K. J. Klabunde, N. F. Woolsey, R. J. Baltisberger, M. Govek and V. I. Stenberg, *Energy Sources*, **3**, 19 (1976).

11. N. F. Woolsey, R. Baltisberger, K. Klabunde, V. Stenberg and R. Kaba, *Am. Chem. Soc.*, Fuel Division Preprints, **21** (7), 33 (1976).

12. R. J. Baltisberger, K. J. Klabunde, V. I. Stenberg and N. F. Woolsey, *ibid.*, **22** (5), 84 (1977).

13. *e.g.*, P. B. Asyscough, "Electron Spin Resonance in Chemistry," London: Methuen and Co. Ltd., 1967, Chapter 5.

14. J. E. Wertz and J. B. Bolton, "Electron Spin Resonance: Elementary Theory and Practical Applications," New York: McGraw-Hill, 1972, p. 462-464.

15. Ref. 13; Appendix 5.

(c) Work Forecast

Further testing of solvents for C-13 nmr will be conducted. s-Triazene which has shown some promise already, and pentofluoro pyridine, in particular, will be tested.

Application of a silylation procedure developed at PERC to SRL and SRC samples for the determination of acidic hydroxyl groups will be carried out to compare results with the titrametric procedure.

Preliminary testing of our uv analytical computer program is nearing completion and some results should be available by the end of the next quarter.

Task II

(a) Objective

This task is intended to elucidate what catalysts and reaction conditions are optimum for hydrotreating of SRL to yield high quality liquid fuels. Also, product studies will yield information as to how the various catalysts function and what the original SRL was like chemically and structurally.

(b) This task is complete as described in the last quarterly report except for one final study. That study involves the detailed GC-MS-Computer studies to obtain type analyses, compound types, and structural information about a series of liquid products from our catalytic SRL hydrotreating work.

The planned analyses have not yet been carried out due to major personnel changes involving both our project and our collaborators at the Grand Forks Energy Research Center. The planned analyses will probably be carried out during the next reporting period.

Task III

1. The Reduction of Model Compounds Under the COSTEAM Conditions

(a) Objectives

To understand both the function of the hydrogen donor solvent and the role of mineral matter in lignite during the formation of solvent refined lignite using and comparing the reducing gas mixtures H_2; H_2, $CO-H_2O$ and $CO-H_2O$.

(b) Introduction

A mixture of carbon monoxide, hydrogen and water is regarded to be superior to either carbon monoxide-water or hydrogen as reducing gases for the liquefaction of lignites.[1-4] The role of carbon monoxide as a reducing agent for coal and lignite reduction is not well defined. In contrast, a considerable volume of literature and knowledge is available on the subjects of converting carbon monoxide into methane, methanol and hydrocarbons and on the water gas reaction.

It is known that a combination of bases and carbon monoxide is effective in the reduction of aromatic carbonyl compounds, and this is likely to proceed through the formate ion. The reduction of other compounds with carbon monoxide is ill-defined both in terms of products as well as mechanism.

Reactions 1-8 are known or postulated pertinent reactions regarding carbon monoxide chemistry. The reactions are as follows:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (1)$$

$$2CO \rightarrow C + CO_2 \qquad (2)$$

$$Na_2CO_3 + H_2O \rightleftharpoons NaOH + NaHCO_3 \qquad (3)$$

$$NaOH + CO \xrightarrow[100\ psi]{120-150^{o},} NaOCOH \qquad (4)$$

$$2NaOCOH \xrightarrow{360^{o},\ base} Na_2C_2O_4 + H_2 \qquad (5)$$

$$HCO_2H \rightarrow H_2 + CO_2 \qquad (6)$$

$$HCO_2H \rightarrow H_2O + CO \qquad (7)$$

$$2HCO_2H \rightarrow CH_2O + H_2O + CO \qquad (8)$$

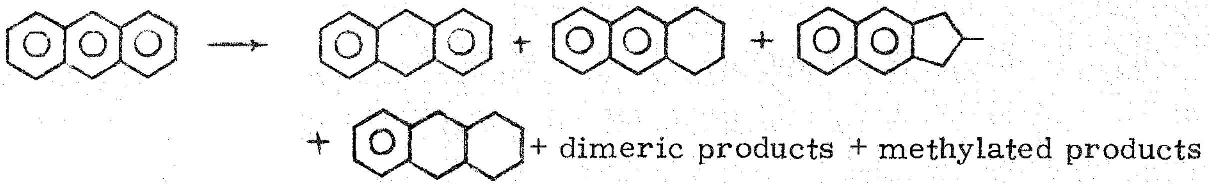
We have previously determined that phenol, diphenylether and diphenylmethane are converted into reaction products via the reducing gases H_2; H_2, $CO-H_2O$ and $CO-H_2O$ in low yields in batch autoclave experiments. The conditions are two hours at reaction temperature of 425°C and pressure of ca. 4000 psi. This quarter, ethylbenzene and carbazole are added to this "inactive" list.

