SECTION 5

GENERAL SESSION

TVA'S GAS PROCESSING EXPERIENCE IN SUPPORT OF METHANOL PRODUCTION FROM COAL

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TVA'S GAS PROCESSING EXPERIENCE IN SUPPORT OF METHANOL PRODUCTION FROM COAL

Previous papers have discussed the need and desirability of methanol production in conjunction with electric power production. A methanol unit would be coupled with an integrated coal gasification combined-cycle power production facility. Those papers also covered the anticipated design needs to overcome some of the unique problems facing methanol production when using coal as the source gas. This paper will cover the operating experience TVA has had with the gas cleaning and processing units when operating in modes compatible with traditional methanol production, that is, with carbon monoxide shift to produce a "balanced" CO and hydrogen ratio. Also covered is experience with the "once-through" methanol production concept with no prior CO shift. The latter operational mode is desirable and offers advantages to the power industry because it conserves both energy and capital costs.

Background and description were given at last year's conference and was mentioned in previous papers at this conference. For the reader's convenience, a brief description of the TVA advanced coal gasification technology facility (formerly the Ammonia from Coal Project) is given here.

The facility was designed to retrofit to the front end of an existing 225-ton-per-day ammonia plant. The purpose of the project was to study the technical, economic, and environmental aspects of substituting coal for natural gas to produce ammonia. The synthesis gas was designed to match the gas composition, temperature, pressure, and 60-percent flow rate of the gas between the high- and low-temperature shift conversion units in the ammonia plant. The coal gasification facility was sized to supply synthesis gas equivalent to about 150 short tons per day of ammonia. The principal operations in the plant are indicated in the flow diagram, Figure 1. The partial oxidation process, licensed by Texaco Development Corporation, is used for gasification. Sized coal (minus 1/2-inch) is fed at about 8 short tons per hour, mixed with condensate from the ammonia stripper at the wastewater treatment unit, and ground to 100 percent less than 14 mesh forming a slurry containing at least 55 percent solids. The slurried coal reacts with oxygen in the upper, refractory-lined section of the

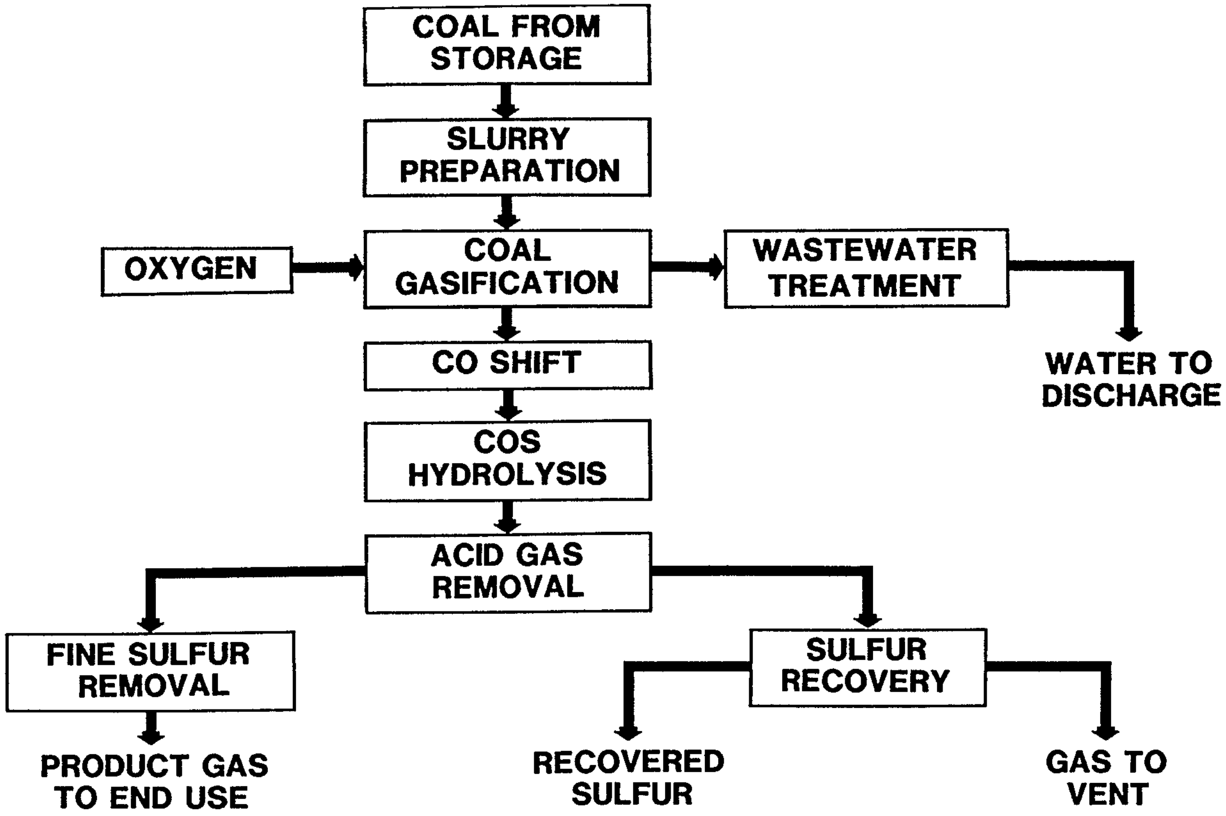


Figure 1. TVA's Coal Gasification Flow Diagram

gasifier. The molten slag is quenched in a water pool in the bottom of the gasifier and removed through a lockhopper to a drag conveyor for dewatering. Wet gas from the quench section is water-scrubbed for particulate removal. Quench water is clarified for solids removal before returning (through the scrubber) to the gasifier. Part of the clarifier overflow is removed to the wastewater treatment unit for control of dissolved solids.

After scrubbing, the raw gas flows to two sulfur-activated carbon monoxide shift catalyst units in series and then to a carbonyl sulfide hydrolysis unit. As much as possible of the carbonyl sulfide must be converted to hydrogen sulfide because carbonyl sulfide cannot be recovered by the Holmes-Stretford sulfur recovery process. The catalyst for all three units was originally supplied by Haldor Topsoe, Inc. However, the shift catalyst has been replaced with Shell Chemical's catalyst.

The shifted gas is cooled and sent to a Selexol unit (licensed by Norton Company) for removal of carbon dioxide and hydrogen sulfide. The acid gas is processed in a Holmes-Stretford unit provided by Peabody Process Systems, Inc., for sulfur recovery. Elemental sulfur is produced and removed as wet filter cake. The Holmes-Stretford unit had two recovery trains--one for cleaning the carbon dioxide to vent standards, another for demonstrating cleanup to urea feedstock specification.

High-purity nitrogen from the air separation plant is added to the purified synthesis gas after acid gas removal. At this point, the gas contains about 1 ppm total sulfur which is reduced to 0.1 ppm by a zinc oxide bed, also provided by Haldor Topsoe, Inc. The gas is then further reheated, and demineralized water is added and vaporized to provide the proper steam-to-dry-gas ratio for final shift conversion in the ammonia plant.

The Selexol acid gas removal system and the COS hydrolysis unit were evaluated in both the CO shift mode and the shift bypass mode. In addition, levels of trace contaminants that are known to poison methanol catalyst were determined. The trace contaminant study was conducted during three coal gasification tests at TVA. These were Utah, Illinois No. 6, and Pittsburgh No. 8 coal tests. Supplementary data were also taken during the Maryland coal test. Results of these studies have been reported to EPRI in proprietary reports.

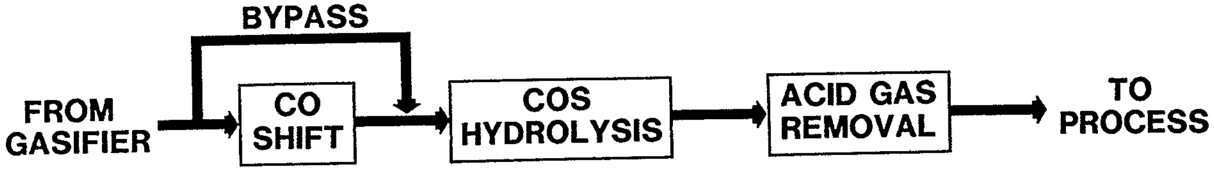
A nonproprietary report for publication covering results for all tests is now being completed. This paper covers the results of trace contaminants in the product gas at the inlet and outlet of the acid gas removal (AGR) system only. A zinc oxide bed is located downstream of the AGR. However, the bed is ineffective during shift bypass operation because heat from the shift operation is unavailable to heat the bed to its design temperature. The design of the once-through methanol project described in papers presented earlier will provide absorbent beds to handle the gas directly from the AGR system.

COS HYDROLYSIS

The COS hydrolysis unit was designed to handle gas with the CO shift reactors in operation. The shift reactors actually convert most of the COS in the process gas to H_2S. Typical COS concentrations in the gas to and from the COS hydrolysis unit for both the shift operation and shift bypass modes are shown on Figure 2. The gas compositions shown are for operations using Pittsburgh No. 8 coal. Operation with other coals, Illinois No. 6 and Maryland, having similar sulfur content was similar. In all cases, the COS level was essentially the same regardless of whether the CO shift units were bypassed. These results verified that the hydrolysis reactor is equilibrium limited at the conditions at our plant. Thus one major concern about operating in the shift bypass mode was eliminated. It was interesting to note one period of CO shift bypass operation during which the temperature of the catalyst bed decreased to about 360°F instead of the usual 400°F, the outlet COS concentration increased to over 50 ppm. As the temperature was brought back into line, the COS concentration decreased to its usual 8-10 ppm range.

SELEXOL ACID GAS REMOVAL

Since one of the main purposes of the study at TVA was to obtain data in support of the Cool Water project, it is important to understand the differences between the Cool Water and TVA's Selexol system. The major differences are listed in Table 1. First and foremost are the process requirements. The TVA unit was designed to produce a near sulfur-free gas (< 1 ppm total sulfur) because of downstream process requirements, in this case, the manufacture of ammonia. The Cool Water unit was designed to remove sulfur compounds to a level dictated by total poundage of SO_2 emission per million Btu. For the Cool Water unit, the total reduced sulfur in the product gas is 400 ppm for high sulfur (3.5 percent) and 70 ppm for low sulfur (0.35 percent) coals.



OPERATION[a]	COS, ppm INLET	COS, ppm OUTLET
WITH SHIFT	41	6
WITHOUT SHIFT	165	5
DESIGN WITH SHIFT	51	10

[a] a—Pittsburg No. 8 Coal

Figure 2. COS Composition of Gas To and From COS Hydrolysis Unit

Table 1

MAJOR DIFFERENCES BETWEEN COOL WATER AND TVA SELEXOL UNITS

Area	Cool Water	TVA
Absorber stages	1	2
Flash vessels, no.	1	4
CO_2 presaturator	no	yes
Stripper	Reboiler	N_2 Stripper
Sulfur recovery, %	97	99.9
Sulfur in clean gas, ppm	400	1

The TVA unit was also designed to remove a sizable fraction of the CO2, whereas the Cool Water unit was designed to remove the minimum amount of CO2. Other major differences are: number of absorption stages, operating temperatures, number and pressures of flash vessels, and method of regenerating the spent Selexol solvent. Figure 3 is a simplified schematic of both processes. The Cool Water unit treats raw gas in a single-stage absorber. The treated gas flows from the unit to downstream process, a gas turbine. Solution regeneration is accomplished by one flash stage (degassing stage) and a stripper operating with a steam-heated reboiler. Solution from the flash stage flows to the stripper and after stripping, flows to the absorber. Waste gases from the AGR unit is sent to sulfur recovery prior to venting. The TVA AGR unit treats the gas from COS hydrolysis in a two-stage absorber to meet the design specifications of one ppm total sulfur leaving the unit. The top absorber section uses lean solution from the stripper that has contacted the gas leaving the top section and has become saturated with CO2. The heat of CO2 absorption is removed prior to this solution being pumped to the top absorber section. Solution from the absorber is regenerated by flowing through the four flash vessels. This semilean solution is then split to flow to the bottom absorber section and to the stripper. The stripped, lean solution then flows to the top absorber section. The stripper operation uses nitrogen to decrease the absorbed gases to near zero levels. Gas from the first flash vessels is returned to the process gas stream upstream of the absorber. Gases from the remaining flash vessels and the stripper are sent to sulfur recovery prior to venting.

