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Co-Oxidative Depolymerization of Coal

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1985

CO-OXIDATIVE DEPOLYMERIZATION OF COAL

A Thesis
Presented to
the Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Renae D. Rosencrans
May 1985

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CO-OXIDATIVE DEPOLYMERIZATION OF COAL

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Renae D. Rosencrans

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CO-OXIDATIVE DEPOLYMERIZATION OF COAL

Renae D. Rosencrans May 1985 69 pages
Directed by: Rita K. Hessley, J. W. Reasoner, J. T. Riley
Department of Chemistry Western Kentucky University

In contrast to current coal conversion technology, co-oxidative depolymerization of coal is a novel approach to coal liquefaction in that the reactions are carried out under relatively mild conditions. This free radical process utilizes air or oxygen and a suitable co-oxidant (solvent) which acts as a radical and hydrogen transfer agent throughout the coal matrix. Ideally, co-oxidation would lead to the formation of hydroperoxide groups at the reactive bridging sites in the coal matrix, which upon decomposition would lead to C-C bond scission.

The effects of several variables on co-oxidation and subsequent post-treatment were investigated. Up to 49% conversion to DMF soluble products was achieved. Further enhancement of solubility is believed to be limited by the failure of hydroperoxide decomposition to lead to C-C bond scission.

INTRODUCTION

The abundance of coal throughout the world provides a tremendous source of carbon and hydrogen, the basis for chemical feedstocks and synthetic fuels. However, the structure of coal on the molecular level is very different from the hydrocarbons found in natural gas or petroleum (the primary source of chemicals and fuels), namely in the ratio of hydrogen to carbon. Fundamentally, conversions of coal to liquids and gases are reductive processes in which the hydrogen to carbon ratio is increased. The amount of hydrogen addition determines the properties of the product and also the cost of carrying out the conversion.(1)

Historically, the objective of coal liquefaction has been to produce liquids which could be processed into high-octane gasoline. On the average, this represents a two-fold increase in hydrogen content. This degree of hydrogenation is very expensive and wasteful. In recent years the goal has become to add just enough hydrogen to the coal to produce a pumpable oil which can be used for industrial and commercial heating and electrical power generation.(2)

Converting coal to combustible gases requires the addition of even more hydrogen. Five-fold increases in hydrogen content are necessary to obtain a high Btu gas from coal.(3)

In the conversion of coal to useful synthetic fuels or chemical feedstocks, liquefaction has advantages over gasification in thermal efficiency and economics: fewer chemical changes are required with milder process conditions to convert coal to liquids than to gases, and the higher density of liquids makes them cheaper to store and transport.(4)

Interest in converting coal into liquids has been rather cyclic, following the availability of petroleum. Coal was the major source of energy at the beginning of the industrial revolution, ca. 1840. After its discovery in 1859, petroleum quickly became the preferred energy source.

During the early 1920's, fear of seriously depleting oil supplies spurred research in coal liquefaction. The growing automobile industry with its demand for gasoline accentuated this interest. But the discovery of oil in Texas in the mid-1920's discouraged further research in coal liquefaction in the United States.

Countries dependent upon the importation of oil continued to develop methods for converting coal to more convenient liquid fuels. Germany, in particular, laid the foundations for most of the present day coal liquefaction processes with Bergius'(5) discovery for direct hydrogenation in 1913, the Pott-Broche(6) solvent extraction process in 1927, and the Fischer-Tropsch(7) process for hydrocarbon synthesis from gasified coal in 1925. During World War II, Germany was able to supply all of her aviation fuel and about 75 percent of her liquid fuel needs by synthetic means.

Coal liquefaction research was again considered in the United States after World War II when the rate of petroleum production could not keep up with the growing demand. But the discovery of massive petroleum reserves in the Middle East in the mid-1940's, coupled with favorable import agreements, once again made coal liquefaction uneconomical. Research efforts then declined until 1973, when unrest in the Middle East threatened our major source of energy. The combination of severely diminished supplies of domestic crude and unpredictable supply and rapidly increasing cost of foreign crude once again focused attention on coal as a potential source of liquid fuels.(8)

Table I (taken from Berkowitz(9)) lists the principle features of some coal liquefaction processes which have been under development. Of these, the SASOL process of South Africa is the only liquefaction process currently in commercial operation (since 1955) and is also the only example in the Table of an indirect route to liquid products. The term "indirect" refers to a two-step process whereby the coal is first gasified and then Fischer-Tropsch synthesis is carried out using the resulting "synthesis gas": carbon monoxide and hydrogen are reacted over an iron or cobalt catalyst to produce light hydrocarbons (C_5-C_{11}).

TABLE I

SOME LIQUEFACTION PROCESSES AND OPERATING CONDITIONS(9)

Process and Sponsor	Characteristics	Temp. °C	Pressure, psi	H_2*
H-Coal by Hydrocarbon Research, Inc.	Coal-oil slurry reacts rich gas in a fluidized bed of cobalt molybdate on alumina	455	2500	
Exxon Donor Solvent by Exxon Corporation	Non-catalytic hydrogen transfer from recycle oil; donor is regenerated by hydrotreatment and recycled; free radicals are stabilized by hydrogen atmosphere and donor.	425-465	1500-2000	
SRC-II (Solvent Refined Coal) by Gulf Oil	Slurry of dry, pulverized coal in recycle oil is preheated to initiate thermal decomposition and dissolution. The slurry is then transferred to a "dissolver" where cold hydrogen is injected	370-465	1500-2000	
CSF (Consolidation Synthetic Fuel) by Consolidation Company	Two Steps: 1. Solvent extraction with recycle oils 2. Catalytic hydrogenation	 400-425 425-455	 150-400 3500-4500	
Synthoil by Pittsburgh Energy Research Center	Coal-oil slurry is agitated in hydrogen rich atmosphere and then hydrogenated over a packed-bed of cobalt molybdate on SiO_2/Al_2O_3	465	4000	
COSTEAM by Pittsburgh Energy Research Center	Coal-oil slurries react with crude syngas (5-60% CO + 30-50% H_2)	455	4000	(a)
SASOL by South African Coal, Oil and Gas Corporation	Indirect liquefaction 1. Lurgi gasification 2. Fischer-Tropsch Synthesis	 925-1035 220-330	 400-450 325-350	 (b) (a)

*H_2 unless otherwise stated; (a)Syngas; (b)Air or O_2.

Direct liquefaction schemes are one-step processes to form liquids which may or may not require further upgrading or hydrogenation.

Table I also shows that all of these processes have two features in common: (1) very high temperatures are used to thermally fracture bonds in the coal and (2) very high pressures of hydrogen gas are used to "cap-off" the resulting fragments. Such severe conditions for liquefaction of coal place extreme technological demands on engineering expertise to produce hardware able to withstand the harsh operating conditions. The overall costs of the facilities and equipment necessary to construct and maintain operation of a commercial synthetic fuels plant must be competitive with other alternatives to be economically feasible.(10)

The keys to economical coal liquefaction are optimizing hydrogen utilization and lowering the very high temperatures and pressures.(11) In an attempt to develop a low temperature, low pressure process for breaking up the coal on a molecular level into smaller, soluble fragments, cooxidation was investigated as an approach to depolymerization. This proposed process is based on four premises, each of which will be discussed separately:

1. Coal is oxidizable
2. Coal is susceptible to reactions involving a free radical mechanism

3. A solvent capable of oxidation and swelling the coal matrix can effectively co-oxidize the coal;
4. Decomposition of hydroperoxides leads to C-C bond cleavage and therefore depolymerization of the coal could be achieved.

Oxidation of Coal

The low temperature air oxidation, or autoxidation, of coal as it occurs during weathering is generally undesirable. Autoxidation is initially limited to the surface of the coal and the pores and crevices within the coal because oxygen cannot penetrate the highly crosslinked coal matrix. As oxidation progresses and the surface layers become saturated, oxygen can then diffuse deeper into the coal.(12) The destructive degradation of the coal substance during oxidation reduces the amount of soluble material, and thus the potential for liquefaction is reduced. There is also a loss in heating value and an alteration of the properties of the coal during oxidation. The exothermic oxidation reactions may even proceed to the point of ignition of the coal.(13) This type of oxidation is unsuitable for liquefaction: there is little control over the reactions and the products.

A study of controlled air oxidation of coal in pyridine at 100°C was undertaken by Solash et al.(14) The coal was first oxidized and then thermolyzed at 415°C in the absence of air. Although total conversions were not high, the study results indicate that the amount of soluble material obtained after thermolysis followed the extent of prior oxidation.

Huntington, Mayo and Kirshen(15) have also attempted to use selective oxidation to break the large coal molecules into smaller, soluble segments. Mild oxidation of the coal was carried out in pyridine at 50°C under 1.1-1.5 atm of oxygen. They found this system to be unpromising for liquefaction: too much oxygen was incorporated into the coal and too much fuel value was lost for the depolymerization achieved.

Controlled oxidation as it was carried out in these studies does not appear to be satisfactory for the liquefaction of coal.

However, oxidation has been successfully applied to the determination of coal structure. Mayo and Kirshen(16) report that coal oxidized by aqueous NaOCl yields high-molecular-weight acids which are suitable for structural analysis by nuclear magnetic resonance spectroscopy.

Other oxidizing agents which have been used to degrade coal into smaller, identifiable molecules to be interpreted in terms of coal structure have been HNO_3, HNO_3-$K_2Cr_2O_7$, $KMnO_4$, O_2, H_2O_2-O_3 and $Na_2Cr_2O_7$.(17)

From this information, it is evident that coal is oxidizable under a variety of conditions; it is certain that coal will be oxidized under the proposed co-oxidative conditions.