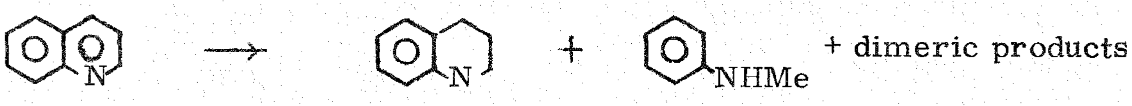
Earlier results have shown that 1,2-diphenylethane, benzophenone, benzhydrol, anthracene and quinoline are reactive. The products, which are condition dependent, are as follows:

$$PhCH_2CH_2Ph \rightarrow PhCH_3 + PhH + PhC_2H_5 + PhCH{=}CHPh + Ph_2CHCH_3^{*}$$

$$Ph_2CO \rightarrow Ph_2CHOH + Ph_2CH_2 + PhCH_3 + PhH$$

$$Ph_2CHOH \rightarrow Ph_2CH_2 + Ph_2CO + PhCH_3 + PhH$$





+ methylated products + other alkylated anilines

* Recently identified.

(c) Results

In Table 1, data is presented which shows that for this list of model compounds H_2 is sometimes superior to CO-H_2O (quinoline), while for Ph_2CO and Ph_2CHOH the reverse is true. For bibenzyl and phenanthrene, there is no difference. Added sodium carbonate and iron compounds range from no effect to a positive effect. For $PhCH_2CH_2Ph$, Ph_2CO and quinoline, the presence of tetralin has no effect on product conversions.

Table 2 summarized the data on thioanisole reductions. The principal conclusions are:

1. the products are benzene, toluene and diphenylsulfide,
2. hydrogen gas is more effective than carbon monoxide-water, cf. runs 1, 2 and 3,
3. sodium carbonate uniformly reduces conversion for the hydrogen reductions, cf. runs 4 and 1, has no effect on the carbon monoxide-water reductions, cf. runs 6 and 3,
4. ferrous sulfide aids the carbon monoxide-water reductions, cf. runs 7 and 2, and retards the hydrogen reduction, cf. runs 8 and 3,
5. the hydrogen donor solvent, tetralin, reduces the conversion, cf. runs 9 and 6,
6. the reactions are thermal in part, cf. run 10 and one thermal process produces toluene and diphenylsulfide and
7. carbon monoxide reduces conversions and increases the toluene yields, cf. 11.

In Table 3, the final results on the reduction of diphenylsulfide are summarized. The principal conclusions are:

1. $H_2 \overset{\sim}{=} H_2, CO\text{-}H_2O > CO\text{-}H_2O$ for the reduction, *cf.* runs 4,5 and 6,
2. sodium carbonate retards the reduction, *cf.* runs 1,2 and 3 with 4,5 and 6,
3. ferrous sulfide further retards the reduction, *cf.* run 8 with runs 3 and 6, and
4. the hydrogen donor solvent, tetralin, also seriously retards the reduction, *cf.* runs 9 and 3.

Ethylbenzene and carbazole are essentially inert to the reduction conditions. Ethylbenzene was converted to 0.4% yield of benzene together with a trace of toluene by the reducing gases, carbon monoxide and water over sodium carbonate during the 425°C, 2 hour reaction. Similarly carbazole is essentially inert to the same conditions using carbon monoxide, water and hydrogen over sodium carbonate.

(d) Experimentation

The reductions of the model compounds were done using the reactors, conditions and work-up described in Quarterly Report 3.

(e) Work Forecast

The results on n-decylalcohol and phenylbenzylether will be completed and 1,2-diphenylethane will be used to survey a series of metal oxides related to minerals present in lignite, in addition to three lignite fly ash samples.