For power production, it is desirable to remove as little CO2 as feasible because of the potential energy of the CO2 at elevated pressures. Selexol's varying degrees of affinity for gases affords the opportunity to selectively remove certain compounds while permitting others to slip through. Table 2 shows the solubilities of various gases in Selexol with reference to methane. CO2 is less soluble than any of the sulfur compounds; therefore, for a given design, the CO2 slip can be varied to some extent by varying process variables. TVA conducted tests to determine the effect of solution temperatures and flow rates on CO2 slip while maintaining the sulfur level within the 1 ppm design limit. Unfortunately, after correcting major design errors in the AGR system, the opportunity to do test work was limited.

Table 3 shows the levels of CO_2 in the cleaned gas while operating in the shift bypass mode. The data were obtained during the Maryland coal run. Under baseline operating conditions, the CO_2 level at the absorber exit was 6.5 percent by

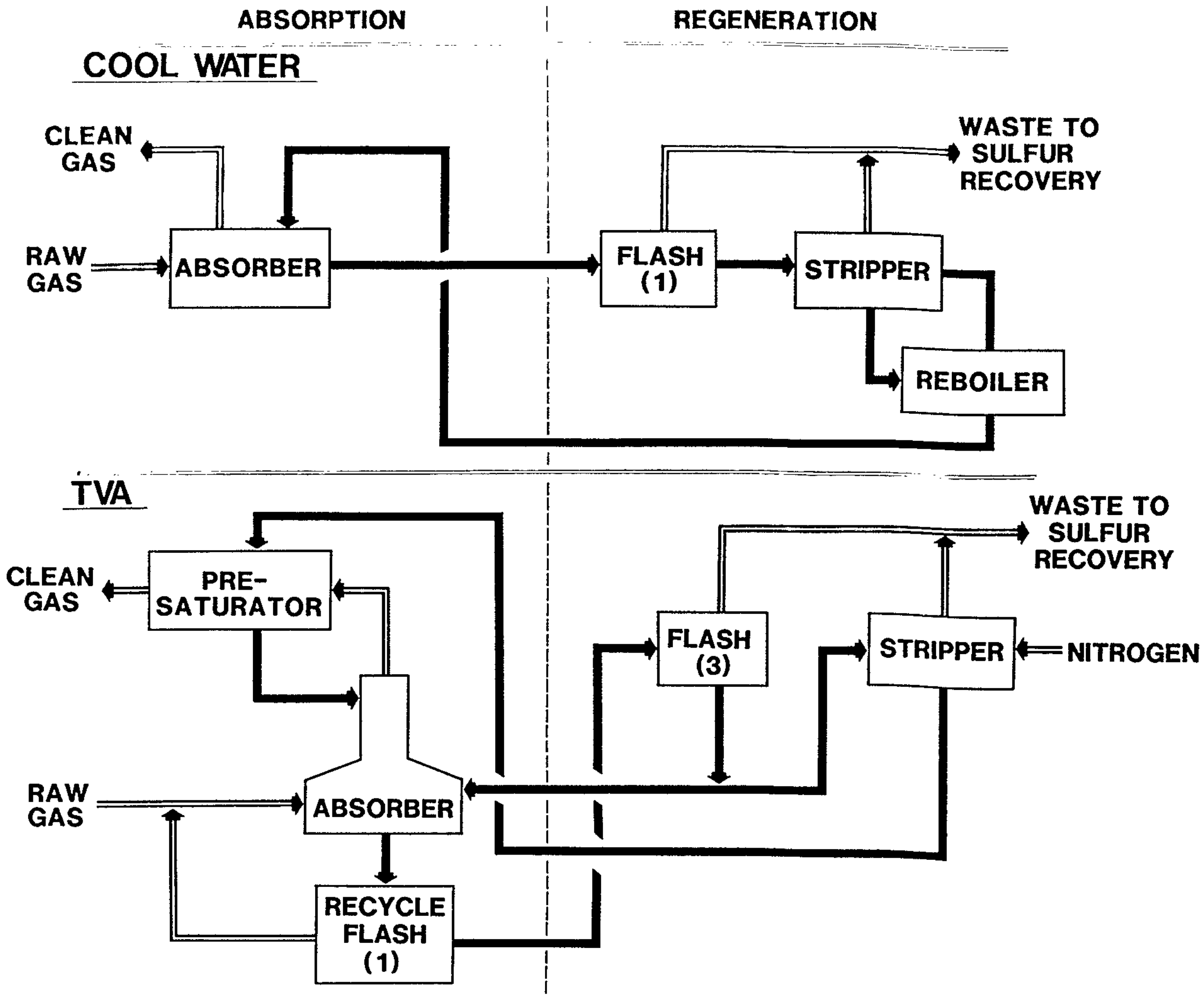


Figure 3. Schematic of Cool Water and TVA Selexol Processes

Table 2

SELEXOL
RELATIVE SOLUBILITIES
(70°F, 1000 PSIA)

Component	KC/KCH_4
H_2	0.20
CO	0.43
CH_4	1.0
C_2	6.4
CO_2	15.
COS	35.
NH_3	73.
H_2S	134.
CH_3SH	340
CS_2	360
H_2O	11,000
HCN	18,000

Table 3

CO_2 SLIP VERSUS SEMILEAN FLOW RATE
MARYLAND COAL TEST
SHIFT BYPASS OPERATION

Selexol flow rate,[a] % of baseline	CO_2, percent by volume			Sulfur, ppm
	To absorber	Exit bottom stage	Exit absorber	Exit absorber
100	18.8	9.7	6.5	0.9
83	18.8	11.0	7.5	NA
61	18.8	13.2	8.8	1.1
Design[b]	42.1	NA	19.5	1.0

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[a] Semilean Selexol to bottom stage; lean solvent to top stage constant at 100 percent of design in all tests.

[b] CO shift operation with 160 percent of baseline flow.

volume. By decreasing the flow of semilean solvent to the bottom section by 39 percent, the CO_2 content was increased to 8.8 percent, a 36 percent increase over the base case. Further increases could be accomplished by varying the temperature of the absorbing solution and adjustments to the lean and semilean solvent flow rates as has been demonstrated by Norton Company's computer-simulated runs.

TRACE CONTAMINANTS

Levels of trace contaminants that are known to affect methanol catalyst life were determined at various locations within TVA's gasification facility. Table 4 lists the components of interest and the design limit set by the catalyst manufacturers as being acceptable for a two-year productive life. There may be other components that should be included on the list. For example, arsenic or its compounds are believed to be involved in deactivating the CO shift catalyst at Tennessee Eastman and could conceivably cause problems with the methanol unit. TVA is working with Tennessee Eastman to determine trace component levels at their installation. Certain information from that work will be included in the final summary report covering the test work at TVA.

Figure 4 shows the location of the sampling points at TVA and the slipstream to which test cells of methanol catalyst were exposed. This paper, as stated before, is concerned only with the results of samples to and from the acid gas removal system. Results of the studies at other locations will be available from the summary report.

Table 5 lists the levels of components found in the gases to and from the AGR system during each of four coal test runs. Most of the data were obtained through gas stream sampling using wet chemical methods to capture and analyze the components. During all tests except the Maryland coal test, data on the metals and chlorides were also determined by analysis of the catalyst test cells. With the exception of the Illinois No. 6 coal run, total sulfur (H_2S plus COS) leaving the AGR unit was approximately 1 ppm or less. The solvent temperature was higher than normal during the Illinois No. 6 run and resulted in abnormally high total sulfur content. Further treatment for sulfur compounds is required, possibly with a "purple sandwich"--two zinc oxide beds separated by a hydrogenating catalyst bed to convert the COS to H_2S for removal by the second zinc oxide bed. Ammonia appears not to be a problem. Ammonia in the gasifier product gas is removed with condensate as the gas is cooled prior to entry into the AGR unit.

Table 4

METHANOL TRACE CONTAMINANT STUDY

Contaminant, ppm	Design Limit, ppm
Total sulfur (Primarily H_2S and COS)	0.06
NH_3	10.
HCN	0.01
Cl	0.01
Fe	0.04
Ni	0.01

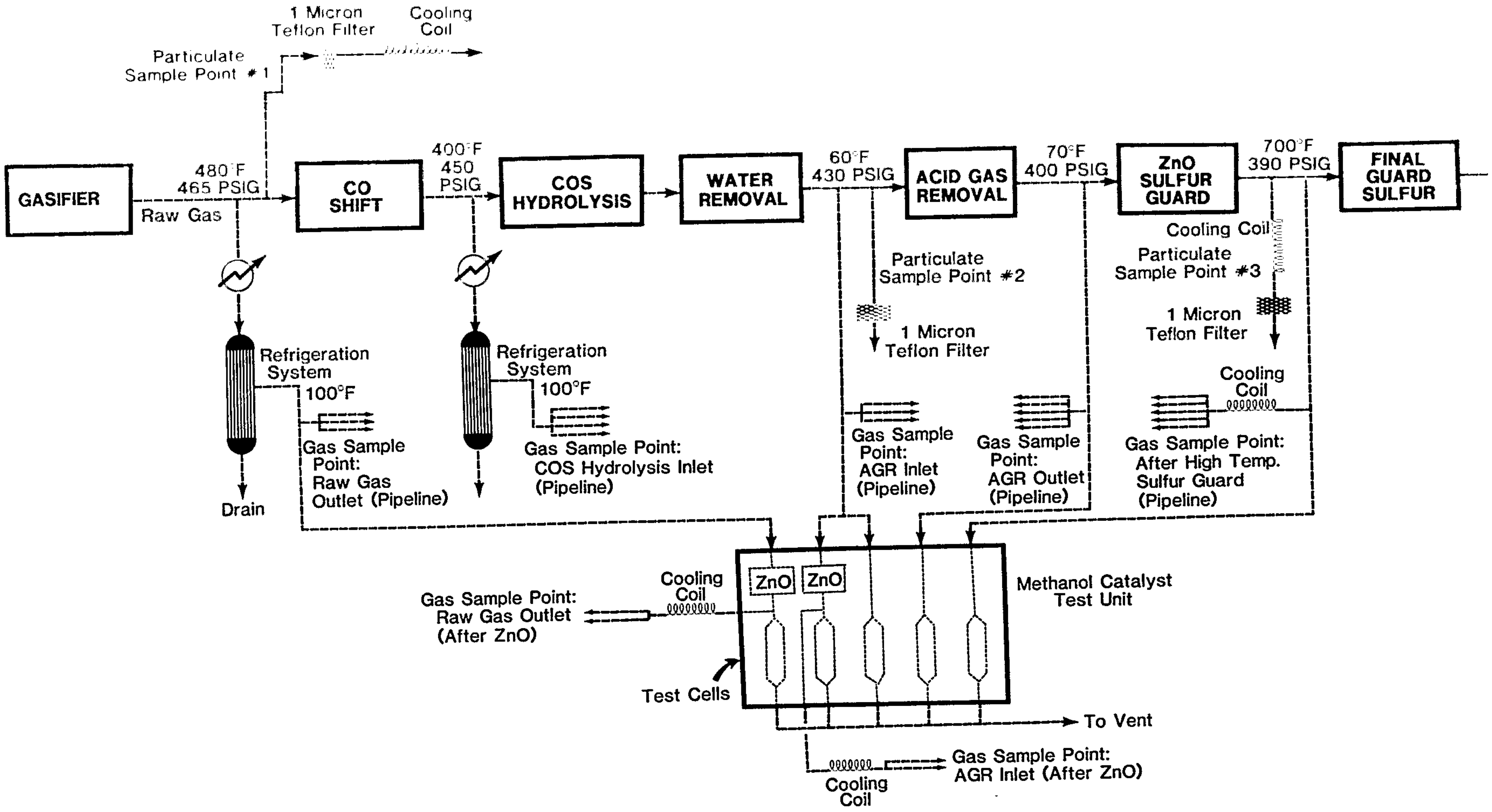

Figure 4. Gas and Particulate Sampling Locations

Table 5

TRACE COMPONENTS AT AGR (PPM)

	Illinois #6 (Unshifted)		Utah (Shifted)		Pittsburgh #8 (Unshifted)		Maryland (Unshifted)		Design Limit
	Inlet	Outlet*	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	
H_2S	13,500	12.4	1000	0.1	9500	0.7	6000	0.5	.06**
COS	18	4.4	2	0.4	6	0.2	10	0.2	-
NH_3	27	< 1	< 1	< 1	< 1	< 1	< 1	< 1	10
HCN	NA	0.22	24	.09	14	< 0.4	7.1	< 0.3	.01
CL	NA	< .001	NA	6.8	120	< 0.3	< .06	< 0.04	.01
FE	NA	.65	< .01	.01	1.2	.8	< .03	< .03	.04
NI	NA	0.2	.04	0.14	< .2	< .2	< 0.02	< 0.02	.01

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*AGR unit temperatures were higher than normal due to operating problems.