The Free Radical Nature of Coal

Oxidation of coal is generally thought to proceed by a free radical mechanism. The first step is the formation of peroxides at aliphatic structures present in coal. The basic mechanism is believed to be as follows:(18)

$$\text{R-H} \xrightarrow{O_2} \text{R}\cdot$$

$$\text{R}\cdot + O_2 \longrightarrow \text{R-O-O}\cdot$$

$$\text{R-O-O}\cdot + \text{R-H} \longrightarrow \text{R-O-O-H} + \text{R}\cdot$$

The mechanism of coal liquefaction is also believed to be free radical in nature,(19,20) and isolated free radicals exist in coal and have been characterized by electron resonance spectroscopy.(21) The role these free radicals play in coal liquefaction has been studied by Petrakis et al.(22-24) They have shown that the more free radicals inherently present in the coal, the greater the potential for conversion.(23) In liquefaction experiments at 400-480°C and 10.9 atm H_2 using tetralin, naphthalene, or a heavy oil as the reaction medium, coal was shown to form radicals which were subsequently stabilized when they reacted with other radical or non-radical species.

Poutsma and Dyer(25) have studied the behavior of model compounds under conditions typical of thermolysis. They showed that thermal cracking at 345-425°C of aliphatic bridges in compounds such as 1,3-diphenylpropane and 1,4-diphenylbutane produces a radical species. Figure 1 depicts the scheme they postulated for the behavior of coal during

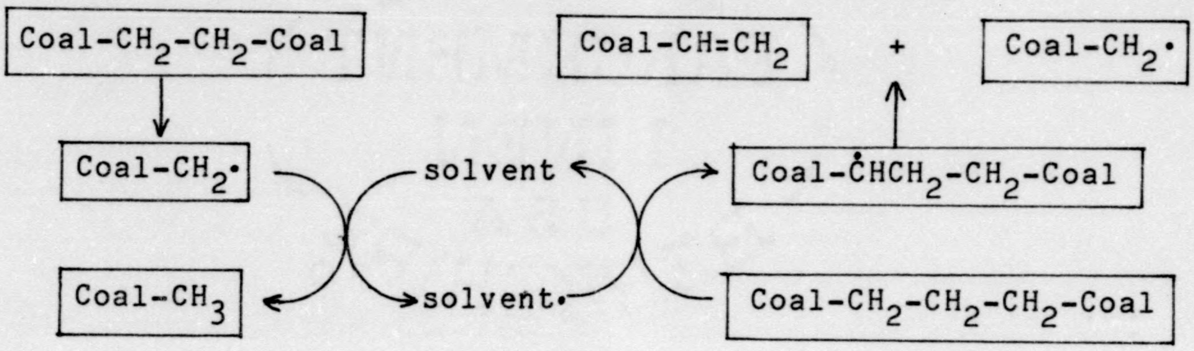

Figure 1. Scheme of Poutsma and Dyer for the Free Radical Reactions of Coal at High Temperature

thermolysis in the presence of a solvent capable of donating hydrogen to the coal. It involves a sequence of reactions between the coal and solvent leading to bond cleavage and coal depolymerization.

Gilbert and Gajewski report their studies of the thermal decomposition of model compounds show that the reactions occur by free radical chain processes. Diphenylpropane, dibenzyl ether and phenethyl phenyl ether were thermolyzed in the temperature ranges of 138-350°C(26) and 335-380°C.(27) These compounds serve as models for the three atom linkages present in coal and therefore indicate that thermal decomposition of coal proceeds by free radical processes.

All of these free radical studies were carried out at temperatures near 400°C except for Gilbert's experiments, which were in the range of 138-350°C. In this study, a free radical initiator was utilized to start the reactions in the lower temperature range. After initiation, the reactions are self-perpetuating.

Based on these studies, it was believed that using co-oxidation, radical initiation and perpetuation of a similar free radical chain reaction could be brought about in coal at temperatures well below 400°C.

Co-oxidation

Co-oxidation of various compounds has been the focus of many studies.(28) The principles involved in co-oxidation suggested a potential means of overcoming the problems encountered with oxidation as a method for depolymerization of coal. It was proposed that a small molecule slurried with coal as a co-reactant in an inert solvent or as the solvent itself might participate in the oxidation reactions in the following manner (RH and rH represent reactive sites in the coal and solvent molecules, respectively):

$$\text{rH} + \text{initiator} \dashrightarrow \text{r}\cdot + \text{initiator H}$$
$$\text{r}\cdot + O_2 \dashrightarrow \text{rOO}\cdot$$
$$\text{rOO}\cdot + \text{RH} \dashrightarrow \text{rOOH} + \text{R}\cdot$$
$$\text{R}\cdot + O_2 \dashrightarrow \text{ROO}\cdot$$
$$\text{ROO}\cdot + \text{rH} \dashrightarrow \text{ROOH} + \text{r}\cdot$$

The co-oxidant peroxy radical, rOO• , being small in comparison to the coal molecule and mobile in the liquid phase may move freely within the coal matrix and attack the otherwise inaccessible reactive sites. The overall process is depicted in Figure 2, adapted from Huyser.(29) Peroxy formation represented by the species ROO• and rOO• has an activation energy of approximately zero and is nearly spontaneous. Abstraction or shuttling of hydrogen would involve labile carbon-hydrogen bonds in either RH or rH, and the cycles shown can occur repeatedly. In terms of coal conversion, the key to this proposed scheme is the formation of hydroperoxide species at critical points within the coal matrix.

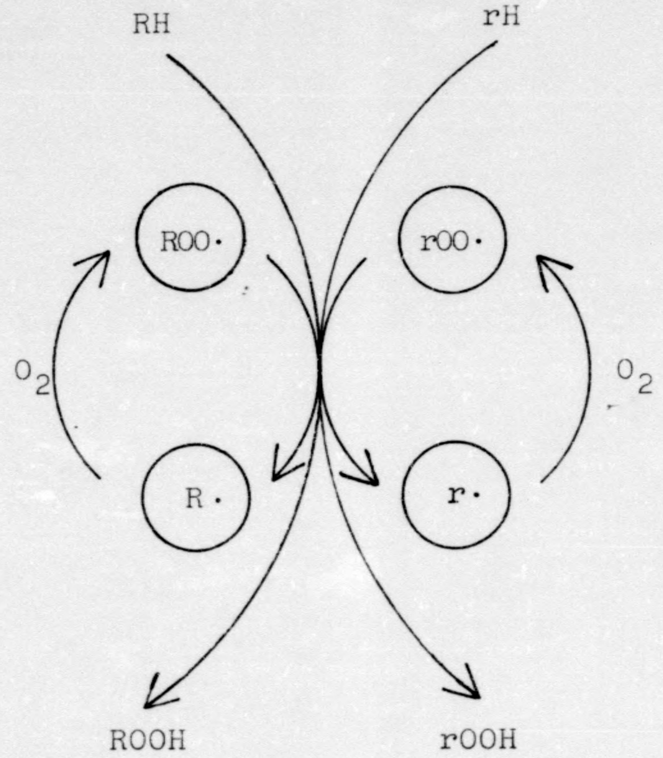

Figure 2. Autoxidation of Mixed Substrates

Isopropyl benzene, or cumene, is known to undergo oxidation at 80-100°C to form cumene hydroperoxide; the decomposition of cumene hydroperoxide occurs as low as 60°C in dilute acid. These reactions, illustrated in Figure 3, constitute an industrial process for the production of acetone and phenol from cumene.(30) In the two-step process, carbon-carbon bond scission has been achieved resulting in two smaller molecules. If the same type of cleavage could be achieved in coal, even at only a few sites, effective depolymerization of the coal molecule would be accomplished.

Figure 4 is a representative drawing of a portion of the three-dimensional coal "molecule."(31) It seemed likely that the aliphatic bridges between aromatic rings would be as susceptible to hydroperoxide formation during co-oxidation as they are during air oxidation.(18) If bond scission, via co-oxidative hydroperoxide formation could be achieved at as few as two of the potential sites (shown by arrows in Figure 4), substantial depolymerization of the coal molecule into smaller, low molecular weight (more soluble) fractions would be achieved. The solubilized coal could then be upgraded and refined using existing petroleum technology.

The proper medium in which to carry out co-oxidation is crucial to the depolymerization scheme. When placed in contact with a solvent for which it has an affinity, coal will absorb the solvent and swell,(32) opening up the