References:

1. Appell, H. R. and I. Wender, The Hydrogenation of Coal with Carbon Monoxide and Water, Div. Fuel Chem. Preprints, *Am. Chem. Soc.*, V. 12, No. 3, 1968, pp. 220-222.
2. Appell, H. R., I. Wender, and R. D. Miller, Dissimilar Behavior of Carbon Monoxide Plus Water and of Hydrogen in Hydrogenation. Div. Fuel Chem. Preprints, *Am. Chem. Soc.*, V. 13, No. 4, 1969, pp. 39-44.
3. Appell, H. R., I. Wender, and R. D. Miller, Solubilization of Low Rank Coal with Carbon Monoxide and Water, *Chem. and Ind.* (London), No. 47, Nov. 22, 1969, p. 1703.
4. H. R. Appell, private communication.

Table 1. Brief Summary of Batch Autoclave Studies of Model Compounds

	Reducing gas effectiveness for conversion	Catalytic effect Na_2CO_3	$CO-H_2O$ catalytic effect of FeS	$CO-H_2O$, catalytic effect of Fe_2O_3	Effect of tetralin
$PhCH_2CH_2Ph$	$CO-H_2O \cong H_2, CO-H_2O \cong H_2$	no effect	no effect	unavailable	no effect on conversions, conv. to naphthalene
Ph_2CO	$CO-H_2O, H_2 > CO-H_2O > H_2$	+	unavailable	+	no effect
Ph_2CHOH	$CO-H_2O \cong CO-H_2O, H_2 > H_2$	-- all give 100% conversion --------------------			unavailable
Anthracene	$H_2 \cong H_2, CO-H_2O \cong CO-H_2O$	none	unavailable	unavailable	unavailable
Quinoline	$H_2 > H_2, CO-H_2O > CO-H_2O$	+	unavailable	+	no effect
Thioanisole	$H_2 \cong H_2, CO-H_2O > CO-H_2O$	-	+	unavailable	-
Diphenylsulfide	$H_2 \cong H_2, CO-H_2O > CO-H_2O$	-	-	unavailable	-

Table 2. Reduction of Thioanisole[1]

Run	Reducing gases[2]	Solvent	Catalyst[3]	Benzene, %[4]	Toluene, %[4]	Diphenyl sulfide, %[4]	Thiophenol, %[4]	Unknown, %[4]	Conversion, %[5]
1	H_2, H_2O	None	None	84.1	1.1	0.	0.0	0.0	85.2
2	CO, H_2O	None	None	5.1	9.7	10.7	0.6	6.6	32.7
3	H_2, CO, H_2O	None	None	80.9	5.6	0.8	0.0	0.6	87.9
4	H_2, H_2O	None	Na_2CO_3	37.7	4.8	1.4	0.0	0.0	43.9
5	CO, H_2O	None	Na_2CO_3	16.1	8.3	6.5	0.0	0.0	30.9
6	H_2, CO, H_2O	None	Na_2CO_3	14.7	8.7	3.2	0.0	0.0	26.6
7	CO,H_2O	None	FeS	15.6	7.9	9.3	0.0	14.3	47.1
8	H_2, CO, H_2O	None	FeS	32.7	8.0	4.5	8.5	8.1	61.8
9	H_2, CO, H_2O	Tetralin	Na_2CO_3	9.3	0.9	1.2	0.0	0.0	11.4
10	Ar, H_2O	None	None	4.4	29.5	38.2	1.4	7.2	80.7
11	CO	None	None	2.7	44.8	15.8	0.0	—	63.3

1. 0.15 mole.
2. Each gas is at 750 psi initial pressure except when hydrogen and carbon monoxide are used simultaneously; then each is at 375 psi initial pressure. Argon is added to bring the total pressure to 1500 psi.
3. 0.015 mole.
4. Normalized to converted starting material.
5. Based on recovered starting material.