**Total Sulfur.

Cyanides leaving the AGR are higher than design limit. However, samples taken downstream of the high-temperature zinc oxide beds showed a decrease in passing through the beds and may not require special treatment other than that provided for the sulfur compounds. Also, HCN is extremely soluble in Selexol. Therefore, it may be possible to obtain the low design levels through operation of the AGR unit under proper steady-state conditions.

The numbers for chlorine are inconclusive. The problem has been partly sampling and partly analytical at the extremely low levels. An absorbent bed may or may not be required for the chlorides.

Iron carbonyls are present at levels slightly above the design limit. Because it decomposes around 300°F, manipulation of the gas temperature may be the best way to handle iron carbonyl.

Nickel carbonyl is also present above the design level. Avoiding use of nickel-containing materials of construction at critical temperatures appears the best solution to this problem.

SUMMARY

The study found that the COS hydrolysis unit hydrolyzes the COS to the same outlet level regardless of the mode of operation, with or without shift. While still maintaining the sulfur in the clean gas to the 1 ppm limit, the Selexol acid gas removal system has some flexibility in control of CO_2 slip. Additional CO_2 slip is possible by manipulating solution temperatures.

Trace components are present in the cleaned gas at levels requiring further treatment ahead of a methanol unit. Cyanides and chlorides may or may not be a problem; in any case, the levels are near the specified design limit. Sulfur compounds are present at levels that will require treatment with the sandwich approach because of the COS. Zinc oxide sandwiching a COS hydrolysis catalyst is expected to handle the sulfur problem. This unit may also be modified to absorb chlorides if they are indeed a problem. Metal carbonyls may require gas temperature control to avoid or destroy the iron carbonyls and use of nonstainless materials at critical temperatures to avoid formation of nickel carbonyls. Arsenic, if present in significant quantities, will have to be addressed. Test work is underway at Tennessee Eastman that may shed more light on the entire trace contaminant problem. With the present knowledge or lack of knowledge, a prudent methanol design would include the ability to add a "final filter" such as a copper-based absorbent immediately prior to the methanol catalyst should the need arise.

SUMMARY

COS Hydrolysis

- 10 ppm COS out, shift or bypass mode

Acid Gas Removal

- 1 ppm Total S out, shift or bypass mode
- CO_2 slip enhanced by solvent flow, temperature control

Trace Contaminants

- Sulfur - Requires sacrificial absorbants
- Ammonia - no problem
- Cyanides, chlorides - Borderline
- Metal carbonyls - require materials and temp. control
- Other contaminants - may require "Final Filter"

CHEMISTRY AND USES OF CARBON DIOXIDE

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CARBON DIOXIDE: BACKGROUND AND SCOPE

Carbon dioxide is found in small amounts, about 0.03 volume percent, in the atmosphere. The gas is a by-product of many commercial processes: hydrogen production, the production of synthetic ammonia, the combustion and gasification of fossil fuels, fermentation, some chemical processes involving carbon monoxide, the calcination of limestone and the reaction of dolomite with sulfuric acid. An increasing amount of CO_2 is being found in wells containing large amounts and percentages of this gas. Carbon dioxide is usually present in a mixture of gases from which it is separated and prepared for commercial use as a gas, liquid or solid.

There is an increasing demand for CO_2 but the problem of inadequate low-cost CO_2 availability is holding down the amount that could be sold.(1) While tremendous amounts of CO_2 are formed as a by-product material, there is nevertheless a shortage of this gas.

Carbon dioxide is generally considered to be of little use chemically since it is a thermodynamic end product. However, this gas is quite reactive under certain conditions and its potential for expanded utilization is high.

It should be noted that transition metals are part of the enzymes which are essential contributors to the biological fixation of CO_2. We shall see later that transition metal coordination compounds may be helpful in realizing the purely chemical processes for reducing CO_2 and in its resultant transformation to organic compounds.

An important aspect which draws our attention towards CO_2 is the fact that the main part of terrestrial carbon is in the form of CO_2 and carbonates (CO_3^{2-}). It is possible to suppose that these sources of carbon, estimated to contain 10^{15}-10^{16} tons of carbon, may some day replace fossil fuels as the carbon source for fuels and chemicals.

It is recognized that the world reserves of fossil fuels are not infinite; these reserves are estimated to be about 10^{13} tons (as carbon). The total amount of CO_2 in the atmosphere and in the oceans, is about 10^{14} tons (also as carbon).

SOME PHYSICAL PROPERTIES OF CARBON DIOXIDE

Some important physical properties of CO_2 are listed below.

SOME PHYSICAL PROPERTIES OF CO_2

Property	
Sublimation point	-78.5°C at 1 atm (101 kPa)
Triple point	-56.5°C at 75.1 psia (518 kPa)
Critical temperature	31.1°C
Critical pressure	1071 psia (734 kPa)
Critical density	467 g/l
Latent heat of vaporization	149.6 Btu/lb. (348 J/g)
Gas density	1.976 g/l at 0°C and 1 atm
Liquid density (at one atm)	914 g/l at 0°C
Viscosity (at one atm)	0.015 mPa.s (=cP) at 25°C
Heat of formation (25°C)	373.4 Btu/mol (393,700 J/mol)

CHEMICAL REACTIVITY OF CARBON DIOXIDE

Carbon dioxide is considered to be unreactive at ordinary temperatures since it is the final oxidation product of carbon. But at the usual temperatures at which many reactions are conducted (100-350°C), CO_2 ranks as a reactive chemical with intriguing potential for commercial use.

Currently, carbon dioxide is not used extensively as a source of carbon in the commercial synthesis of chemicals. Although CO_2 has points of chemical attack, its lack of reactivity and hence chemical commercial utilization can, in part at least, be ascribed to thermodynamic aspects. Biologically, however, CO_2 is very reactive and an important carbon source in many natural enzymatic and biological syntheses of organic molecules.

The extended goal of utilizing CO_2 as a source of fuels and chemicals necessitates an understanding of the basic chemistry of the molecule. Carbon dioxide is a linear molecule with equivalent carbon-oxygen bond distances of

$$O=C\overset{1.16\text{Å}}{=}O$$

1.16 Å (2). The molecule has a high electron affinity so that it is susceptible to electron attack.

The oxygen atoms in CO_2 are electron-attracting so that the carbon atom is electron poor. Accordingly, the carbon should react as a good electron acceptor (an electrophile) and a poor electron donor. On the other hand, the oxygen atoms in CO_2 have partial negative character and should tend to react as nucleophiles or electron donors.

Because of the thermodynamic stability of CO_2, the key problem in the chemical exploitation of this molecule is its activation, essentially by an input of energy. The supply of energy can be furnished by carbanions, hydrogen, electrode processes, irradiation and importantly by electrons or negative species supplied by metals (especially transition metals) or by transition metal complexes.

Chemical perturbation of CO_2 leading to reaction proceeds mostly by interaction either at the electrophilic carbon atom or at the nucleophilic oxygen atoms. In many examples of CO_2 reduction and incorporation, hydrogen is a necessary reactant. For example, the reduction of CO_2 to hydrocarbons over transition metal catalysts proceeds as follows:

$$nCO_2 + (3n+1)H_2 \rightarrow C_nH_{2n+2} + 2nH_2O \qquad (1)$$

$$nCO_2 + 2nH_2 \rightarrow C_nH_{2n} + nH_2O \qquad (2)$$

Some hydrogen is incorporated into organic products but much of it is consumed in the production of water. Thus, water serves as a "sink" for the excess oxygen in CO_2, providing a thermodynamic driving force for the reaction. When the focus is not on CO_2 as a reactant, then CO_2 itself is often used as an "oxygen sink," a thermodynamically stable repository for oxygen.

Carbon dioxide can be used in the preparation of methane, methanol, high hydrocarbons, alcohols and amines as well as formates, oxalates, lactones, and carbonates. Three main types of reactions are involved (3): (a) reductions with concomitant loss of all or part of the oxygen in the CO_2 (methanol, methane and products of the Fischer-Tropsch reaction), (b) reactions involving reduction of CO_2 with retention of both its oxygen atoms (formates, oxalates) and (c) reactions, such as reductive carbonylations in which both of the oxygen atoms in CO_2 are also retained (lactones).

All of these reactions of CO_2 may be accomplished by the use of heterogeneous catalysts (methanol, methane, Fischer-Tropsch products) or with heterogeneous catalysts and/or soluble transition metal complexes. Some (formates, oxalates) may also be obtained using other catalyst types or by the addition of electrons.

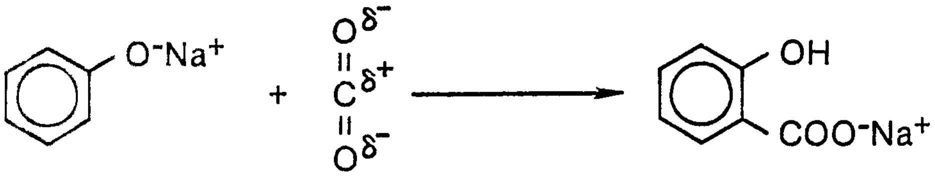
COMMERCIAL USES OF CARBON DIOXIDE

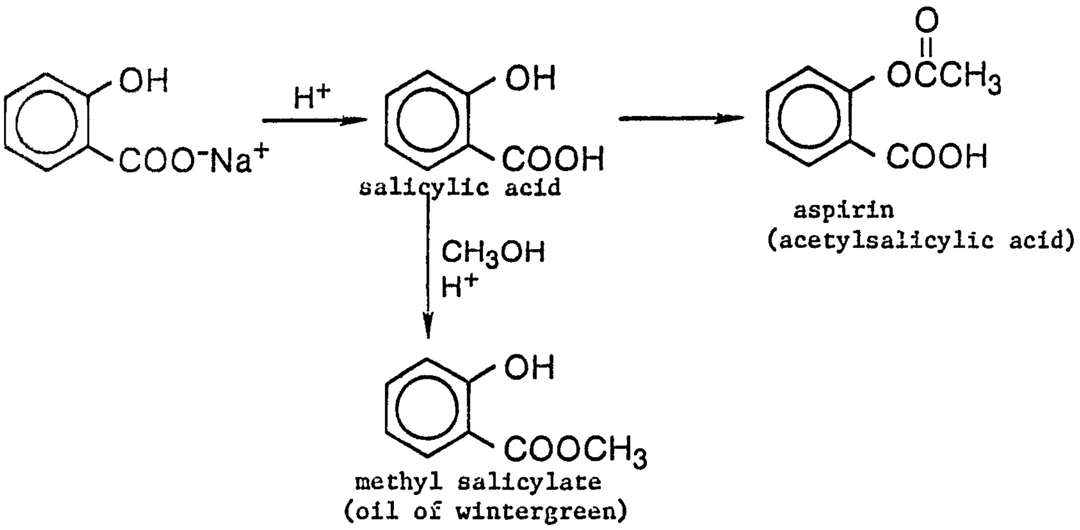
It has been reported that 7.80 billion pounds (3.898 thousand tons) of liquid and solid CO_2 were produced in 1984 in the U.S. (4). This figure is undoubtedly low since captive uses of liquid and solid CO_2 are not reported. Carbon dioxide, as a liquid or a solid only (not gaseous CO_2) ranked eighth among organic chemicals produced in the same year. Although listed in this way as an organic chemical, the uses of liquid and solid CO_2 depend almost entirely on their physical properties.