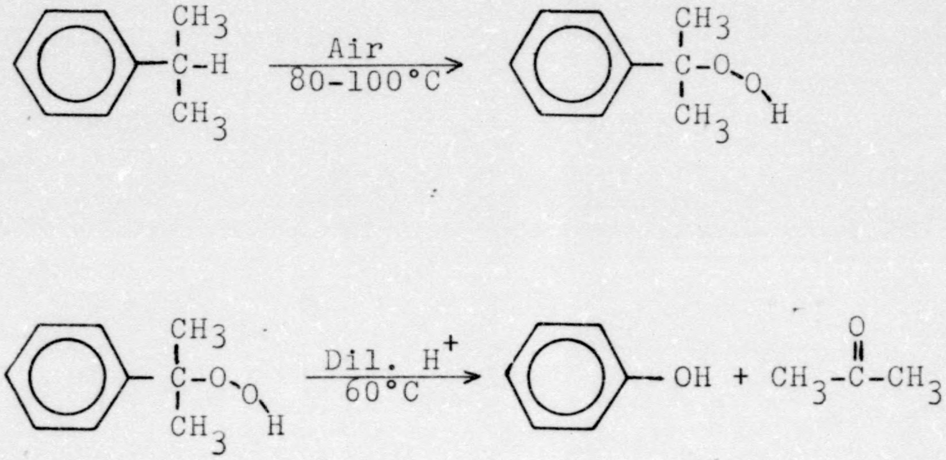

Figure 3. The Oxidation of Cumene and the Decomposition of Cumene Hydroperoxide

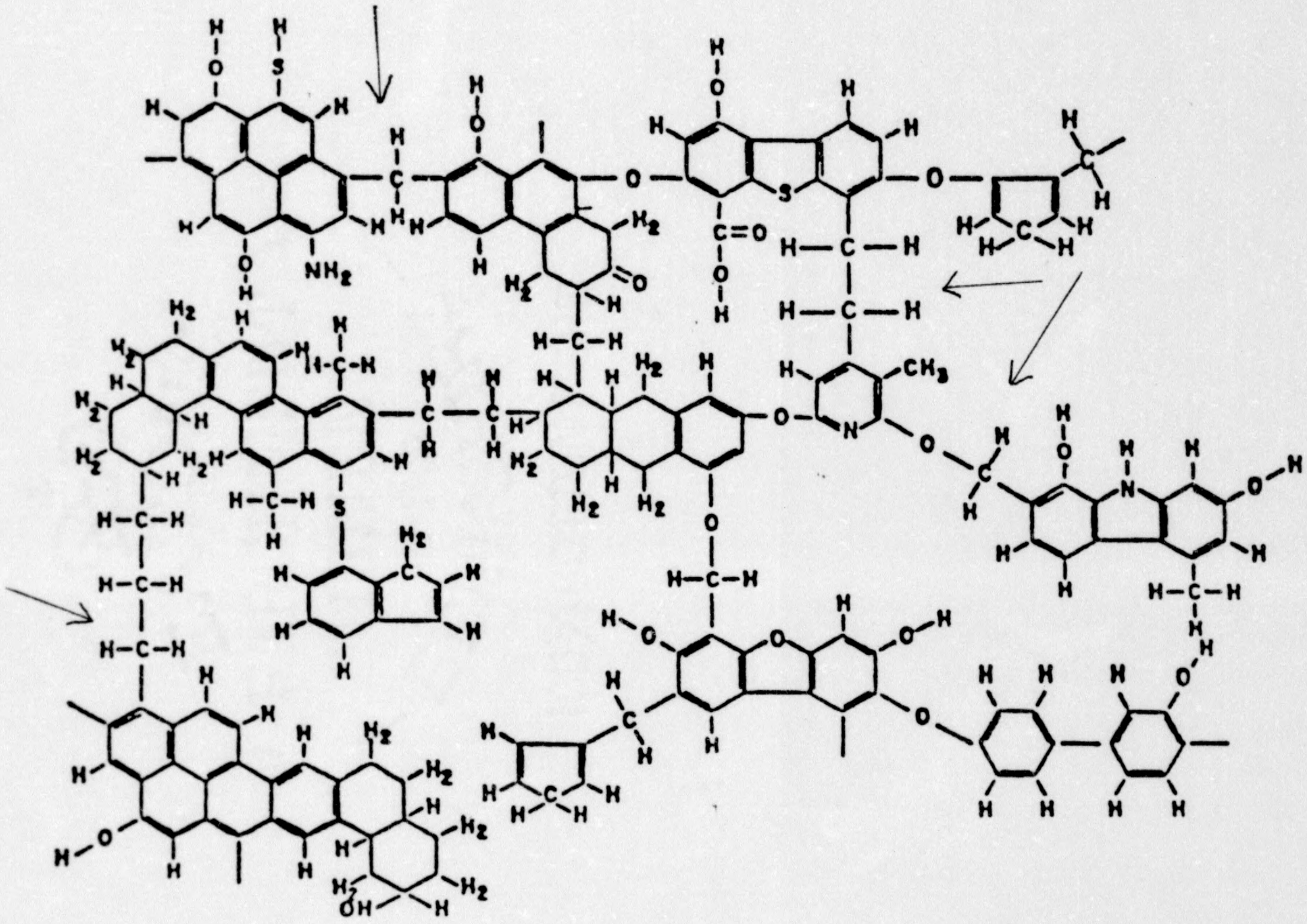

Figure 4. Schematic representation of structural groups and connecting bridges in bituminous coal

crosslinked structure. A solvent suitable for co-oxidation with coal will be oxidizable and also possess the ability to swell the coal, allowing repetition of the co-oxidation reactions deep within the coal matrix.

Much research has been carried out on the swelling of coal by solvents. From swelling data, the average molecular weight between crosslinks can be calculated using an equation developed by Peppas and Lucht.(33) Similar determinations of coal structure have been carried out by Sanada and Honda(34) and Larsen.(35)

N,N-dimethylformamide, dimethylsulfoxide, pyridine,(36,37) carbon disulfide(37) and cumene(38) are some solvents which have been shown to have a high affinity for coal and are therefore good swelling solvents. Used in the co-oxidation mixture, any one of these solvents could facilitate the co-oxidation of coal.

In selecting a suitable co-oxidant, cumene is a reasonable choice; it is known to undergo the desired oxidation reactions at low temperatures using air as the oxidant(30) and it possesses the ability to swell coal. Using a co-oxidant such as cumene, the depolymerization of coal at low temperatures and pressures could be made possible.

Hydroperoxide Decomposition

The formation of hydroperoxides in the coal during co-oxidation is the key to subsequent C-C bond cleavage and depolymerization of the coal. Decomposition of hydroperoxides in coal produces various oxygen-containing compounds, e.g., acids, peracids, alcohols, ketones, aldehydes, esters, and ethers(18) via beta-bond scission. Figure 5 is a possible mechanism for thermal hydroperoxide decomposition.(39) First, there is homolytic cleavage of the O-O bond which is then followed by scission of the beta-bond.

Organic hydroperoxides are generally unstable above 200°C,(39) well below the temperature range necessary for thermolysis of C-C bonds in coal (350-500°C).(40) Therefore, C-C bond cleavage could be achieved in co-oxidized coal at substantially lower temperatures than are necessary for C-C bond thermolysis in raw coal.

Hydroperoxides can also be decomposed chemically, e.g., the acid catalyzed decomposition of cumene hydroperoxide.(30)

Summary

The proposed process of co-oxidative depolymerization of coal is based on the novel application of known chemistry to coal. The process consists of two steps:(1) the coal is first co-oxidized at low temperatures using air or oxygen as the oxidant (in contrast to the high temperatures and high hydrogen pressures necessary for current processes); and (2) thermal or chemical treatment for hydroperoxide decomposition, consequently cleaving C-C bonds and depolymerizing the coal. The soluble products could then be upgraded and refined using existing petroleum technology.

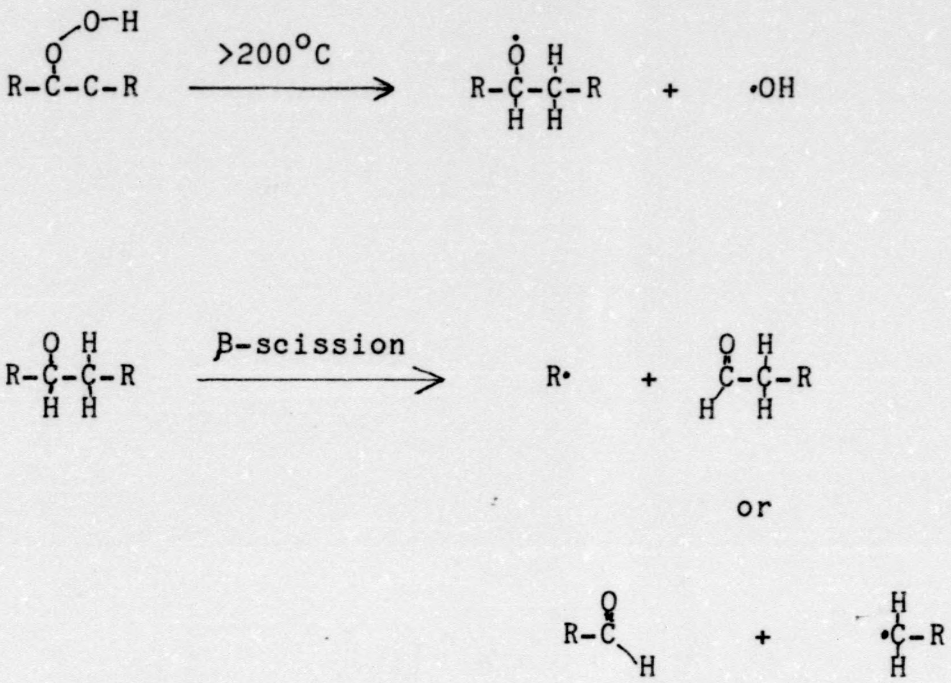

Figure 5. Thermal Decomposition of Hydroperoxides via β-scission

EXPERIMENTAL

The experimental section describes the materials, equipment and procedures utilized in this investigation.

I. Materials

A. Coal

Four coals were selected for use throughout this investigation. All were western Kentucky hvB or hvC bituminous coals obtained from the coal bank at Western Kentucky University. The complete analyses for the four coals are shown in Table II.

B. Solvents

Solvents screened for potential use as co-oxidants were ethylenediamine, cumene, cyclohexene, and 4-picoline obtained from Aldrich Chemical Company; diphenylmethane, benzonitrile, o-dichlorobenzene, fluorene, diphenylether and carbon disulfide obtained from Matheson, Coleman and Bell; tetralin and acetic acid obtained from Fisher Scientific Company; dioxane obtained from Sargent Welch. All solvents were high quality chemicals and were used without purification. All Soxhlet extractions were carried out using reagent grade dimethylformamide (DMF) obtained from Fisher Scientific Company. Methanol and acetone used to

TABLE II

PROXIMATE AND ULTIMATE ANALYSES OF COALS CHOSEN FOR STUDY

Coal	M[a]	A	VM	FC	%C	%H	%N	%S	%O[b]
9036	5.33	6.44	46.8	46.6	76.48	5.37	1.60	3.29	6.79
9072	6.92	8.44	41.8	49.6	74.15	5.24	1.23	3.21	7.71
9100	7.09	8.36	40.6	50.9	74.08	5.11	1.50	3.59	7.34
7827	2.84	9.49	35.9	50.5	74.49	5.22	1.53	3.33	5.94

[a] Moisture as determined, other values are on a dry basis.

[b] By difference.

rinse the co-oxidized and extracted coal were also high purity and received from Fisher Scientific Company.

C. Free Radical Initiators

Four chemical initiators were chosen for use in co-oxidation reactions over the temperature range of 70-200°C. Azobisisobutyronitrile (ABIN), di-tert-butyl peroxide (DTBP), and tert-butyl hydroperoxide (TBHP) were obtained from Matheson, Coleman and Bell. Cumene hydroperoxide (CHP) was obtained from Pfaltz and Bauer. The temperature range in which each of these decomposes with a half-life of 5-10 hours is shown in Table III.(29) Micromolar concentrations were used in the co-oxidation reactions.

D. Gases

Oxygen obtained from Airco and air were used as oxidants. Nitrogen obtained from Airco was used to create an oxygen-free atmosphere.