Table 3. Reduction of Diphenyl sulfide[1]

Run	Reducing gases[2]	Solvent	Catalyst[3]	Benzene, %[4]	Toluene, %[4]	Thiophenol, %[4]	Unknown, %[4]	Conversion, %[5]
1	$CO-H_2O$	None	Na_2CO_3	41.8	1.3	1.1	0.0	44.3
2	H_2	None	Na_2CO_3	50.9	0.0	0.0	0.0	50.9
3	$CO-H_2O, H_2$	None	Na_2CO_3	40.7	0.4	0.5	0.0	41.5
4	$CO-H_2O$	None	None	31.9	2.3	3.4	22.7	60.2
5	H_2	None	None	100.0	0.0	0.0	0.0	100.0
6	$CO-H_2O, H_2$	None	None	96.7	3.4	0.0	0.0	100.0
7	None	None	FeS	2.7	0.0	0.0	0.0	2.3
8	$CO-H_2O, H_2$	None	FeS	61.4	3.0	0.0	11.5	24.2
9	$CO-H_2O, H_2$	Tetralin	Na_2CO_3	17.7	0.4	0.0	0.0	18.1

1. 0.15 mole.
2. Each gas is at 750 psi initial pressure except when hydrogen and carbon monoxide are used simultaneously; then each is at 375 psi initial pressure. Argon is added to bring the total pressure to 1500 psi.
3. 0.015 mole.
4. Normalized to converted starting material.
5. Based on recovered starting material.

Task IV

1. Mechanism of the CO Reducing System

(a) Objective

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

(b) Introduction

This task deals with the 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 liquefaction processes. Since the $CO-H_2O$ system is very effective in the 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 oxides.

In previous Quarterly Reports we have reported that well degassed surfaces of MgO, CaO, SrO, BaO, and ThO_2 gave rise to a paramagnetic species upon exposure to a CO atmosphere. No other oxides have been found to give rise to an observable paramagnetic species. The results of the oxide survey are presented in Table I.

The activity of the alkaline earth oxides toward formation of a paramagnetic species upon CO exposure has been reported to follow a systematic pattern: MgO > CaO > SrO >> BaO. However, this trend is reversed (i.e., SrO > CaO > MgO) when the activity is corrected for surface area. This order correlates roughly with either the Lewis basicity or the number of reducing sites.[1,2] A basic site could be an electron pair from oxygen or isolated hydroxyl groups, whereas a one electron reducing site is an area of high electron density, for example, a cationic vacancy. Thus, the order of activity/area could be explained by either the number of basic or reducing sites.

Heat treatment of the alkaline earth oxides can effect the number of both the Lewis basic[3] and reducing sites.[1,3] In the last Quarterly Report we stated that "lower heat treatment (400-600°) favors basic sites, while higher heat (700-900°) increases the concentration of reducing sites". Upon examination it was determined that the data used for the statement concerning the number of reducing sites was obtained for alkaline earth oxide samples heat treated in air. Our MgO/CO samples were heat treated under vacuum. Thus, we have endeavored to determine the effect of heat treatment temperature upon the number of reducing sites in MgO.

We have examined in detail the relationship between the heat treatment temperature and the formation of radicals in the MgO/CO system. The MgO/CO data and the number of reducing sites as a function of the heat treatment temperature correlate very strongly and, thus, support our earlier contention that the primary site for CO radical formation is a reducing site.

(c) Results and Discussion

(A) Oxide Survey. The oxide survey has been completed. The results are summarized in Table I. As indicated earlier, only the alkaline earth oxides and thorium oxide gave rise to a paramagnetic species upon exposure to carbon monoxide. It was further noted[4] that these oxides possess both basic and reducing sites. Oxides that have only basic (*e.g.*, NaOH, ZnO) or only reducing sites (*e.g.*, TiO_2) show no activity upon CO exposure.

It was hoped to include the alkaline metal oxides in the survey, but because of experimental problems this does not appear possible. When Na_2O was heat treated at 600° the oxide fused with the quartz tube. However, it was possible to heat treat Na_2O in quartz at a lower temperature. Next a stainless steel reactor was used to try a heat treat Na_2O at a higher temperature. Evidently, the oxide was reduced to Na metal by the iron[5] present in the reactor as the temperature was increased.

(B) Chemistry of the CO-Derived Surface Species. A study of the effect of the heat treatment temperature of MgO on the amount of radical formed upon exposure to carbon monoxide has been undertaken. The MgO samples were heat treated at 300-1000°C in 100° intervals. After addition of 150 torr CO the epr spectra was monitored at frequent intervals up to ca. 2400 hrs. The relative radical concentration, $[CO]_{rel}$, was estimated using the following equation:

$$[CO]_{rel} = \frac{H_{CO}}{H_{(int\ Mn^{2+})}}\ H_{(ext\ Mn^{2+})} \qquad (1)$$