The very large and growing amounts of gaseous CO_2 used in the production of fuels and chemicals has not been well documented. The amount of gaseous CO_2 produced is not known; its growing use in enhanced oil recovery (EOR), mostly obtained from natural CO_2 gas wells, may now be the largest use of CO_2. Most CO_2 is produced from drilled wells and there is no good estimate of this production other than it must be large and growing. It is not unusual for an oil company to consume its entire production of CO_2 from gas wells in its own EOR operations. These and other uses will be discussed in the following sections.

Much of the CO_2 produced during the synthesis of ammonia (more than a ton of CO_2 is generated per ton of ammonia synthesized) is captive and not reported. The use of CO_2 in the production of urea is steady (much of it is also captive). Large amounts of CO_2 are produced by the fermentation of agricultural products in the production of beer, distilled beverage and ethanol. The production of ethanol for use in "gasohol" (about 10% ethanol, 90% gasoline) is expanding rapidly in the U.S. and CO_2 recovery plants are being constructed adjacent to these plants. Tax incentives are needed to make gasohol nearly competitive with unleaded gasoline and this source of CO_2 may become tenuous in the future.

The chief commercial chemical use of CO_2 is in the production of urea (H_2NCONH_2).While only small amounts of CO_2 are consumed in the synthesis of aspirin, its synthesis illustrates probably the most important way in which CO_2 undergoes reaction. The mechanism of this and related reactions correspond to the attack of a nucleophile ($C_6H_5O^-$), an energy rich reagent, on the positive carbon of CO_2. Aspirin is synthesized by the Kolbe reaction; treatment of the salt of phenol with CO_2 resulting in the substitution of the carboxyl group, -COOH, for a hydrogen atom of the aromatic ring in phenol. In the first step of the synthesis, the negative (nucleophilic) phenoxide ion attacks the positive (electrophilic) carbon atom in the CO_2 molecule.





Other uses of CO_2 depend largely on its physical properties. Carbon dioxide has extensive uses as a refrigerant. Gaseous CO_2 may be liquefied at any temperature between its triple point ($-56.6^{0}C$) and its critical temperature ($31^{0}C$) by compression. The liquid CO_2 is stored and transported at ambient temperature in cylinders which usually contain 22.7 kg. Insulated refrigeration tanks and trucks, kept at $-18^{0}C$ and 20 atm, are used to store and transport liquid CO_2. Liquid CO_2 is very useful in quickly freezing large quantities of perishable foodstuffs.

When liquefied CO_2 is allowed to expand into the chamber of a hydraulic press, so much heat is absorbed during expansion and evaporation that some 50% of the CO_2 is cooled to carbon dioxide "snow" ($-78^{0}C$) while the remaining is recovered as CO_2 gas for recycling. Compression of the snow with a hydraulic ram with a force of about 250 tons converts it to a block of dry ice. This solid form of CO_2 is about 1.7 times as dense as ice made from water but its net refrigerating effects on a weight basis is about twice that of water ice. Dry ice has extensive use in inhibiting bacterial growth, weepage and shrinkage in the preservation of meats and other foods. Dry ice is highly effective in the storage and shipment of ice cream, frozen foods and many other perishables. It is important as a refrigerant for many reasons, one of which is that it leaves no residue upon evaporation. This allows dry ice to be mixed with molded substances that must be kept chilled. It is used to chill the center of golf balls before winding. It is also used to chill aluminum rivets to prevent their hardening at room temperature. There are a variety of other uses of both liquid and solid CO_2.

Carbonation continues to be a growing use of CO_2. The first significant commercial use of CO_2, in fact, was in the attempt in Europe, is about 1785, to duplicate the effervescence of the continent's popular natural springs. In 1975, more than 2,000 plants in the U.S. produced about 4 trillion cases of eight ounce beverages (per capita consumption of 43.9 bottles) with an estimated value in excess of $9 billion. Growth in consumption of soft drinks continues to outpace population growth.

Carbon dioxide is responsible for the taste or bite of carbonated beverages. It is useful in inhibiting the growth of microorganisms, depending on the amount of CO_2 in the preparation. At one atmosphere and 15°C, one volume of water absorbs an equal volume of CO_2.

There are many other commercial uses of CO_2. Carbon dioxide is one of the most effective fire extinguishing agents, for it smothers fires by (a) displacing the oxygen needed to support combustion and (b) cooling temperatures below ignition points with dry ice snow. No damaging residue remains behind.

Carbon dioxide is also used in welding as an agent to shield the weld zone from the surrounding atmosphere. It excludes oxygen and other gases, maintains visibility in the weld area and reduces slag formation.

Many municipalities soften hard water by adding excess slaked lime to dissolve the magnesium and calcium bicarbonates that make the water hard. Carbon dioxide is added to remove surplus lime which precipitates out.

Carbon dioxide is used for many types of environmental and low temperature testing (aircraft and electronic components). With liquid CO_2 or dry ice, test chamber temperatures can be dropped to -78°C in seconds.

Carbon dioxide's cooling ability is used in the shrinking of machined metal parts to produce tight fit. For example, when automobile valve seats are fitted into an engine block, the valve seat is cooled with CO_2 until it is shrunk to a size small enough to allow them to fit easily into the block. It is then securely bound in place on expansion to normal size.

Fresh fruit and vegetables continue to respire after harvesting. This "breathing" is due to the release of CO_2 and burning up of oxygen. The result is aging and deterioration. Refrigeration and blanketing with CO_2 reduces the respiration rate and maintains freshness. Depending on the particular commodity, oxygen content is reduced from 21% (atmospheric) to less than 5% and the CO_2 content is raised from 1 to 12%.

The miscellaneous uses of CO_2 are legion and cannot all be even mentioned here. Cattle are now branded with a mixture of dry ice and alcohol, eliminating damage to the hides due to hot branding together with dangers of infection. CO_2 vapor is used for setting ink in printing operations and for firming adhesives.

Other uses of CO_2 are listed in the most recent Kirk-Othmer encyclopedia (5).

SUPERCRITICAL EXTRACTION WITH CARBON DIOXIDE

A supercritical fluid (SCF) is a material heated to or beyond its critical temperature (T_c) under a pressure equal to or higher than its critical pressure (P_c). In the supercritical state, the fluids exhibit a combination of physical (and chemical) properties that allow them to become very powerful and unusual solvents.

Several supercritical heavy oil and residuals processes have been put forward, often in order to reduce energy requirements. The Residual Oil Supercritical Extraction (ROSE) process, developed by the Kerr-McGee Refining Corporation, is probably the most successful, with about a dozen plants either already on stream or due to begin operation by 1986 (6). The solvent used is generally n-butane or n-pentane but the choice of solvent varies with the type of feedstock to be treated and the nature of the products to be recovered.

In a typical SCE process, there are two major steps. The first one is the loading step during which the desired product is dissolved in the supercritical fluid by contacting the solvent and the feedstock under selected conditions. The second step is the separation of the extract from the solvent which occurs mostly by reducing the solvent power as a result of small changes in pressure or, if need be, in temperature. In connection with this, it is worth mentioning that fractionation of the extract is also possible. One way to do this is by inducing incremental changes in solvent power in either one of the two above mentioned steps.

Critical Data for Some Supercritical Solvents

Substance	Critical Temperature (^oC)	Critical Pressure (atm)	Critical Density ($g.cm^{-3}$)
Methane	-82	46	0.162
Ethylene	9.2	49.7	0.218
Freon 13	28.8	38.7	0.579
Carbon Dioxide	31.1	72.9	0.468
Ethane	32.4	48.3	0.203
Nitrous Oxide	36.5	71.7	0.457
Propylene	92	46	0.233
Propane	96.8	42	0.217
Ammonia	132.3	112.5	0.235
n-Butane	152.0	37.5	0.228
n-Pentane	196.6	33.3	0.237
Methanol	240.5	78.9	0.272
Benzene	288.9	48.3	0.302
Toluene	320.8	41	0.292
Water	374	220	0.322

At this point, one is led to discuss another property which is at least as important as the extraction yield, namely the selectivity of the process. Because most of the feedstocks of interest are complex mixtures, selectivity must be considered. For example, to eliminate nicotine from tobacco, it is imperative to leave the aroma and flavor in the raffinate. The first attempt to deal with such a problem is to find the right solvent as well as the right conditions. General rules on solubility, selection of gases, and operating conditions may be helpful in approaching the problem; however, it is not always possible to discover a satisfactory solution. In such cases, a promising way to investigate would be the use of mixtures of gaseous solvents, as they exhibit an extended flexibility of properties.

This report is concerned specifically with the use of CO_2 in supercritical extraction. It is informative to learn that effective SCE can be obtained in the temperature range of 10 to 100^oC above the critical temperature of the gas used while the accompanying pressure range is 50-300 atm. Particularly effective gases are those having critical temperatures that are neither very low nor very high. Carbon dioxide ($T_c = 31^oC$, $P_c = 73$ atm) is a particularly effective gas for SCE.

Other gases which have given good results are ethylene, ethane, propane, propene, and ammonia. But CO_2 has physical properties that make it especially suitable for SCE. It is unreactive unlike gases such as ethylene, propylene and ammonia. Carbon dioxide is "inert", even in the supercritical state. There is no objection to its use from a health point of view which is an advantage over organic solvents. Carbon dioxide is neither flammable nor toxic, and does not maintain combustion. The gas is ubiquitous in nature, being found in air, in mineral waters and, in conjunction with some other gases, often found as a major constitutent in drilled wells. As mentioned earlier, it is a by-product in the synthesis of ammonia and in the production of alcoholic beverages, as well as in other fermentations.

Carbon dioxide is regarded as a "natural" non-toxic substance and is not considered as an additive. It is therefore the supercritical gas predominantly used with natural products to extract unstable substances and in several other SCE processes. However, it should be mentioned that prolonged exposures to CO_2 at concentrations higher than 5% are definitely harmful.

Carbon dioxide uses in supercritical extractions will continue to grow. It is almost the supercritical gas "of choice". The amount of CO_2 that will be used in present and new applications is quite large but the principle use of CO_2 at or near supercritical conditions will be in enhanced oil recovery.

With today's technology and economics, about two barrels of oil are left in the ground for each barrel of oil recovered. An increase of only 1% in oil recovery efficiency for the U.S. represents about 4.5 billion barrels of oil - more than is produced in this country in one year.

A fast growing application of supercritical or near supercritical extraction is the use of high pressure CO_2 to recover crude oil not recovered by conventional methods from porous reservoir rocks. Oil in a newly discovered reservoir will usually be driven to the surface by pressure in the formation and by expansion of the gas dissolved in the oil. In light oil reservoirs this primary production generally recovers about 10-25% of the oil in place. Primary recovery is usually less in reservoirs containing heavy, viscous crudes.

Secondary oil recovery methods have been in use since the 1940s, resulting in recovery of an added 20 to 50% of the original oil in light oil reservoirs. Most secondary oil recovery is carried out by waterflooding; this technique now accounts for almost half the oil produced in the U.S. But water is not miscible with oil and therefore many interfaces are present in the reservoir rock during displacement by water. Resulting capillary forces trap oil in small channels in the rock pore spaces.

These interfaces between the oil and the injected fluid could be eliminated by injection of a fluid miscible with the oil. Low boiling hydrocarbon solvents can be used but these are generally more valuable than the crude oil displaced.