E. Catalysts

Three transition metal compounds were used as catalysts in selected reactions throughout the course of this work. Cobalt(II) acetylacetonate ($Co(acac)_2$) was prepared according to a standard procedure.(41) Cobalt(III) acetylacetonate ($Co(acac)_3$) was prepared according to the procedure of Shalhoub.(42) Co(II) naphthenate was obtained as a 6% solution in mineral oil from Pfaltz and Bauer. A

TABLE III

USEFUL[*] TEMPERATURE RANGES FOR FREE RADICAL INITIATORS

Initiator	Useful Temperature Range, °C
azobisisobutyronitrile	65-88
di-tert-butyl peroxide	117-143
tert-butyl hydroperoxide	121-147
cumene hydroperoxide	154-194

---

[*] By 'useful' is meant with half-life between 0.5 and 10 hours.

dilute solution (50 ug Co(II)/ml) was prepared by dilution with decane.

F. Chelating Reagents

Nitrilotriacetic acid (NTA) and 2,2′-bipyridine were obtained from Eastman Kodak Company. These compounds were used in trials to remove mineral matter from coal.

G. Other Reagents

Sodium borate and sodium carbonate obtained from Matheson, Coleman and Bell were used in the preparation of pH 10 buffer.(43) Potassium hydroxide obtained from J. T. Baker and tert-butyl alcohol obtained from Fisher Scientific Company were used in a 10% w/v base in alcohol solution. Sodium iodide from Fisher Scientific and sodium thiosulfate from Aldrich Chemical Company were used in the titrimetric determination of hydroperoxides. Sodium stearate received from Matheson, Coleman and Bell was used as an emulsifying agent. Potassium iodide, hydrogen peroxide (50% solution), and hydrazine (85% hydrate solution) obtained from Aldrich Chemical Company and sulfuric acid, acetic acid, chloroform, isopropyl alcohol and acetonitrile obtained from Fisher Scientific Company were used in trials for the chemical decomposition of hydroperoxides.

II. Equipment

Co-oxidations carried out at atmospheric pressure were run in standard taper laboratory glassware. A 3-neck 500-ml round bottom flask was fitted with a condenser, an O_2 dispersing tube and a thermometer attached to an automatic temperature controller (I^2R model L-71). A 300-ml stainless steel Parr reactor equipped with a thermocouple temperature control and an internal mechanical stirrer was used for reactions at elevated O_2 pressures.

A Fisher Isotemp vacuum oven (model 281) was used to dry all samples.

A Sartorius (model 16091 MP 8) electronic analytical balance was used for all analytical weighings to the nearest 0.001 g.

Gas chromatographic analyses of co-oxidation filtrates were carried out using a Varian model 3700 gas chromatograph equipped with a 6-ft column of 3% Dexil on Chromasorb W and a flame ionization detector. Chromatograms were recorded and integrated by a Hewlett Packard (model 3390 A) integrator interfaced to the chromatograph.

Elemental and proximate analyses were performed using the LECO MAC-400, SC-132, and CHN-600 instruments.

Infrared analyses of co-oxidized coals were performed on a Nicolet MX-1 Fourier-transform infrared spectrometer.

A Fisher titrimeter (model 35) was used for titrimetric determination of hydroperoxides. The electrodes used were a Corning platinum inlay indicating electrode and a saturated calomel reference electrode (SCE).

Thermolysis reactions were carried out using a Lindberg Hevi-Duty SIB tube furnace.

Standard Soxhlet apparatus and Whatman cellulose extraction thimbles (33 x 80 mm) were used for all extractions.

III. Procedures

Figure 6 shows the flow diagram for the processes by which the effect of co-oxidation on coal was investigated. The project was divided into three principle sub-sections: (1) co-oxidation; (2) post-oxidative analysis and treatment; (3) solvent extraction of reacted coal.

A. Co-oxidation

Determination of the optimum conditions for the co-oxidation of coal required that a number of variables be tested. Solvent system, temperature, pressure, and reaction time were identified as the four principle co-oxidation reaction variables. These were varied with limits selected to maintain a useful range for ultimate application on a larger, commercial scale. Temperatures were tested in the range 30°C to 185°C; gas pressures were varied from 1 atm (air) to 7 atm (O_2); reaction times were varied from 0.5 to 24 hours.

1. Effects of temperature, pressure, time, and solvent system. Typically, the reaction mixture consisted of 10 g coal ground to -60 mesh, 100 ml solvent, and 1.0 g or 1.0 ml initiator. For reactions at atmospheric pressure, air or oxygen was passed continuously into the reaction

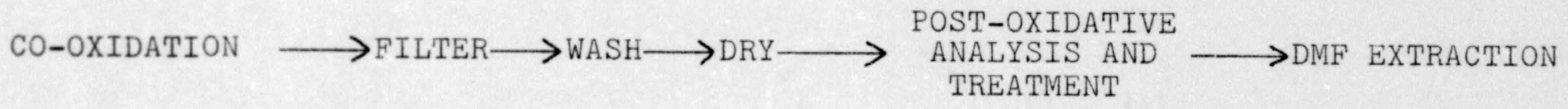

Figure 6. Flow Diagram for the Co-oxidation of Coal

slurry at a rate sufficient to maintain a moderately turbulent system. At elevated pressure, the reactants were added to the bomb reactor which was then sealed and pressurized to the desired initial gas pressure. All reactions at elevated pressure involved pure oxygen only.

Many solvents were tested for their ability to co-oxidize coal. These solvents are listed in Table IV.

2. Effect of swelling solvent. Mixed solvent systems in varying proportions were used to test the possible synergistic effects of solvents known to swell coal (cumene, DMF, and CS_2) used in conjunction with potential co-oxidants.

3. Effect of base. Based on the process for the commercial production of cumene hydroperoxide,(30) some reactions were carried out with aqueous (pH 10 buffer or pH 10 Na_2CO_3) or alcoholic (10% w/v KOH in tert-butyl alcohol) base in the ratio 2:1 base to solvent. One gram of sodium stearate, an emulsifying agent, was added to two-phase systems. The base reacts with phenolic species which may inhibit oxidation.

4. Effect of catalysts. First row transition metal ions strongly promote hydroperoxide decomposition.(44) The reactions are cyclic and are illustrated in the following equations for the Cobalt(II)-Cobalt(III) ions:

$$\text{ROOH} + \text{Co}^{2+} \longrightarrow \text{RO}^{\cdot} + \text{Co}^{3+} + \text{OH}^{-}$$

$$\text{ROOH} + \text{Co}^{3+} \longrightarrow \text{ROO}^{\cdot} + \text{Co}^{2+} + \text{H}^{+}$$

Hydroperoxide decomposition occurs in these reactions, but more reactive free radical species ($\text{RO}^{\cdot}$ and $\text{ROO}^{\cdot}$) are formed which generally permit more rapid and more extensive oxidation.

The addition of catalysts was tested for the effects on co-oxidation. Micromolar quantities were added to some reaction mixtures.

5. Effect of removal of mineral matter. The effects of removal of mineral matter on co-oxidation were studied in two ways. A comparison was made of the co-oxidation of a coal before and after commercial cleaning by the float-sink method. Also, chelating reagents were used in an attempt to remove mineral matter from the coal or to minimize its potential reactivity by forming metal chelates. Several trials were carried out by slurrying the coal with 1.0 g of the reagent in aqueous solution before co-oxidation or by adding the reagent directly to the co-oxidation reaction slurry.

6. Filtration of the co-oxidation mixture. After a pre-determined reaction time, the slurry was cooled and filtered through a medium porosity sintered glass filter. The filtrate was kept for gas chromatographic analysis and the coal was washed thoroughly with 200 to 300 ml acetone.

7. Drying of co-oxidized coal. The co-oxidized coal was dried for a minimum of 16 hours at 150°C in vacuo.

B. Post-oxidative Analysis

1. Extent of oxidation of the solvent. Gas chromatographic analysis of the co-oxidation filtrate was used to detect the extent of oxidation of the solvent. Knowing the retention time of the solvent, the percentage of unoxidized solvent could be read directly from the integrated chromatogram.

2. Determination of hydroperoxides. The method described by Huntington(45) was used to titrimetrically detect the presence of hydroperoxides in coal after co-oxidation. This is a classic reaction in which the iodine liberated by the oxidation of iodide (accompanied by the reductive decomposition of peroxides) is titrated with sodium thiosulfate.

The dried, co-oxidized coal was slurried in a solution of 2 g sodium iodide and 25 ml acetic acid which had been purged 5 minutes with nitrogen. Some reactions were carried out at room temperature, and some were run under reflux to ensure the exclusion of oxygen from the system. The flask was covered to exclude light; and after 25 minutes with continued nitrogen purge, the solution was decanted and immediately titrated to the null endpoint.

A blank was run in the absence of coal, and a 1% solution of cumene hydroperoxide was reacted in the same manner to verify the accuracy of the method. Co-oxidized solvent was also analyzed to determine the extent of hydroperoxide formation.

3. Oxygen uptake analysis. To determine the extent of oxygen uptake by coals during co-oxidation, ultimate analyses were carried out using LECO equipment in the Coal Testing Laboratory at Western Kentucky University.

Infrared analysis to detect structural alteration in the coal, particularly in oxygen functionality, was made by preparing a sample of co-oxidized coal in KBr (1% w/w).

C. Post-Oxidative Treatment

1. Hydroperoxide decomposition.

Four methods were used in an effort to decompose hydroperoxides formed in the coal matrix during co-oxidation. After chemical decomposition, samples were filtered, dried and extracted.

(a) Thermolysis

Thermolysis at 250°C under an N_2 atmosphere was carried out by weighing aliquots of the dried, co-oxidized coal into ceramic boats. The boats were transferred to the combustion tube, and the tube was flushed with N_2 for several minutes before the heating period was begun. The oven reached 250°C in less than 10 minutes and heating was continued for 10 additional minutes. The N_2 purge was continued over the coal samples until they were cool. The samples were stored under vacuum or in a desiccator prior to being extracted.

(b) Acid catalyzed decomposition

The industrial process for decomposition of cumene hydroperoxide(30) was tested. The dried, co-oxidized coal was stirred at 60°C in 100 ml 2% H_2SO_4 in acetone for 1 hour.