where H_{CO} is the height of the high field component of the unsymmetric epr spectra as measured from the base line, $H_{(int\ Mn^{2+})}$ is the total height of the nearest high field component of Mn^{2+} in the MgO sample, and $H_{(std\ Mn^{2+})}$ is the total height of the same Mn^{2+} peak of a standard Mn^{2+} sample in the other cavity system. The high field component (the epr spectra) of the CO derived radical was used rather than the total signal because of the problems associated with the presence of O_2. At heat treatment temperatures of 400 and 500°C the epr signal of the CO derived radical was distorted on the low field side. In an earlier Quarterly Report, these low field components were shown to arise from incomplete O_2 removal. The $H_{(int\ Mn^{2+})}$ term in Eq (1) corrects the relative radical concentration for differences that result from varying amounts of MgO in each sample, i.e. the assumption is made that $H_{(int\ Mn^{2+})}$ is directly proportional to the MgO sample weight. The term $H_{(std\ Mn^{2+})}$ insures that each temperature run can be compared to the other runs.

The relative radical concentration in the MgO/CO generally reached a maximum in 30-60 days at room temperature. The results of this study, along with those of the MgO/nitrobenzene system to be described later, are shown in Figure I. There has been some problem with obtaining reproducible data for the 500° run in the MgO/CO system. This is most likely related to the incomplete O_2 removal problem noted above. Thus the experimental conditions may have to vary only slightly around 500° (i.e., the actual temperature or final pressure) to have large differences in the amount of O_2 removed. It is clear, however, that radical formation reaches a maximum value around 500°.

As mentioned earlier in the last Quarterly Report, we assumed that MgO would have a maximum number of basic sites when heat treated at 500° and a maximum number of reducing sites at 700-800°C. However, the data for the reducing sites was for MgO heat treated in air rather than under vacuum as is the case for the present study. Thus it was determined that a study of the number of reducing sites as a function of heat treatment temperature would be undertaken. The number of reducing sites can be measured by adsorption of nitrobenzene on MgO, forming, by a one electron transfer, the nitrobenzene anion radical.[2,6]

A small sample (∿ 20 mg) of MgO is heat treated for 12-16 hrs at a given temperature under ca. 10^{-6} torr vacuum in a normal quartz epr tube equipped with a 4 mm offset stopcock. The sample is then exposed to nitrobenzene[7] vapor (ca. 0.2 torr) at room temperature for two hours. Upon adsorption of nitrobenzene vapor, the solid immediately turned bright yellow but within a few minutes turned a permanent dark grey color. The samples were left exposed to the nitrobenzene vapor for two days at room temperature before excess nitrobenzene was removed by pumping through a liquid nitrogen trap. The epr spectra of the nitrobenzene anion radical, which agrees with the literature data,[2,6,8,9] were then monitored at frequent intervals. The relative radical concentration was estimated[10] as follows:

$$[\phi NO_2]_{rel} = \frac{A_x}{A_s G_x M} \tag{2}$$

where A_x is the area[11] of the nitrobenzene anion radical, A_s is the area[11] of a standard $\sim 10^{-4}$M solution of 1,1-diphenyl-2-picrylhydrazine (DPPH) in benzene, G_x is the instrument gain for the MgO/nitrobenzene sample, and M is the weight of the MgO sample before heat treating.

Initially, the 300, 400, and 500° runs have the highest radical concentrations[12] with the lines being noticeably broadened. The linewidth and the radical concentrations of these runs decrease with time. The initial period with very broad epr signals appears to be related to surface adsorbed water or hydroxyl groups.[13] The runs at 600° and above gave radical concentrations that varied only slightly with time.

The data[14] for the MgO/nitrobenzene system, after ca. 2-4 weeks and removal of excess nitrobenzene, is shown in Figure I. As can be seen, the curves for both the MgO/CO and MgO/nitrobenzene follow each other very closely and strongly suggest that the primary site for CO derived radical formation on MgO is a reducing site. Evidence presented in the last Quarterly Report suggests that basic sites also play a role as a site for CO adsorption as a nonradical species with, perhaps, later migration to a reducing site. The strongest evidence for the secondary role of basic sites is as follows: (1) only oxides with both basic and reducing sites give a paramagnetic species upon CO exposure and (2) if excess CO is removed immediately after exposure to a well degassed MgO surface, the CO radical is formed and grows in intensity to a radical concentration only slightly less than a similar sample exposed continuously to a 150 torr CO atmosphere.