In the mid 1970s, a number of companies started to investigate EOR projects utilizing supercritical CO_2 injection. Millions of cubic feet of CO_2 are presently used in EOR and its use could approach trillions of cubic feet of CO_2 in future years. The amount of CO_2 used to recover a barrel of oil is surprisingly large. It usually requires 5 to 7 thousand cubic feet of CO_2 to recover a barrel of oil but there are numerous oil wells where as much as 25 thousand cubic feet of CO_2 are used to recover that barrel of oil (7). Purchased CO_2 from wells containing large percentages of this gas costs about 1.35 to 1.50 dollars per MCF but the CO_2 can be recycled for about 50-60 cents per MCF (8).

The most desirable source of CO_2 is that found in naturally occurring underground wells capable of producing CO_2 at a minimum pressure of 8 atm. Such underground reservoirs, believed to contain an estimated 30 trillion cubic feet of CO_2, are located in the states of New Mexico, Colorado, Wyoming, Utah and Mississippi (9). Underground sources of CO_2 likely exist in neighboring states. These wells contain high concentrations (15-90%) of CO_2. Recovery and purification of this gas will involve compression, dehydration, and recovery of methane and natural gas liquids (NGL) for sale.

The raw gas quantity, CO_2, and H_2S contents may vary several fold over the life of an EOR project. In the early years, the CO_2 content may vary from 10-15% rising to 80-90% in ensuing years. The content of H_2S may vary from a few percent at the start of the EOR to a few thousand parts per million in later years.

Carbon dioxide from ammonia synthesis plants often approaches 98% purity and can be used directly for oilfield flooding after compression and drying. Carbon dioxide from these plants is potentially available in several major oil production areas: the Los Angeles Basin, Colorado, Utah, Texas, Wyoming, New Mexico and Louisiana. The amounts of CO_2 available from ammonia plants varies from less than a million to as much as 50 to 70 million cubic feet per day.

The potential to provide CO_2 in large amounts from gasification plants is quite promising. About 80 million cubic feet of CO_2 per day are already being produced from two SNG plants in Illinois using naphtha and NGL feedstocks. The Great Plains gasification plant had planned to transmit millions of cubic feet of CO_2 per day; this would be delivered to pipelines if the plant is allowed to operate. Sales of this CO_2 by-product could bring in revenues of over $17 million per year. As much as 300 million cubic feet per day could be generated by some coal gasification plants; this would amount to about a trillion cubic feet over a decade. Integrated combined cycle coal gasification second generation plants for generation of electricity could well be a prime source of needed CO_2. The major impurity here would be H_2S. In 10 to 20 years, this could be a major source of CO_2 for EOR in various parts of the country.

The most widely distributed source of CO_2 is that found in power plant stack gas. Hundreds of million of cubic feet of CO_2 per day could be available from this source. The CO_2 content of stack gas varies from 6 to 16% depending on the fuel burned. It is available at atmospheric pressure after purification and transmission. Separation and recovery of CO_2 from this source is not feasible at present. Dow Chemical has announced a two-stage technology that, the company claims, can recover CO_2 from flue gas streams at about $22 per ton (10). Alkalis remove SO_2 to below 5 ppm. The final gas stream extracts up to 95% of the available CO_2.

Various fermentations are yielding large amounts of CO_2. The largest amounts are associated with the fermentation of agricultural products to ethanol. Plants for recovery of this CO_2 are under construction.

The use of CO_2 flooding in EOR depends on the physical and to a smaller extent on the chemical properties of CO_2. The mechanisms involved in CO_2 flooding are complex and not completely understood; the fact that CO_2 flooding interacts with oil underground in various kinds of reservoir rock types, at various temperatures and pressures, with different crude oil viscosities, with pores and channels of many sizes, etc. makes the subject particularly difficult to understand. Much of the prediction of utility of CO_2 flooding in EOR therefore depends on empirical type tests made in the laboratory; extreme caution must be exercised when field scale projects are designed.

Although several injection schemes using CO_2 have been suggested, the so-called WAG process is now in general use (Figure 1). This process alternates small volumes and water until the required CO_2 volume has been injected. The water reduces the ease with which the CO_2 can flow and improves the contact between the displacing and the displaced fluid. After a number of alternating injected slugs of CO_2 and water, continuous injection of water is begun.

As of late, various foams and direct thickeners are being tested to improve sweep efficiency and lower the amount of CO_2 used.

It is important to note that H_2S is undesirable in CO_2 flooding in EOR. H_2S is a safety hazard and it is corrosive. Typically, residual H_2S levels in CO_2 floods are less than 100 ppm. A few percent of H_2S has been used in some cases of flooding but its removal to very low levels is desirable.

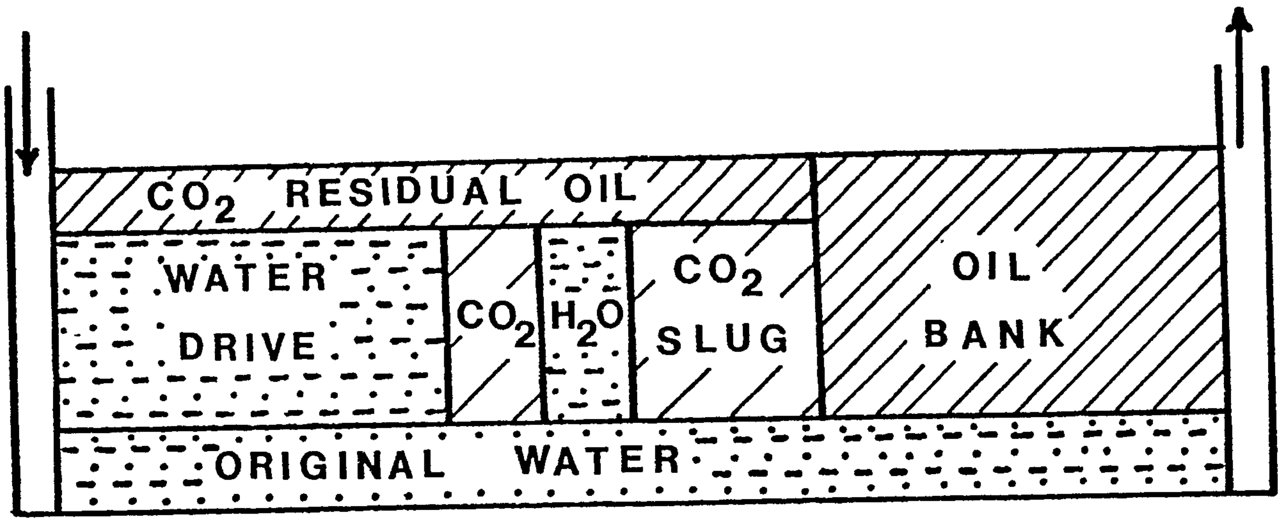


Figure 1: Schematic of CO_2 flooding (WAG Process).

ROLE OF CARBON DIOXIDE IN THE COMMERCIAL SYNTHESIS OF METHANOL

About 6% of CO_2 is routinely added to the synthesis gas used in the industrial manufacture of methanol. Only lately has attention been paid to the role of CO_2 in this synthesis. We shall present evidence, some of it controversial, but inevitably leading to the conclusion that under commercial conditions, the CO in the feed synthesis gas forms methanol by first being converted to either CO_2 or to a surface CO_2 intermediate. The combination of CO and CO_2, on certain catalysts, seems to form a unique system. The promise is that CO_2 will play (and already is playing) a larger role in the synthesis of methanol and of higher alcohols. The products of the gasification of fossil fuels may perhaps be used in syntheses with considerable amounts of CO_2 left in the gas mixture produced. Further research to clarify the role of CO_2 in these syntheses promises to have a high pay-off.

It has been pointed out that all industrial processes for the synthesis of methanol use a synthesis gas containing 3-8% of CO_2. Newer plants use feed gases containing considerably more CO_2 than CO. If the CO_2 is completely removed from the feed gases in the commercial synthesis, the catalyst generally deactivates. However, in spite of the tremendous role played by CO_2 in the methanol synthesis, the mechanism by which CO_2 intervenes has remained, until recently, a rather complete mystery.

IS THE CARBON IN THE METHANOL DERIVED FROM CO, FROM CO_2 OR FROM BOTH COMPONENTS?

Until fairly recently, there was a general belief that the methanol synthesis proceeds via the hydrogenation of CO. This equation is logical and the possibility that the synthesis of methanol would occur through CO_2 appeared highly improbable. Yet the evidence that the methanol prepared commercially involves the synthesis of methanol from a surface intermediate derived from CO_2 (rather than from CO) is now generally accepted.

As a matter of fact, all the chemistry of CO_2 hydrogenation has until recently been associated with that of CO assuming that the transformation of CO_2 to CO takes place through the reverse water-gas shift (wgs) reaction. It is then considered that the CO is further hydrogenated, for example to methanol. Acceptance of this route to methanol may be a major reason why the detailed contribution of CO_2 to the methanol synthesis has been overlooked.

There has been significant progress, recently, in providing a scientific base for understanding the operation of methanol synthesis catalysts although some research groups have taken points of view that appear incompatible. Experimental results reported so far, as well as the interpretations that followed, are confusing.

Kagan, Rozovskii and coworkers (11,12) reported a really surprising finding: not only does the conversion of CO_2 to methanol not proceed through a free CO intermediate, but the conversion of CO to methanol occurs, under industrial conditions, almost entirely via the intermediacy of CO_2. This finding was arrived at by studying the isotopic distribution of ^{14}C among the reaction products of the conversion of CO_2 to methanol in the presence of a small amount of ^{14}CO. The authors performed the reaction on a commercial catalyst ($Cu/ZnO/Al_2O_3$), at 50 atm using a gaseous feed consisting of $CO_2/CO/H_2/N_2$ = 22/1.2/73/4.

The comparison between the specific radioactivity of CO, CO_2 and CH_3OH enabled the authors to conclude that (a) the hydrogenation of CO does not occur, and (b) not only does the transformation of CO_2 into methanol proceed without the intermediacy of free CO, but under industrial conditions, the synthesis of methanol from CO and H_2 takes place through CO_2 as an intermediate.

Other workers repeated the same type of experiments carried out by Kagan et al.. The reaction temperature and pressure as well as the catalyst ($Cu/ZnO/Al_2O_3$) pretreatment were similar to those used industrially. An equimolar mixture of CO + $^{14}CO_2$ was hydrogenated at varying but high flow rates so that the wgs reaction does not interfere (13). The results reported confirm the major role played by

CO_2 in the synthesis of methanol, namely that the synthesis proceeds primarily via CO_2 (Figure 2).

A very interesting experiment has been performed in which the catalyst bed was preceded by a zeolite CO_2 trap. The starting mixture contained, besides H_2 and CO, 0.5% of CO_2. The rate of CH_3OH formation was initially low. For $t < t_b$, the CO_2 is adsorbed by the zeolite; the breakthrough of CO_2 occurs at $t = t_b$ and it is immediately accompanied by a fivefold increase in the rate of conversion to methanol (Figure 3).

The following conclusions may be made:

a. CO_2 hydrogenates to methanol more readily and more selectively than does CO.

b. There is strong evidence that, under industrial conditions, CO_2 is the major species that yields methanol without the intermediacy of CO. The carbon monoxide is probably transformed into CO_2 via the wgs reaction.

c. The methanol synthesis conducted under other than industrial conditions may well follow a different reaction mechanism.

In spite of the fairly good agreement about the nature of the catalyst, at least as many as four different sites have been claimed to be active in the synthesis of methanol: $-Cu^+$, $-Cu^o$, $-Cu^o$ in the vicinity of an oxidized site and $-Cu^{2+}$.

SOME POSSIBLE REACTION MECHANISMS IN THE SYNTHESIS OF METHANOL

A number of mechanisms have been proposed for the methanol synthesis over Cu/ZnO catalysts. Three proposed mechanisms are outlined below. It is perhaps more likely that the first two routes to methanol take place when synthesis gas is used in the absence of CO_2.