(c) Reduction by iodide ion

The co-oxidized coal was slurried with 50 ml saturated KI solution and 50 ml 3:2:1 acetic acid: chloroform:isopropyl alcohol according to the procedure described by Lundberg.(46) Two trials were run for 24 hours, one at ambient temperature, the other at 50°C.

(d) Reduction by hydrazine

Szmant(47) described the reaction of oxy- and peroxy-species with hydrazine. This reaction was used for several trials. Dried, co-oxidized coal was slurried in 50 ml hydrazine and refluxed for 24 hours.

2. Cleavage of keto groups. Three methods were used to achieve the cleavage of ketone species formed in coal during co-oxidation. After treatment, samples were filtered, dried and extracted.

(a) By t-butoxide

Doering and Haines(48) have reported that C-C bonds in several aldehydes and ketones can be cleaved during oxidation in the presence of tert-butoxide ion.

Their procedure was followed in several reactions. Co-oxidized coal was reacted with 200 ml potassium t-butoxide (10% KOH in t-butyl alcohol) under: (1) 2 atm O_2 for 1 hour at ambient temperature; (2) reflux for 1 hour; (3) under 2 atm O_2 at 130°C for 2.5 hours.

(b) By sulfuric acid

The procedure of Pavlyuk and Chervikskii(49) was also followed to achieve acid cleavage of ketones. In this system, a catalytic quantity (0.3 g) of H_2SO_4 was dissolved in 60 ml acetonitrile and the co-oxidized coal was added to the solution. The temperature was raised to 60°C with stirring for 1 hour and then was raised to 80°C for an additional hour.

(c) By peracid

Robertson and Waters(50) reported that any peracid is capable of cleaving aryl ketones. Peracid oxidation and dissolution of coal has also been described by Deno et al.(51) A co-oxidation reaction was followed by a reaction using peracetic acid. The solution consisted of 30 ml 50% H_2O_2 in glacial acetic acid and 5ml concentrated H_2SO_4. This solution must be added to coal very slowly and with cooling to prevent the rapid generation of heat. The temperature of the slurry was raised to 60°C for 2 hours.

D. Extraction

After co-oxidation and post-treatment, extraction of the coal was carried out to test whether the solubility of the coal had been enhanced. The extraction data of co-oxidized coal compared to that of the unreacted coal is an indication of the extent to which co-oxidation has altered the macromolecular coal structure.

Duplicate samples of the dried coal residue (about 5 g each) were weighed into pre-dried and pre-weighed extraction thimbles. Exhaustive Soxhlet extraction of each sample was carried out with about 250 ml refluxing DMF for 24 hours. The DMF was then drained and replaced with methanol for rinsing of the coal for a minimum of 6 hours to remove any residual DMF.

The thimbles were then dried using the previously described drying procedure.

The dried thimbles and residues were again weighed, and the loss in weight was calculated to give the percent extracted as follows:

$$\frac{\text{wt loss after extraction}}{\text{wt of pre-extracted residue}} \times 100\% = \text{percent extracted}$$

Data were reported on a relative basis as compared to the extractability of the raw coal.

RESULTS

Table IV through Table XV summarize the results of over 250 reaction trials. Each piece of data is an average of duplicate trials and is reported as compared to the extractability of the raw coal. Tables IV through VII present the results of preliminary studies carried out to determine the most effective solvents and conditions for co-oxidation. Tables VIII through XI show the effects of metal ion catalysts and the presence of mineral matter on co-oxidation. Tables XII and XIII and Figures 7 and 8 show analyses of the residues and soluble products after co-oxidation. Tables XIV and XV give results of post-oxidative treatments.

I. Solvent Screening

Table IV is a summary of 50 trials to determine a suitable co-oxidant for coal. From this data, cumene was chosen for further study because extraction values were as high for cumene as for any of the other potential solvents or mixed solvent systems: diphenylmethane, cumene/fluorene, tetralin, cumene/tetralin, acetic acid/dioxane and o-dichlorobenzene.

The reported values are for the extraction of co-oxidized coals only, i.e., no post-treatment for

TABLE IV

SOLVENT SCREENING[a]

Trial	Solvent	Temp., °C	Δ%Extracted[b]
22	cumene	100	-3
23	cumene	130	-1
4	1:1 cumene:DMF	100	-21
6	DMF	100	-18
19	benzonitrile	100	-9
20	1:1 cumene:benzonitrile	100	-7
2	o-dichlorobenzene	100	-2
10	1:1 cumene:o-dichlorobenzene	100	-4
11	diphenylmethane	100	-3
12	1:1 cumene:diphenylmethane	100	0
13	benzonitrile	150	-18
15	o-dichlorobenzene	150	-15
16	1:1 cumene:o-dichlorobenzene	145	-2
17	diphenylmethane	180	-8
18	1:1 cumene:diphenylmethane	160	-5
25	1:1 diphenylmethane:benzonitrile	130	-6
26	o-dichlorobenzene + 20g fluorene	130	-1
27	benzonitrile + 20g fluorene	130	-11
28	cumene + 20g fluorene	130	+1
29	tetralin	130	+2
30	1:1 cumene:tetralin	130	+2
31	diphenylmethane	130	-3
32	1:1 cumene:diphenylmethane	130	-1
32	1:1 cumene:diphenyl ether	130	-1
H-9	diphenyl ether	130	-4
100	dimethoxyethane	75	-9
101	cyclohexene	75	-5
102	dioxane	75	-6
103	1:4 4-picoline:dioxane	75	-13
105	1:4 ethylenediamine:dioxane	75	-14
106	1:4 acetic acid:dioxane	75	-2

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[a] All co-oxidations: 1:10 w/v coal to solvent, suitable initiator for temperature range, 1 atm O_2, stirred for 2 hours.

[b] Relative to extractability of raw coal into DMF.

hydroperoxide decomposition other than drying at 150°C was carried out prior to extraction. The data all show, at best, only a small increase in extractability after co-oxidation. Benzonitrile and DMF consistently gave poor results, as did the organic bases dioxane, 4-picoline and ethylenediamine.

II. Effect of Oxygen Pressure, Temperature and Time

Table V gives results of varying co-oxidation reaction conditions. Both increased temperature (above 100°C) and increased pressure (above 1 atm) had little influence on the extractability of co-oxidized coal. Increased reaction time (beyond 2 hours) also did not enhance extractability. From this data, a "standard" co-oxidation was established as a basis for comparison of post-oxidative treatments:

1:10 w/v coal:cumene
1 g ABIN
100°C
1 atm O_2
stirring for 2 hours.

III. Effect of Swelling Solvents

Table VI shows that using a solvent known to swell coal prior to or during co-oxidation did not enhance extractability. Cumene has been shown to swell coal(52) and in reactions with cumene as the co-oxidant (shown in previous tables), no additional benefits from swelling were observed.

TABLE V

EFFECT OF TEMPERATURE, PRESSURE, AND TIME ON CO-OXIDATION OF COAL[a]

Trial	Temp, °C	O_2 Press, atm	Time, hrs	**Δ**% Extracted[b]
22	100	1	2	-2
23	130	1	2	0
41	130	6.8	1	+8
65	168	2.7	0.5	-6
69	185	1.7	1.0	-7
71	130	3.4	0.5	-6
72	85	1	0.5	-7
73	31	2.9	0.5	-4
75	69	2.6	0.5	-5
113	85	1	6.5	+1
78	160	1	0.75	-8

[a] 1:10 w/v coal:cumene and appropriate initiator.

[b] Relative to extractability of raw coal into DMF.

TABLE VI

EFFECT OF SWELLING SOLVENTS ON THE CO-OXIDATION OF COAL

Trial	Swelling Treatment	Co-oxidation[a]	Temp, °C	Time, hrs	Δ %Ext'd
33	60 hr soak in 50 ml CS_2 prior to co-oxidation	Cumene	130	2	-2
34	"	1:1 cumene:tetralin	130	2	-1
35	"	tetralin	130	2	+1
37	"	o-dichlorobenzene	130	2	0
97	Co-oxidation with DMF	3:1 cumene:DMF	85	2	-8
236	"	3:1 cumene:DMF	85	26	+2
237	"	8:1 cumene:DMF	85	21	-2

[a] 1:10 w/v coal:solvent, appropriate initiator, 1 atm O_2.

[b] Relative to extractability of raw coal into DMF.

IV. Effect of Base

The highest extraction results, up to 49% (Δ = +18%), were obtained after co-oxidation in the presence of aqueous or alcoholic base. Table VII shows the effect of base on co-oxidation. Using elevated temperatures and pressures with an alkaline solvent system had the same negative effect on the extractability of the co-oxidized coal as was found in the neat solvent systems (Tables IV-VI).

V. Effect of Metal Ion Catalysts

Table VIII shows the results of trials carried out to determine the effect of metal ion catalysts on co-oxidation. No increase in extractability was observed when catalysts were added to the co-oxidation mixture.

VI. Effect of Mineral Matter

Table IX gives the proximate and ultimate analyses of a coal before and after commercial washing. Ash and pyritic sulfur were significantly reduced. Table X shows the extraction data for these coals before and after co-oxidation. The co-oxidized washed coal showed a slight increase in extractability relative to the unwashed co-oxidized coal.

The use of chelating reagents to remove or bind mineral constituents had a negative effect on co-oxidation (Table XI).