It has also been shown that the formation of the CO derived radical is, at least in part, a reversible process. The radical was allowed to form on a MgO surface heat treated at 800° under a 90 torr CO atmosphere. The radical was then partially removed[15] by heating to 650°K in the presence of the CO atmosphere. The radical was able to regrow at room temperature to almost the same pre-heat concentration. The rate of growth, however, seemed to be somewhat slower than the initial radical growth.

(d) Work Forecast

Work will continue on the detailed surface chemistry of adsorbed radicals on MgO, CaO, SrO, BaO, and ThO_2.

(1) Study of effect of the heat treatment temperature on the basic sites and sufrace areas of MgO.

(2) $^{13}CO/MgO$, $^{13}CO/MgO/H_2O$, and related systems.

(3) Determination of Fe impurities[15] present in various MgO samples.

(4) Determination of the ratio of adsorbed CO radical to total adsorbed CO on MgO surface.

References and footnotes

1. Private communications with K. Tanabe, Distinguished Foreign Scientist, University of North Dakota (1976).

2. T. Iizuka, H. Hattori, Y. Ohno, J. Sohma, and K. Tanabe, J. Catal., **22**, 130 (1971).

3. K. Tanabe, "Solid Acids and Bases," Academic Press, New York-London, (1970).

4. See last Quarterly Report, Task IV.

5. See, for example, T. P. Whaley, "Comprehensive Inorganic Chemistry," Vol, I, A. F. Trotman-Dickenson (Ed.), Pergamon Press Ltd, Oxford, (1973), Chap. 8.

6. H. Hattori, M. Itoh, and K. Tanabe, J. Catal., **38**, 172 (1975).

7. The nitrobenzene was degassed several times by the freeze-pump-thaw method at liquid nitrogen temperature and then at -46°C to remove any dissolved carbon dioxide. The nitrobenzene was then stored in glass with a greaseless stopcock.

8. A. J. Tench and R. L. Nelson, Trans. Faraday Soc., **63**, 2254 (1967).

9. It is interesting to note, however, that the superhyperfine splittings are much more evident at higher heat treatment temperatures.

10. The double cavity was used and the sample positions were kept constant. The gain of the standard sample, G_s, does not appear in Eq (2) as it was kept constant throughout these experiments as were most of the other instrument variables.

11. The area under the first derivative curves were determined by a numerical double integration technique. See, P. B. Ayscough, "Electron Spin Resonance in Chemistry," Methuen, London, (1967), appendix 5.

12. The initial order is $300^{\circ} >> 400^{\circ} > 500^{\circ}$.

13. The evidence for this observation is as follows: (A) A 600° heat treated MgO sample on exposure to nitrobenzene was exposed to water vapor. After several days the line became broad. (B) A sample of MgO washed with D_2O, heat treated at 400° and exposed to nitrobenzene gave a spectra with narrower lines than H_2O washed material.

14. The data for the 300° run is not included because of the very broad nature of the epr signal. This is related to the fact that H_2O is not physically desorbed from MgO except at temperatures in excess of 330°C under our conditions.[1]

15. For a similar sample with CO atmosphere removed, heating to 650°K would result in almost complete loss of adsorbed CO derived radical. Furthermore, no additional radical growth would be observed.

16. As discussed in the last Quarterly Report, J. H. Lunsford and J. P. Jayne [J. Chem. Phys., 44, 1492 (1966)] indicated that Fe impurities in MgO play an important role in CO radical formation. Our results indicate otherwise, but more quantitative data would be helpful.

Table I Oxide Survey[a]: Paramagnetic Species observed on Metal Oxides and Related Species Upon Exposure to CO.

ACTIVE	NON-ACTIVE	NON-ACTIVE
MgO	BeO	Fe_2O_3/Al_2O_3
CaO	Na_2O[b]	GeO_2
SrO	NaOH[b]	ZnO
BaO	$NaOH/SiO_2$	ZrO_2
TiO_2/MgO	NaOOCH[b]	La_2O_3
ThO_2	Na_2CO_3	CeO_2
	Al_2O_3	Nd_2O_3
	Al_2O_3/SiO_2	Eu_2O_3
	SiO_2	Dy_2O_3
	TiO_2(α and β)	UO_3/U_2O_5
	FeS/SiO_2	

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[a] The oxides were normally water washed before being heat treated at 600° (unless noted otherwise), for ca. 12-18 hrs under a high vacuum (10^{-5} to 10^{-6} torr). The samples were then exposed to 150 torr CO. See Quarterly Report, April - June, 1977 for details.