The scheme in mechanism C is based on the work of those investigators who have established that methanol is formed not from CO but via a CO_2 surface

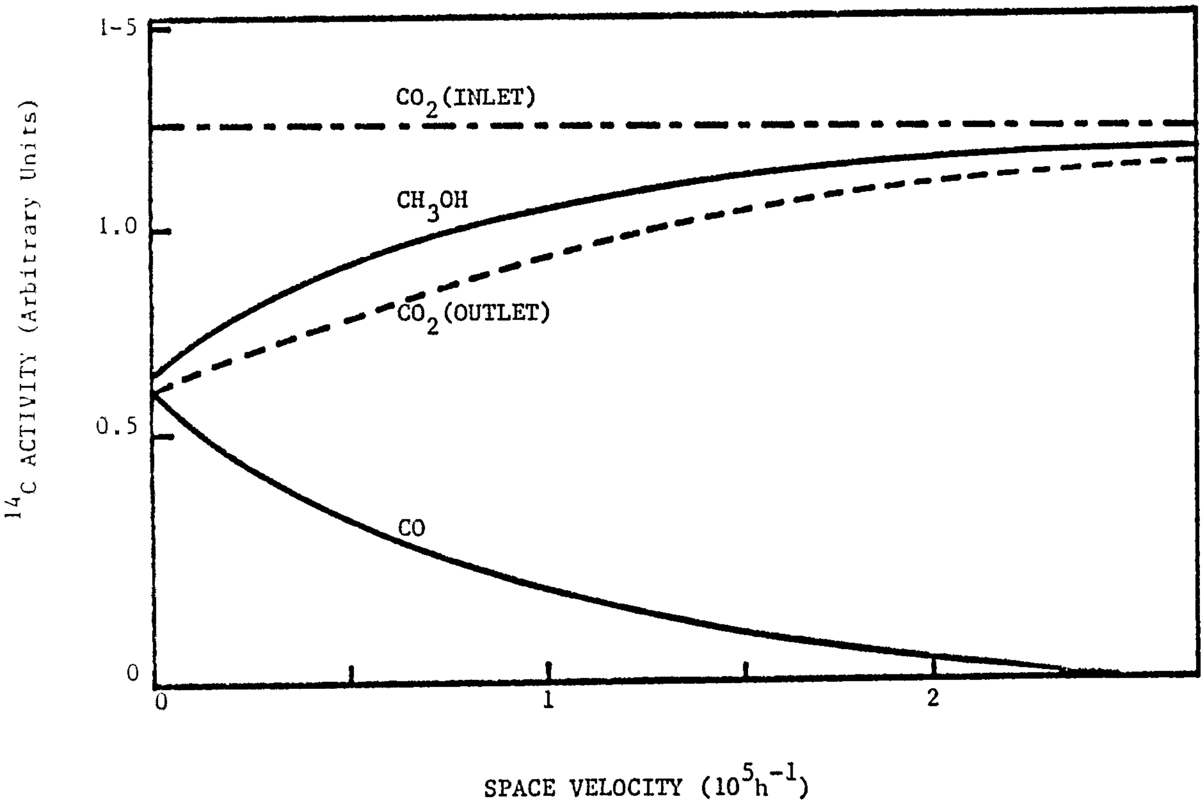


Figure 2: Distribution of ^{14}C radioactivity versus reactant space velocity. Adapted from Ref. (13).

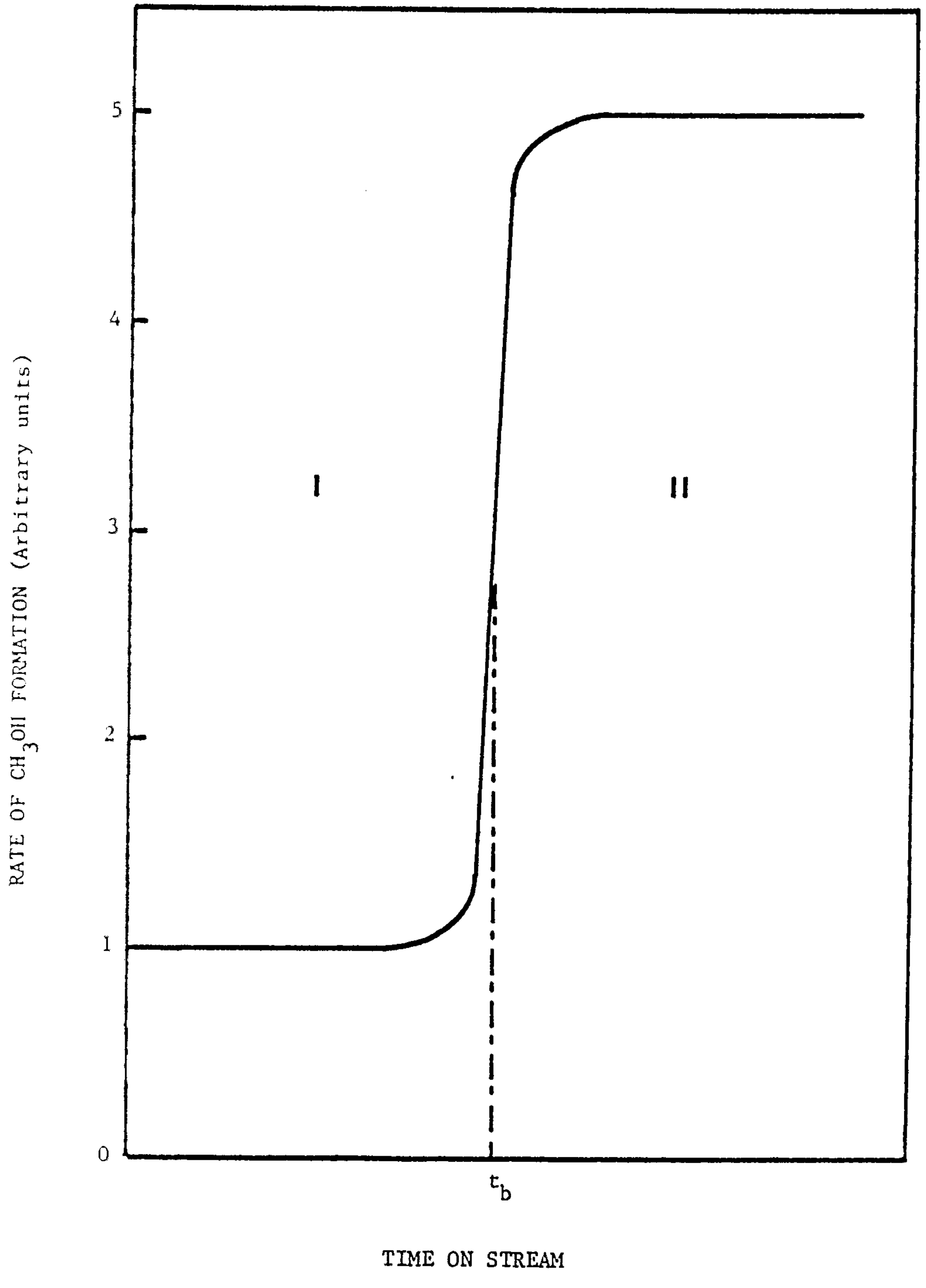


Figure 3: Methanol formation as a function of time on stream. t_b: CO_2 breakthrough (see text).

intermediates. M may be a copper atom or a metal derived from the accompanying oxide, usually ZnO. It should be noted that step 2 is not reversible with CO and H_2 when CO_2 is present. The participation of hydroxide (OH^-) species is not excluded. When the CO_2 pressure is zero or very low, the catalyst surface will be more reduced.

A final point may be made. The commercial methanol synthesis is conducted with CO_2 added to the synthesis gas. It is believed that synthesis plants using a ratio of CO_2 to CO approaching five are now in operation.

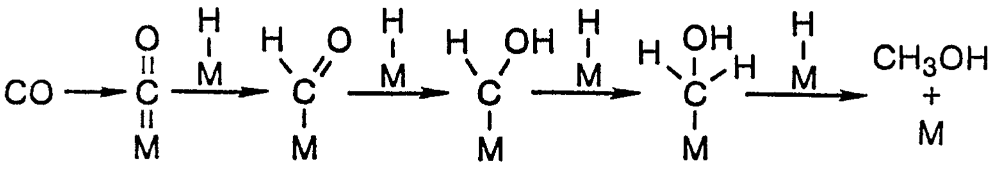
The answer to the following question is of utmost importance to the future chemical and fuel uses of CO_2. Is there a special chemistry of the $H_2/CO/CO_2$ system? Support for this idea has been furnished by this discussion of the role of CO_2 in the methanol synthesis. As for the methanation of CO_2, there is conclusive evidence that it proceeds through the intermediacy of CO.

THE ORGANOMETALLIC CHEMISTRY OF CARBON DIOXIDE: AN AREA OF POTENTIAL GROWTH IN ITS UTILIZATION

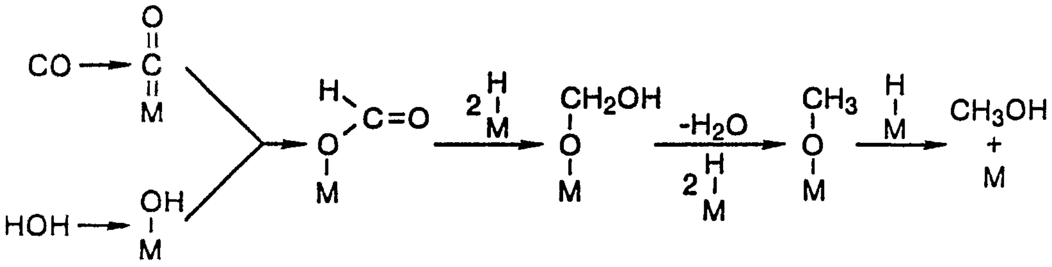
The huge amounts of CO_2 available from minerals on earth, in the air from the combustion of fossils fuels, and in the ocean, make CO_2 an attractive source of carbon for the synthesis of fuels and chemicals. Carbon monoxide produced from methane, petroleum fractions or from coal is already a growing source of fuels and chemicals, but there is a large driving force to substitute CO_2, often a waste product, for CO.

A promising route to the utilization of CO_2 for industrial chemical processes is via reactions usually catalyzed by transition metals. Both CO_2 and CO undergo useful reactions over heterogeneous catalysts, as in the synthesis of methanol, methane and Fischer-Tropsch type reactions, but CO rather than CO_2 again plays the major role.

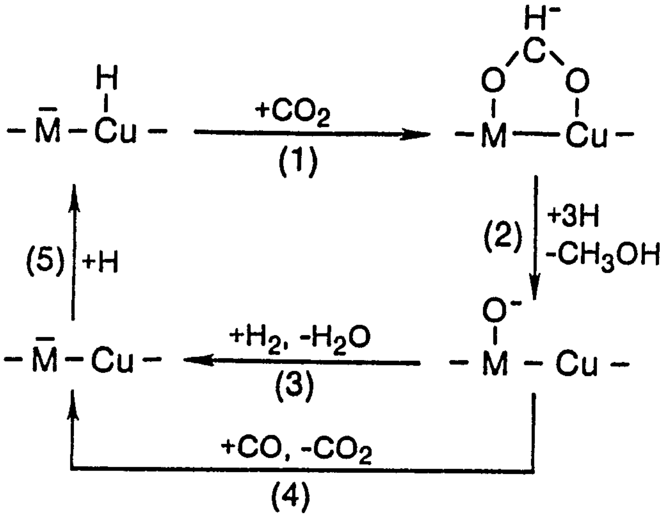
Mechanism A (M = metal surface species)



Mechanism B



Mechanism C



Another route to the chemical use of CO_2 and CO is via catalysis by homogeneous (soluble) transition metal complexes. This chemistry has been explored in great depth for CO but the organometallic chemistry of CO_2 is still in its infancy. However, there may be quite a bit of truth in the statement that, with recent progress in research, organic synthetic reactions using carbon dioxide should soon assume a position of equal importance to CO (14). That sounds optimistic but it is not at all unlikely that CO_2 will eventually find important commercial uses via catalysis by transition metal complexes.