TABLE VII

EFFECT OF BASE ON THE CO-OXIDATION OF COAL[a]

Trial	Base[b]	Temp, °C	O_2 Press, atm	Time, hrs	Δ%Ext'd[c]
45	pH 10 Na_2CO_3	100	1	1.5	+13
46	pH 10 Na_2CO_3	100	1	3	+4
52	pH 10 Buffer	100	1	1	+18
81	pH 10 Buffer	160	1.5	0.75	-10
84	pH 10 Buffer	160	1	0.75	-9
91	10% KOH in t-butyl alcohol	130	1.5	0.75	-9
94	10% KOH in t-butyl alcohol	85	1	3	+6
95	10% KOH in t-butyl alcohol	85	1	1	+10
85	pH 10 Buffer[d]	100	1	1	-6
96	10% KOH in t-butyl alcohol[d]	85	1	1	+13
121	10% KOH in t-butyl alcohol[d]	85	1	1	+17
107	10% KOH in t-butyl alcohol[e]	85	1	1	+7

[a] 1:10 w/v coal:cumene, appropriate initiator.
[b] 2:1 base:solvent.
[c] Relative to extractability of raw coal into DMF.
[d] No cumene present.
[e] No cumene or O_2 present. (N_2)

TABLE VIII

EFFECT OF METAL ION CATALYSTS ON CO-OXIDATION OF COAL

Trial	Co-oxidation Conditions	Catalyst	Δ% Extracted[a]
120	"Standard"[b]	none	-4
108	"	Co^{2+}naphthenate	-4
119	"	Co^{2+}naphthenate	-7
69	185°C,1.7 atm O_2,1 hour[c]	$Co(acac)_3$	-7
78	160°C,1 atm O_2, 0.75 hour[c]	$Co(acac)_2$	-9
206	90°C,1 atm O_2, 2 hours[c]	$Co(acac)_2$	-6
207	130°C,1 atm O_2, 2 hours[c]	$Co(acac)_2$	-3

---

[a] Relative to the extractability of raw coal into DMF.

[b] 1:10 w/v coal:cumene, initiator, 100°C, 1 atm O_2, 2 hours.

[c] 1:10 w/v coal:cumene, initiator.

TABLE IX

ANALYSIS OF A COAL BEFORE (No.82039) AND AFTER (No.82040) COMMERCIAL CLEANING

PROXIMATE ANALYSIS[a]	82039	83040
Moisture	6.88	8.62
Ash	25.97	10.71
Volatile Matter	33.08	40.95
Fixed Carbon	34.07	39.72
ELEMENTAL ANALYSIS[a]		
Carbon	50.02	62.53
Hydrogen	3.88	4.72
Nitrogen	.87	1.12
Total Sulfur	5.63	3.41
Pyritic	2.91	1.19
Organic	2.09	2.14
Oxygen (by diff.)	6.74	8.88

[a] As determined.

TABLE X

CO-OXIDATION OF A WASHED COAL vs AN UNWASHED COAL

Sample	Δ% Extracted
Unwashed, unoxidized	17
Unwashed, co-oxidized[a]	17
Washed, unoxidized	27
Washed, co-oxidized[a]	19

[a] "Standard" co-oxidation.

TABLE XI

EFFECT OF CHELATING REAGENTS ON THE CO-OXIDATION OF COAL

Trial	Procedure	Δ% Extracted[a]
125	"Standard" co-oxidation + 1g NTA in 100 ml acetic acid	-10
126	Coal slurried in 200 ml water + 1g NTA, stirred for 2 hours at ambient temperature followed by filtration and "standard" co-oxidation	-3
127	"Standard" co-oxidation + 100ml acetic acid (no NTA)	-14
129	Coal slurried in 200 ml pH 10 buffer + 1g NTA, stirred for 2 hours at ambient temperature, followed by filtration and "standard" co-oxidation	-10
502	"Standard" co-oxidation + 1g 2,2'-bipyridine	-7

[a] Relative to extractability of raw coal.

VII. Oxygen Uptake Analysis

Table XII shows the ultimate analyses of three coals before and after co-oxidation. It is demonstrated that coal is taking up oxygen during co-oxidation, but the nature of the oxygenate species cannot be determined from this data.

Figure 7 shows a partial infrared spectrum of coal before and after co-oxidation. The peak at 1697 cm^{-1} corresponds to the presence of the carbonyl group, in particular one of a keto-type structure. This observation does not support the proposed formation of the hydroperoxide groups during co-oxidation which is fundamental to the depolymerization scheme.

VIII. Co-oxidation Filtrate Analysis

Gas chromatographic analysis of the filtrate from co-oxidation was used to determine the extent of oxidation. Cumene oxidized in the absence of coal was found to achieve up to 50% conversion to oxidation products (acetone, phenol, acetophenone, and phenylethyl alcohol). Figure 8 is a chromatogram of the filtrate recovered from a standard coal/cumene co-oxidation. Some of the peaks correspond to the oxidation products of cumene,and the remainder are cumene soluble oxidation products from the coal. The reduction in percent cumene (100% before co-oxidation) taken from the integrated peak area confirms that some oxidation of the solvent has taken place. However, since the extent of cumene oxidation in the absence of coal was as much as

TABLE XII

ANALYSES OF COALS BEFORE AND AFTER CO-OXIDATION (SELECTED TRIALS)

Coal (Trial)	M**	VM	Ash	C	H	N	S	O**
9100	7.09	40.6	8.36	74.08	5.11	1.50	3.59	7.34
(1-40[a])	1.67	37.01	7.68	73.72	5.05	1.68	2.93	8.94
9036	5.33	46.8	6.44	76.48	5.37	1.60	3.29	6.79
(253[b])	0.87	36.59	5.71	75.38	5.09	2.08	2.71	9.03
7827	2.84	35.88	9.49	74.49	5.22	1.53	3.33	5.94
(66[c])	2.01	36.64	9.28	75.20	5.24	1.50	3.10	5.68
(A-1[d])	0.45	37.06	9.32	73.59	5.00	1.58	3.19	7.32
(A-2[e])	1.08	35.86	9.51	73.10	4.98	1.56	3.01	7.84

** Moisture, as determined; other values on dry basis; Oxygen by difference

[a] 2 hr., 1 atm.O_2, 90°C, 1:10 (w/v) Coal:Cumene

[b] 15 hr., 1 atm.O_2, 115°C, 1:10 (w/v) Coal:Cumene + 0.1M $Co(ac)_2$ and 0.1 M HBr

[c] 0.5 hr., 20 psig. O_2, 165°C, 1:15 (w/v) Coal:Cumene

[d] 3 hr., 1 atm.O_2, 90°C 1:15 (w/v) Coal:Cumene

[e] 2 hr., 20 psig. O_2, 115°C, 1:2 (w/v) Coal:Cumene, + 0.1M $Co(ac)_2$ and 0.1M HBr

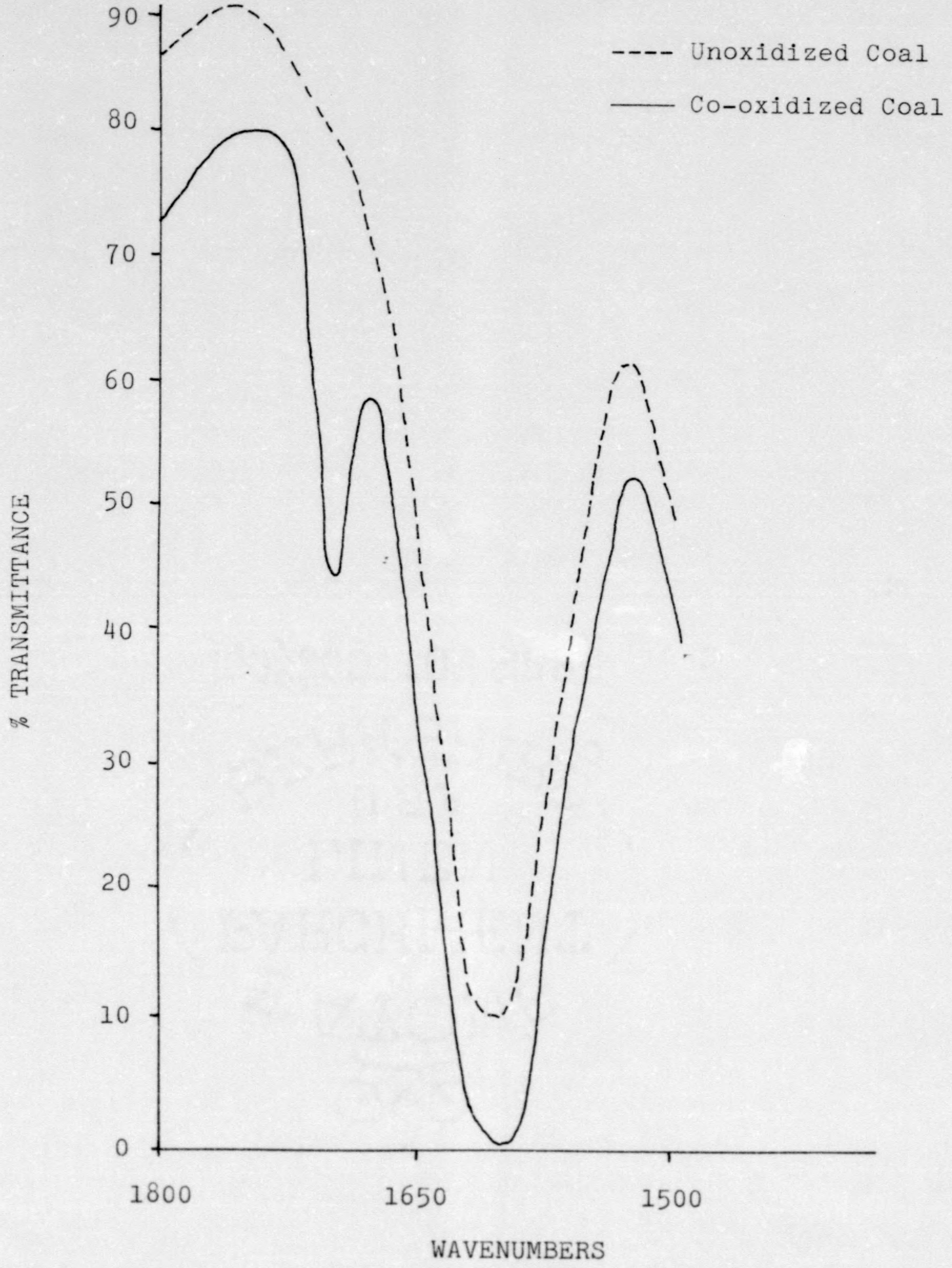
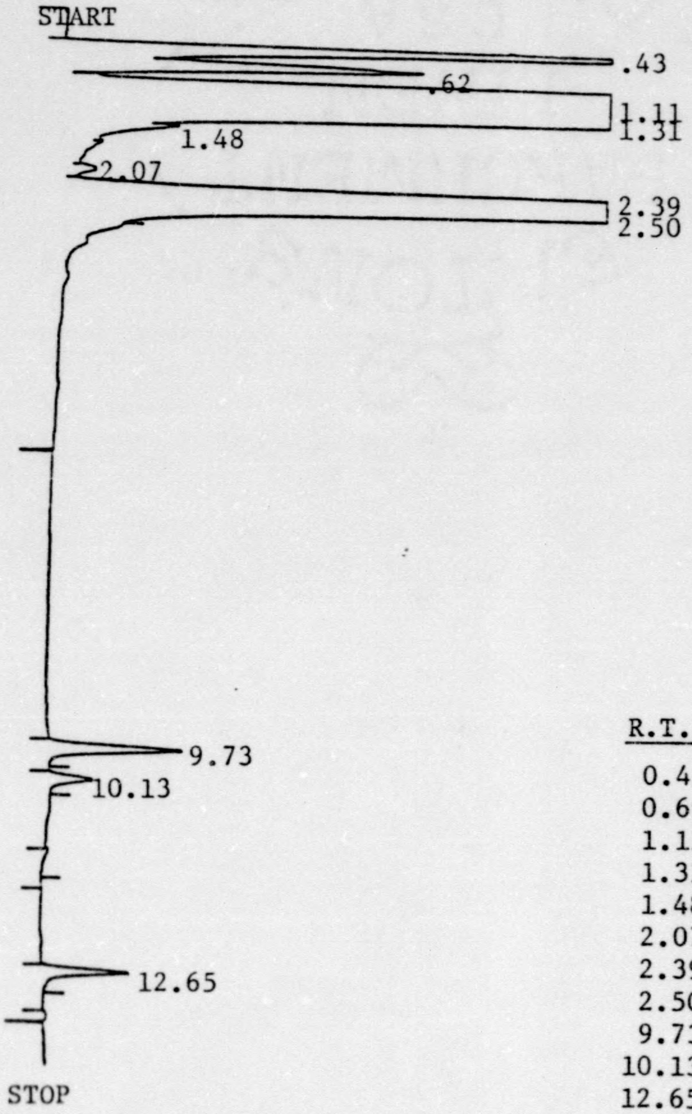