[b] Heat treated at lower temperature because of experimental problems.

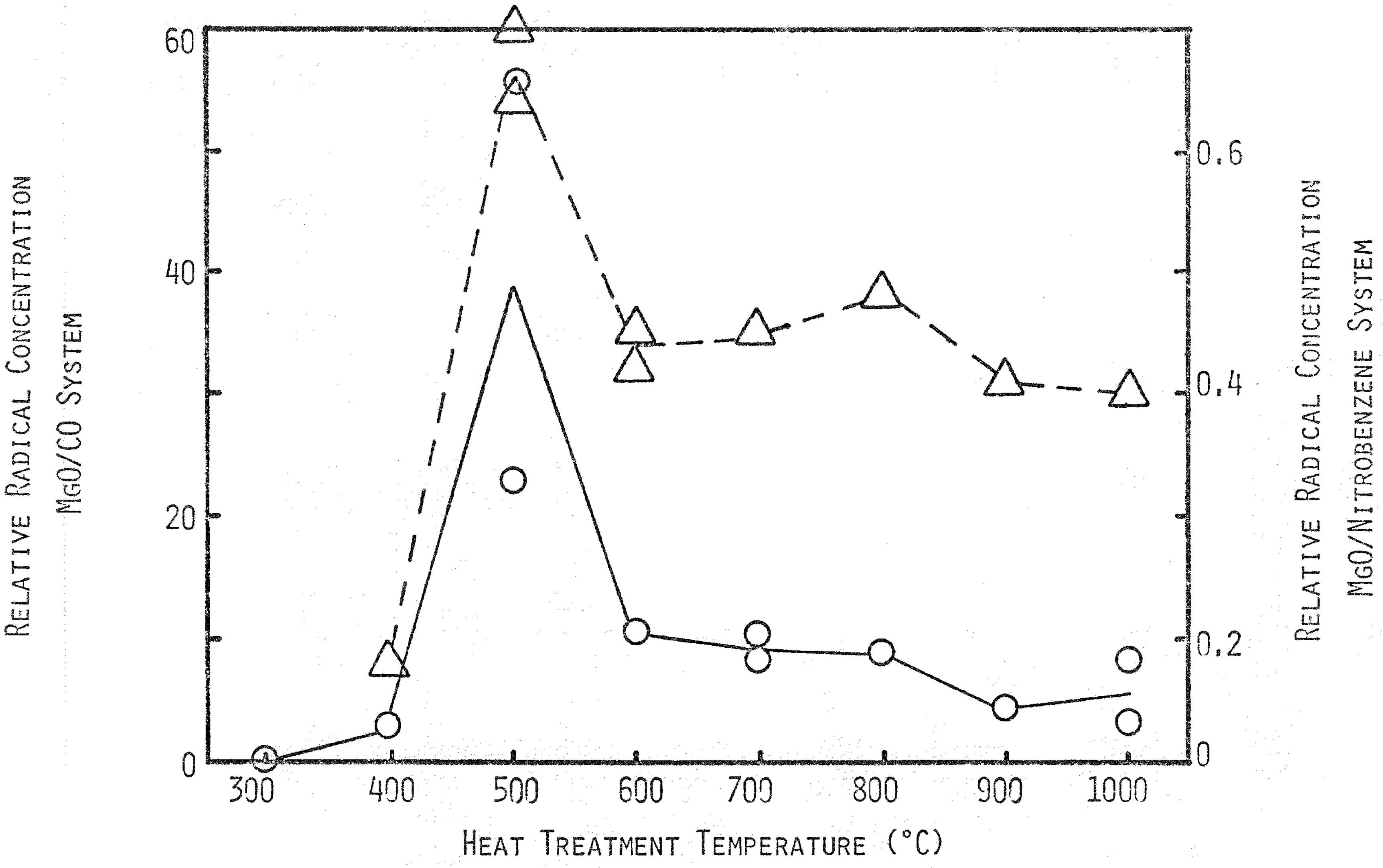

Figure I. Relative radical concentration (arbitary units) of the MgO/CO system (LHS and solid curve) and the MgO/nitrobenzene system as a function of the heat treatment temperature. N.B. Radical concentrations in the two systems are given in different arbitary units.

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