Carbon dioxide can be activated by interaction with transition metals, either on a heterogeneous catalytic surface or by the formation of transition metal complexes of definite structure (Figures 4 and 5), usually used in homogeneously catalyzed reactions (15). It is well known, of course, that a catalyst increases the rate of a reaction by offering the reactants an alternative, lower energy, pathway to the final products. The catalyst complex "activates" one or more of the reactants and then positions them so that they react together.

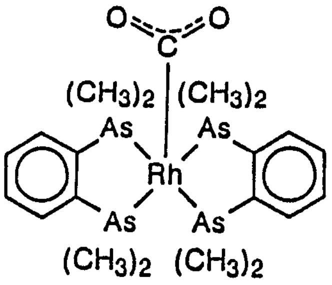
It is established that CO_2, like CO, can undergo further reactions such as insertion of CO_2 into M-C, M-H, M-O, and M-N bonds.

We can look forward to new syntheses of fuels and chemicals by the interaction of CO_2 with transition metals. These should assume great importance in the next decade or two. Some examples of some ways of metal-CO_2 coordination are shown in Figure 6.

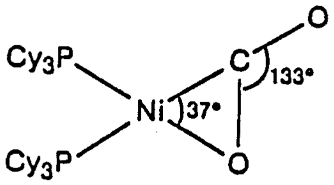
Carbon dioxide has promising uses in the preparation of important polymers including polycarbonates, polyureas and polyurethanes.

The future of CO_2 in the polymer area has not been fully exploited but there is potential for significant utilization in this connection.

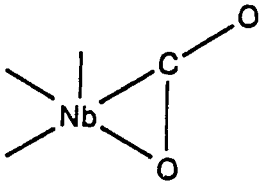
Ethylene carbonate (1,2 glycol carbonate) has been synthesized commercially from ethylene oxide (EO) and CO_2:



η^1-CO_2



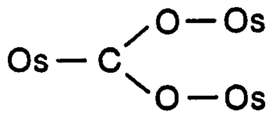
η^2-CO_2



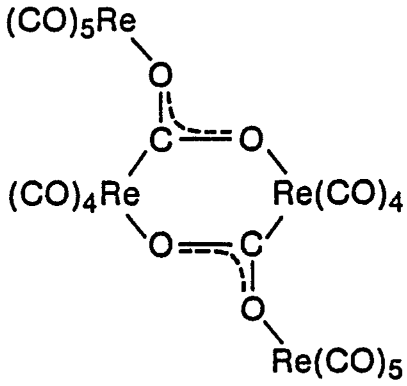
$Nb(\eta\text{-}C_5H_4CH_3)_2(CH_2Si(CH_3)_3)\,\eta^2\text{-}CO_2$

η^2-CO_2

Figure 4: Some Stable Transition Metal Complexes with CO_2 Ligands



η^1-CO_2



η^1-CO_2

Figure 5: Other Transition Metal Complexes with CO_2 Ligands

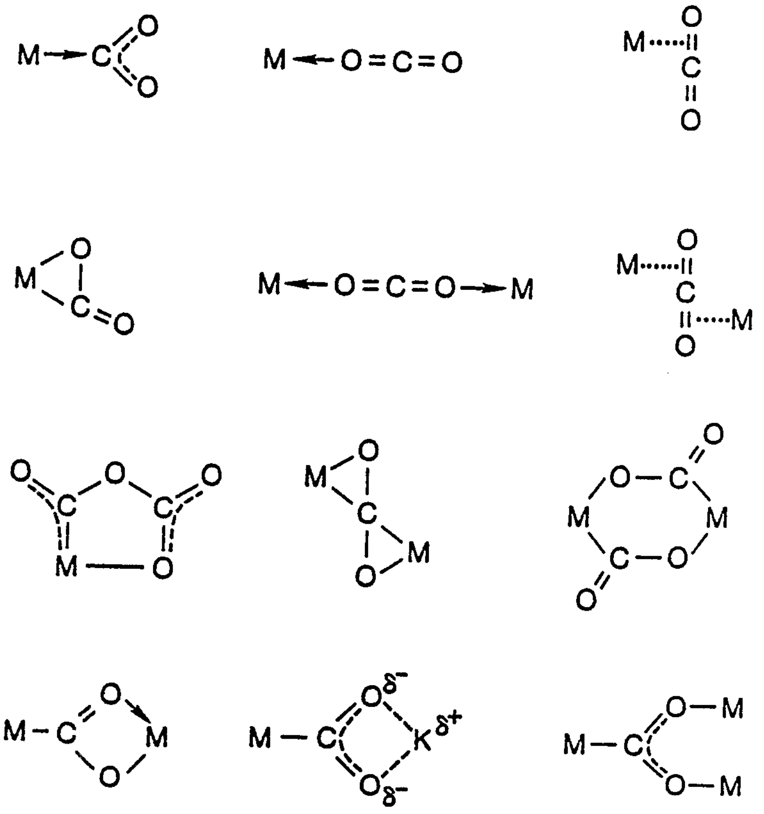
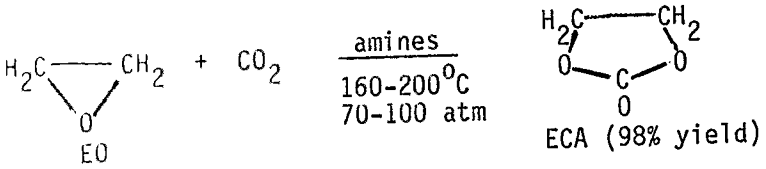


Figure 6: Coordination of CO_2 to a Metal: Some Possible Structures



EO

ECA (98% yield)

Ethylene carbonate is a high-boiling component of and solvent (b.p. = 238°C) for polymers and resins. It is also an intermediate in several organic syntheses.

Ethylene carbonate has other uses that are now under development. Ethylene oxide, a very large article of commerce, is difficult and costly to transfer over long distances. Halcon SD is developing a method of transporting ethylene oxide safely by converting it to ECA. This stable compound can be shipped without a problem and then cracked to give ethylene oxide at high selectivity and modest cost.

III. USE OF LIQUID CO_2 FOR ULTRAFINE COAL CLEANING

There is great interest in the preparation of ultrafine clean coal for combustion. Workers at the University of Pittsburgh are developing the so-called "LICADO" process which uses liquid CO_2 to provide a unique separation method for the fine coal (and other fine particles) cleaning (16).

Conceptually, the use of liquid CO_2 for ultrafine coal cleaning is a surface property controlled process. In preliminary experiments, it was observed that the "clean" coal is completely wettable by liquid CO_2; clean coal particles tend to form aggregates and migrate to the liquid CO_2 phase while mineral particles remain dispersed in the aqueous phase. It is based on such selective transport of particles across the water/liquid CO_2 interface that removal of mineral material from clean coal can be achieved.

At first glance, liquid CO_2 seems to operate simply as a selective agglomeration agent. However, further consideration indicated that the relatively rapid migration of coal particles from the aqueous phase to the liquid CO_2 phase cannot be fully accounted for by the agglomeration process alone. Indeed, the formation of microscopic CO_2 bubbles at nucleation sites on coal particle surfaces is likely due to small fluctuations of temperature or pressure (CO_2 partial pressure) in the system. These bubbles attached to the coal surface can cause a significant reduction is apparent density of coal particles from the (heavier) aqueous phase to the (lighter) liquid CO_2 phase.

Experiments are under way for the use of liquid CO_2 to transport coal in gasification systems or in pipelines. Results are encouraging.

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STRUCTURE AND REACTIVITY OF A WYODAK SUBBITUMINOUS COAL

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ABSTRACT

This paper reports on the continuation of our research efforts on the structure and reactivity of a Wyodak subbituminous coal using potassium-crown ether reagent, operating at room temperature and atmospheric pressure. Optimization of the amounts of potassium, crown ether and coal used has resulted in an enhanced alkali soluble fraction amounting to 44.8% after the first coal-K.CE reaction itself. Using model compound studies it has been demonstrated that the potassium-crown ether reagent reduces some phenolic hydroxyl groups in the coal to carbonyl groups. Field ionization mass spectrometry analysis has shown that dihydroxy one, two, and three ring aromatics represent a major structural component of the Wyodak coal. Tandem mass spectrometry has confirmed the identification of these dihydroxy aromatics. The mono and dihydroxy one, two, and three ring aromatics and their alkyl analogs are not present as monomer units, but are in all probability produced by thermal cleavage products of the coal oligomer fragments in the alkali soluble fraction of the K-CE reaction. This is supported by the FIMS thermal evolution profile which shows that these volatile compounds do not appear until a temperature of 350°C is reached. Size exclusion chromatrography showed a biomodal molecular weight distribution for the coal oligomer fragments of the alkali soluble fraction of the K-CE reaction. The lower molecular weight (number average molecular weight, M_n=632; weight average molecular weight, M_w=5839) predominates, although the M_w values are slightly higher for the fraction from the second K-CE reaction.

STRUCTURE AND REACTIVITY OF A WYODAK SUBBITUMINOUS COAL

Ramani Narayan and Shuyen Huang

INTRODUCTION

Coal conversions typically involve reacting coal under severe conditions of temperature and pressure. As a result, bond cleavage is nonselective and often accompanied by retrogressive (bond forming) reactions. This has resulted in less than satisfactory results in deducing coal structure, coal behavior, and reactivity. Incorrect models of the basic structural units of the coal and the nature of the linkages joining these units have been postulated.

Coal is a network polymer (Figure 1). A more graphic representation of the coal macromolecule is shown in Figure 2. The figure depicts aromatic clusters of varying sizes linked to each other by connecting bonds which could be ether linkages or alkane linkages or hydrogen bonds resulting in a network polymer structure. Trapped in the macropores created by this networking could be some small molecules which presumably are polymethylene type compounds.

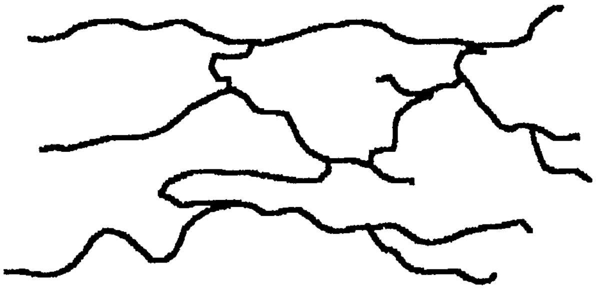


Figure 1. Structure of Network Polymers

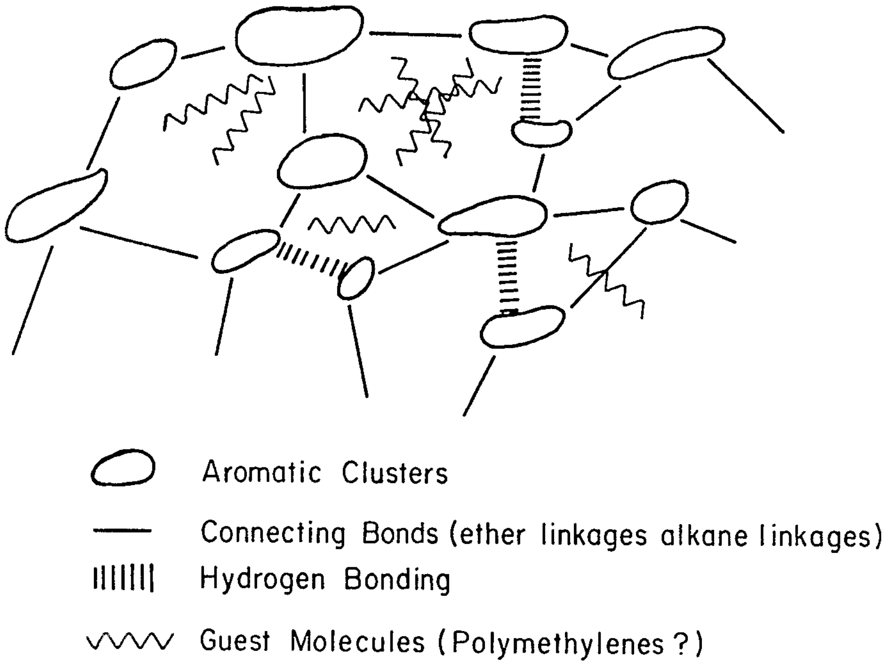


Figure 2. Coal Macromolecular Structure

Our approach has involved using site specific reagents to snip at the linkages holding the coal macromolecular matrix at room temperature and atmospheric pressure. This would result in the gentle dismantling of the macromolecular matrix with the formation of soluble chunks of coal oligomer fragments. These representative coal structural fragments are now amenable to detailed chemical and spectroscopic analysis.