Figure 7. Partial Infrared Spectrum of a Coal Before and After Co-oxidation



R.T.	Area %
0.43	6.195
0.69	1.012
1.11	72.281
1.31	4.060
1.48	0.413
2.07	0.069
2.39	9.396
2.50	5.738
9.73	0.440
10.13	0.139
12.65	0.252

Figure 8. Gas chromatogram of the filtrate recovered from a standard co-oxidation (72% cumene)

twice that of the oxidation of cumene in the presence of coal, coal appears to be inhibiting oxidation of the solvent and therefore may be inhibiting co-oxidation of the mixture.

IX. Hydroperoxide Determination

Table XIII gives the results of hydroperoxide determination by iodine titration. No appreciable quantity of hydroperoxide was detected in co-oxidized coal or solvent.

X. Effect of Post-oxidative Treatment

Table XIV shows the effects of thermolysis as a method for hydroperoxide decomposition. Although several entries in the Table show relatively high increases in extractability, these results could not be duplicated. Thermolysis did not consistently enhance extractability. Extraction after thermolysis of raw coal gave -4% relative extractability to the raw coal.

Table XV shows the results of various chemical methods tested for hydroperoxide decomposition or ketone cleavage. Of these methods, a basic rather than an acidic system resulted in higher extractability.

TABLE XIII

DETERMINATION OF HYDROPEROXIDES BY IODINE TITRATION

Sample	mMoles Hydroperoxide
cumene hydroperoxide, commercial	12.8[a]
cumene, recovered from co-oxidation	2.4[b]
coal, unreacted	0.5[c]
coal, unreacted	0.5[d]
coal, co-oxidized	0.5[e]
coal, co-oxidized	0.1[f]

[a] 90% calculated titer

[b] 12% conversion to products as determined by gas chromatography. This titration value corresponds to less than 1% hydroperoxide content. Average of four determinations.

[c] Average of six determinations made at room temperature.

[d] Average of two determinations made under reflux.

[e] Average of eight determinations made at room temperature.

[f] Average of four determinations made under reflux.

TABLE XIV

EFFECT OF THERMOLYSIS ON THE EXTRACTABILITY OF CO-OXIDIZED COAL[a]

Trial	Δ% Extracted[b]
1	+10
2	+ 6
3	+20
4	+19
5	0
6	- 2
9	+ 3
10	- 8
13	-20
14	- 6
15	- 6
17	- 6
18	- 3
19	+ 5
20	- 3
21	-19
22	+ 5
23	+ 2
24	-12
25	-14
26	-11

---

[a] Samples held at 260°C for 10 minutes in N_2 atmosphere.

[b] Relative to the extractability of the co-oxidized coal.

TABLE XV

EFFECT OF POST-OXIDATIVE TREATMENT ON THE EXTRACTABILITY OF CO-OXIDIZED COAL[a]

Trial	Post-oxidative Treatment	Δ% Extracted[b]
109	Coal + 50ml N_2H_4; reflux for 24 hrs.	-8
110	Coal + 50ml sat'd KI + 50ml 3:2:1 acetic acid:chloroform:isopropyl alcohol; stirred for 24 hours at ambient temperature	+7
112	Coal + 50ml sat'd KI + 50 ml 3:2:1 acetic acid:chloroform:isopropyl alcohol; stirred for 24 hours at 50°C	+1
111	Coal + 150ml 2% H_2SO_4 in acetone; stirred for 2 hours at 60°C.	-3
128	Coal + 200ml 2% H_2SO_4 in acetone; stirred for 1 hour at 60°C	-13
117	Coal + 200ml KOH/alc + 2atm O_2; stirred for 1 hour at ambient temperature	+3
119	Coal + 200ml KOH/alc + ABIN + Co^{2+}; reflux 1 hour at 82°C	+12
123	Coal + 200ml KOH/alc + 2atm O_2; stirred for 2.5 hours at 130°C	0
124	Coal + 50ml CH_3CN + 10ml(CH_3CN + 10 drops H_2SO_4); reflux at 80°C for 2 hours	-8
133	Coal + 60ml glacial acetic acid + 5ml H_2SO_4 + 30ml H_2O_2; refluxed at 60°C for 2 hours	-7

---

[a] "Standard" co-oxidation.

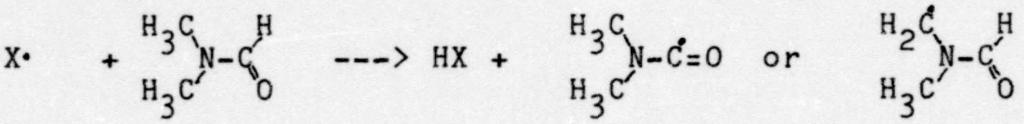
[b] Relative to extractability of raw coal.

DISCUSSION

I. Solvent Screening

A successful co-oxidant will contain an alkyl C-H bond which is reactive toward homolytic cleavage and will thus perpetuate the desired co-oxidation reactions. The data supports this in that trials using cumene, tetralin and diphenylmethane resulted in higher extraction values than trials using benzonitrile or o-dichlorobenzene which do not readily lend themselves to homolytic cleavage and free radical formation.

Under oxidative conditions, DMF has been reported to undergo free radical addition reactions:(53)



(X• represents the RO• product of the decomposition of peroxy compounds). Both DMF radicals selectively attack protonated heteroaromatic bases to form the corresponding substitution products.

Heteroaromatic units are present in coal.(54) Therefore these addition reactions could possibly account for the extremely low extraction values obtained in trials using DMF as the co-oxidant: DMF may be incorporated into the coal under the co-oxidative conditions.

The organic bases were used in an attempt to disrupt hydrogen bonding within the coal matrix. Extraction values were not enhanced using these solvent systems. The highly crosslinked coal matrix may also be a barrier to sufficient penetration of the bases into the network for effective disruption of hydrogen bonds.

II. Effect of Oxygen Pressure, Temperature and Time

Although the rate of oxidation of coal is increased with increasing temperature,(55,56) using elevated temperatures during co-oxidation did not enhance extractability. Temperatures approaching the boiling point of the solvent system lower the oxygen solubility and therefore the extent of co-oxidation can be expected to be diminished. The higher temperatures may also be promoting undesirable reactions such as char formation or dehydrogenation. Using elevated pressure to raise the boiling point of the system and to permit reactions at higher temperatures was not successful. Increased oxygen pressure alone may cause further crosslinking of the coal matrix through the formation of ether or peroxy linkages.(15,18)

The failure of extended reaction times to lead to higher extraction values may be an indication that the maximum extent of hydroperoxide formation has been achieved under these conditions in a relatively short amount of time.

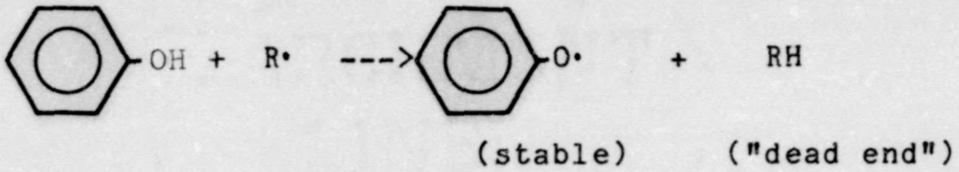
III. Effect of Swelling Solvent

It was proposed that if coal was subjected to swelling by a solvent, co-oxidation could occur more extensively within the coal matrix. This was not observed. Carbon disulfide has been shown to swell coal, and yet extractability of co-oxidized coal was not enhanced by prior treatment with CS_2. A possible explanation for this may be that at the co-oxidation reaction temperature (130°C), well above the boiling point of CS_2 (46.3°C), the CS_2 is boiled off and the molecular structure of the coal returns to its original dimensions (the swelling action of solvents on coal has been shown to be a reversible process).(57)

DMF is known to be an excellent solvent for swelling coal. That the benefits of swelling by DMF when used as a co-solvent during co-oxidation were not observed may be due, at least in part, to the fact that DMF undergoes addition reactions under oxidative conditions. Effective inhibition of co-oxidation by DMF could therefore be occurring. Reducing the ratio of DMF to cumene did not overcome the barrier of inhibition.

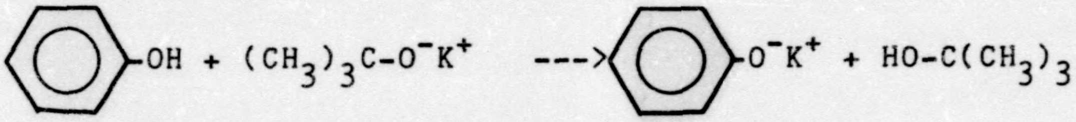
IV. Effect of Base

It is known that phenol and phenolic species are inhibitors of oxidation.(58) Phenolics can react with any free radical to form a radical stabilized by resonance and a "dead end" in the cycle of oxidation reactions, e.g.,



Phenolic species are present in coal(59) and phenol is an oxidation product of cumene. Effective inhibition of the desired co-oxidation reactions could occur as phenolics accumulate in the reaction mixture.

In the commerical production of acetone and phenol from cumene, an emulsion is used which keeps the oxidizing cumene in contact with aqueous base, thus neutralizing the phenolics as they are formed. This is a reasonable explanation for the dramatic increase in extractability for the solvent/base systems over the neat solvent or co-solvent systems. In the presence of base, the phenolics are neutralized, e.g., with potassium t-butoxide:



There is evidence that reactions other than co-oxidation are taking place in this basic system since enhanced solubility was also observed when the co-oxidation reaction was carried out in alcoholic alkali in the absence of an oxidizable co-solvent. It is believed basic hydrolysis is occurring at ester groups inherently present in the coal molecular structure. This was supported in an experiment in which coal and base were reacted under nitrogen and the standard co-oxidation conditions. Enhanced solubility was observed under non-oxidizing conditions.

It has been shown that refluxing alcoholic base alone does enhance the solubility of coal.(60-62) The principle reaction is considered to be hydrolysis. At temperatures of 335-400°C, Ross and Blessing(60) propose a hydride transfer process whereby hydrogen is transferred to the coal from the alcohol or alkoxide salt, e.g., in the case of isopropyl alcohol and KOH:

$$^{-}OCH(CH_3)_2 + \text{coal} \dashrightarrow O{=}C(CH_3)_2 + \text{coal}H^{-}$$

$$\text{coal}H^{-} + HOCH(CH_3)_2 \dashrightarrow \text{coal}H_2 + {}^{-}OCH(CH_3)_2$$

Although co-oxidation in the presence of base resulted in relatively high extraction values, it was decided that this was not a co-oxidative process at all. No further investigation was made of this medium.

V. Effect of Metal Ion Catalyst

Transition metal ions are known to catalyze the production of oxy- and peroxy-free radicals.(63-65). It was thought that addition of a metal ion catalyst to the reaction mixture would aid the proposed co-oxidation scheme. Although not drastic, effects to the contrary were observed. This was an indication that undesired reactions were possibly taking place under the co-oxidation conditions. Indeed, a review of the literature revealed that several investigations have been carried out showing that transition metal ions catalyze the formation of ketones in organic hydrocarbons under oxidative conditions.(66) The decomposition of tetralin hydroperoxide in the presence of transition metal ions yields tetralone rather than C-C bond cleavage.(67) This reaction occurs as low as 80°C in 2 to 3 hours, so it is possible this reaction could also occur during co-oxidation.

If keto groups are in fact formed from hydroperoxides during co-oxidation, the possibilities for hydroperoxide decomposition and C-C bond cleavage do not exist. Since extraction values were not increased with the addition of transition metal ion catalysts to the co-oxidation mixture, the formation of keto groups could be a possible explanation.

VI. Effect of Mineral Matter

Since the addition of catalysts to the co-oxidation mixture was found to decrease the solubility of the coal, it was proposed that metal ions present in coal may be causing spontaneous peroxide decomposition during co-oxidation of coal, and were thus preventing the necessary formation of peroxy and hydroperoxy species in the solvent and in the coal.

Two methods were employed to remove mineral matter from coal. A comparison was made of the co-oxidation of a coal sample before and after commerical cleaning. Co-oxidation of the unwashed sample did not appear to affect the extractability into DMF. For the washed coal sample, the decreased extraction value after co-oxidation was consistent with previous co-oxidation trials. In comparing the co-oxidation of the washed and unwashed samples, it is important to note the slight increase in extractability of the co-oxidized washed coal (+19%) over the co-oxidized unwashed coal (+17%). This may be an indication that metal ions which catalyze the formation of ketones from hydroperoxides were removed during the cleaning process.

The use of chelating reagents to bind or remove mineral matter from coal appeared to have little or no effect on co-oxidation. This may be due to an insufficient quantity of the chelating agent or insufficient chelation under the conditions and time period used.

VII. Oxygen Uptake Analysis

Elemental analysis confirmed the incorporation of oxygen into coal during co-oxidation. Infrared analysis did not reveal the presence of peroxy groups in co-oxidizezd coal. Although a characteristic O-O stretching frequency is not very strong and cannot be assigned with any certainty, the overall range where one may expect to observe the O-O stretching band is 1000 to 830 cm^{-1}.(68) No peaks were found in this range. However, enhanced absorbance was observed in the carbonyl range, 1650 to 1790 cm^{-1}. The carbonyl stretching band of simple aliphatic ketones is found at approximately 1715 cm^{-1}; aryl group conjugation lowers this frequency.(68) A carbonyl group on an aliphatic bridge in coal is very likely to be in conjugation with one or possibly two aryl groups. Therefore the peak at 1697 cm^{-1} is believed to indicate the presence of a keto-type carbonyl structure.

The formation of ketones in coal during co-oxidation can be explained by contrasting the tertiary hydroperoxide of cumene with the secondary hydroperoxides which would be formed at the aliphatic bridging sites in coal. The tertiary site ensures C-C bond cleavage on subsequent decomposition of the hydroperoxide via beta-scission, whereas the secondary site provides a C-H bond which would preferentially cleave,(69) leading to the formation of a ketone. Also, mineral matter inherently present in the coal may catalyze the formation of ketones from hydroperoxides.

VIII. Co-oxidataion Filtrate Analysis

Oxidation of the solvent is essential for the formation of hydroperoxides in coal during co-oxidation. Gas chromatographic analysis of the filtrate from co-oxidation revealed the oxidation of cumene to be greatly inhibited in the presence of coal. Phenolic species in the coal could account for this inhibition.

IX. Hydroperoxide Determination

The failure of infrared analysis and titration to detect hydroperoxides in co-oxidized coal or solvent does not imply that hydroperoxides were never formed; hydroperoxide decomposition may occur during co-oxidation. For example, hydroperoxides may be catalytically converted to ketones or thermally decomposed during the co-oxidation reaction. The role of mineral matter in the catalysis of ketone formation has already been suggested.

Standard co-oxidations were run at 100°C; peroxygen complexes in coal are markedly unstable above approximately 70°C.(55) Therefore, post-oxidative titration may not reveal the maximum amount of hydroperoxide formation.

Also, the inability of titration to detect hydroperoxides may lie in the method itself. The reaction

$$\mathrm{HOOH} + 2\mathrm{I}^- + 2\mathrm{H}^+ \ \text{--->}\ \mathrm{I}_2 + 2\ \mathrm{H}_2\mathrm{O}$$

between coal and sodium iodide takes place in acetic acid which also participates in the reaction; iodine is then titrated and the quantity of hydroperoxides is calculated. Acetic acid is not expected to be a good swelling solvent for coal,(47) and therefore would not enter into the pore structure to any great extent. For this reason, too, the maximum amount of hydroperoxide formation may not be detected.

X. Effect of Post-Oxidative Treatment

It was proposed that thermal decomposition of hydroperoxides would be the most efficient method by which C-C bond scission could be achieved. However, the results of thermolysis were erratic. It is believed that undesirable reactions were occurring at the thermolysis temperature (250°C). Char formation would account for reduced extractability. Productive reactions resulting in C-C bond cleavage are also likely to have occurred. This would account for solubility enhancement. Overall, consistent results were not obtained. It was decided that the high temperature of thermolysis may not be necessary and that effective hydroperoxide decomposition could be achieved during the drying of co-oxidized coal at 150°C.

Although slight solubility enhancement was observed with chemical decomposition of hydroperoxides by reduction by iodide, chemical methods did not appear to be successful. Hydroperoxide decomposition may have occurred during co-oxidation or during the drying stage. Also, the media in which these reactions were run, e.g., acetone or acetic acid, were not good swelling solvents for coal and therefore hydroperoxide decomposition reactions are unlikely to have taken place within the coal matrix.

It was proposed that if ketones were being formed in coal during co-oxidation, subsequent treatment for ketone cleavage would result in C-C bond scission in coal.

Slightly positive results were obtained with the basic media for ketone cleavage--based on the work of Doering and Haines,(48) who showed that ketones and esters undergo C-C bond scission in t-butoxide media. These results are consistent with the observation that coal does exhibit enhanced solubility after treatment with alkaline solution.

The treatment of co-oxidized coal with peracid in order to achieve ketone cleavage did not appear successful. The strongly oxidizing medium of peracid may have caused additional oxygen uptake in coal via Baeyer-Villiger type oxygen insertion reactions.(50)

CONCLUSIONS AND RECOMMENDATIONS

Co-oxidation has been shown to alter the structure and solubility of coal. However, the alteration does not appear to be beneficial. Many trends were observed which provide the basis for several recommendations:

1) Co-oxidation of subbituminous coals or lignites may yield more soluble products than the hvC or hvB bituminous coals used in this study.
2) Chemical demineralization of coal prior to co-oxidation may eliminate the catalyzed formation of ketones from hydroperoxides.
3) Lower temperatures (less than 70°C) during co-oxidation may prevent the spontaneous decomposition of hydroperoxides.
4) Further investigation of aqueous base/solvent systems for co-oxidation may prove beneficial.
5) Lower temperatures (less than 150°C) may be effective for thermal decomposition of hydroperoxides after co-oxidation and may eliminate char formation.

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