The questions to be addressed are: (1) molecular weight and molecular weight distribution of the solubilized coal oligomer fragments (aromatic clusters); (2) nature of the linkages/crosslinks joining these aromatic clusters of the coal macromolecule; (3) nature of the oxygen functionalities in this coal; (4) the basic structural units comprising the aromatic clusters; (5) the chemistry of the coal oligomer fragments--this would allow one to predict the chemistry of the coal macromolecule.

The site specific reagents we are working with are (1) potassium-crown ether reagent and (2) periodate-perohydrite. These reagents have been reacted with coal at room temperature and atmospheric pressure. The potassium-crown ether reagent generates a stable solution of electrons. The small size and high reactivity of the electron solution promotes cleavage reactions at ether, ester, and diarylethane linkages resulting in depolymerization and solubilization of coal. Reduction of aromatic rings to dihydro and tetrahydro analogs also occur. The chemistry of the reaction, experimental procedures followed, and some of the results obtained were presented at the last contractors' conference (1,2). In this report we present our further findings on the structure and reactivity of the subbituminous coal using the potassium-crown ether reagent.

RESULTS AND DISCUSSION

The workup of the coal-K-CE reaction and separation into different soluble fractions are shown in Figure 3. This is a slightly modified workup plan than what we had originally presented. Modification of the reactant stoichiometries (crown ether is to potassium is equal to one is to one) resulted in an enhanced alkali soluble fraction of 44.8% after the first K-CE reaction itself. Incidentally, the alkali soluble fraction is also pyridine soluble! Methylation of the phenolic hydroxyl group of the alkali soluble fraction resulted in 62-80% THF extractability of this fraction. These results are summarized in Table 1.

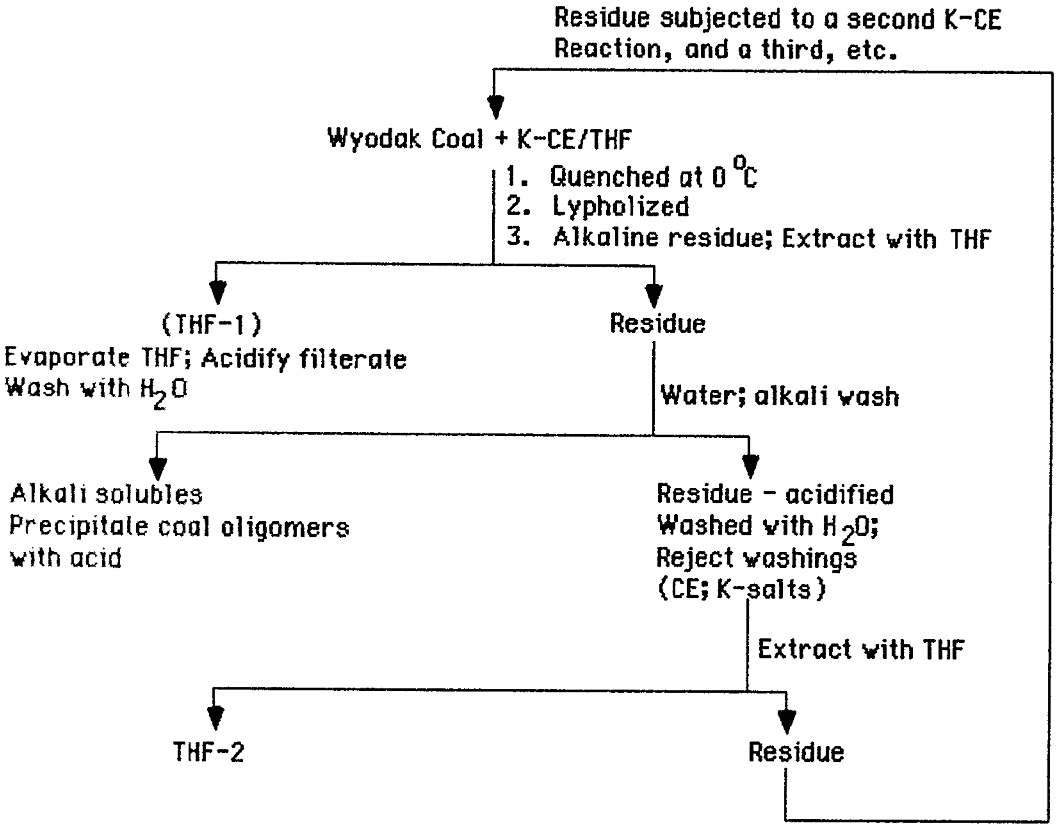


Figure 3. Work-Up of the Coal/K-CE Reaction

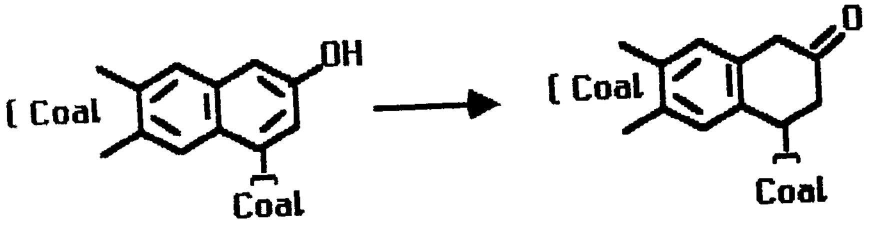
Table 1. Solubility Data

	THF-1	ALKALI SOLUBLE	THF-2
1st K-CE Rxn	2.8%	44.8% (PYRIDINE SOLUBLE!!!)	3%

Total solubility of up to 70-80% after 2nd and 3rd K-CE reactions

Methylate (-OH to $-OCH_3$)
60-80% THF soluble

Figure 4 shows the FTIR spectra of the untreated Wyodak coal, the alkali soluble fraction of the Wyodak coal from the K-CE reaction, the residue after the THF and alkali extractions from the 1st and 2nd K-CE reactions, respec- tively. Very interestingly, a sharp carbonyl stretching vibration at 1700 cm^{-1} was visible in addition to the broad and strong hydroxyl stretching vibration at 3500 cm^{-1} in each of the the K-CE reacted coal fractions. The appearance of the carbonyl seems to indicate that in addition to cleavage reactions reduction of the aromatic ring is taking place with the formation of a carbonyl compound, i.e.,



The carbonyl groups are distributed both in the alkali fraction as well as in the residue. Apparently, carbonyl groups attached to coal clusters which contain phenolic groups are rendered alkali soluble and carbonyl groups attached to coal clusters which are predominantly nonphenolic in nature are in the residue. The reduction of phenolic structures to carbonyl compounds has been confirmed by model compound studies. Thus, reaction of 2-naphthol with the potassium-crown ether reagent under similar conditions of the coal reaction produced a mixture of tetralone, a tetrohydro product, and a dihydro product (Figure 5). Table 2 gives a quantification of the peak intensities, in the aliphatic CH stretch and C=O stretch regions. The aliphatic CH content in all the three components, namely alkali soluble residue fraction (WE1) from 1st K-CE reaction (WR1) and residue from 2nd K-CE reaction (WR2) have increased corresponding to reduction of some aromatic ring systems in the coal to dihydro and tetrohydro products by the potassium-crown ether reagent. The methyl content is also increased after the K-CE reaction supporting the fact that diaryl alkane linkages have been cleaved which promoted depolymerization to soluble coal oligomer fragments. The carbonyl absorptions have increased considerably in the alkali soluble fraction and to a lesser extent in the residues. The increase in aliphatic CH corresponding to reduction of aromatic

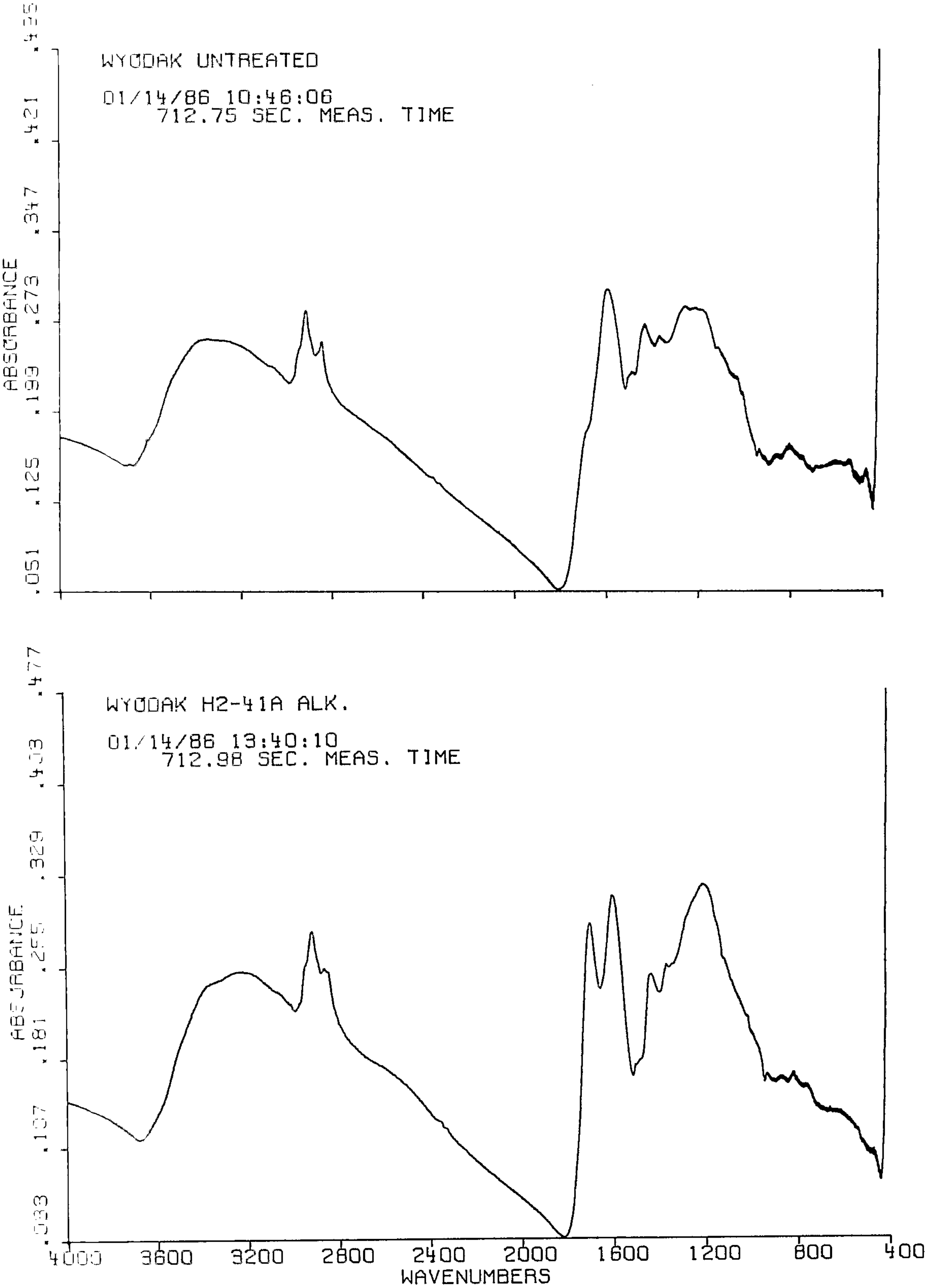


Figure 4. FTIR Spectra of the Wyodak Coal

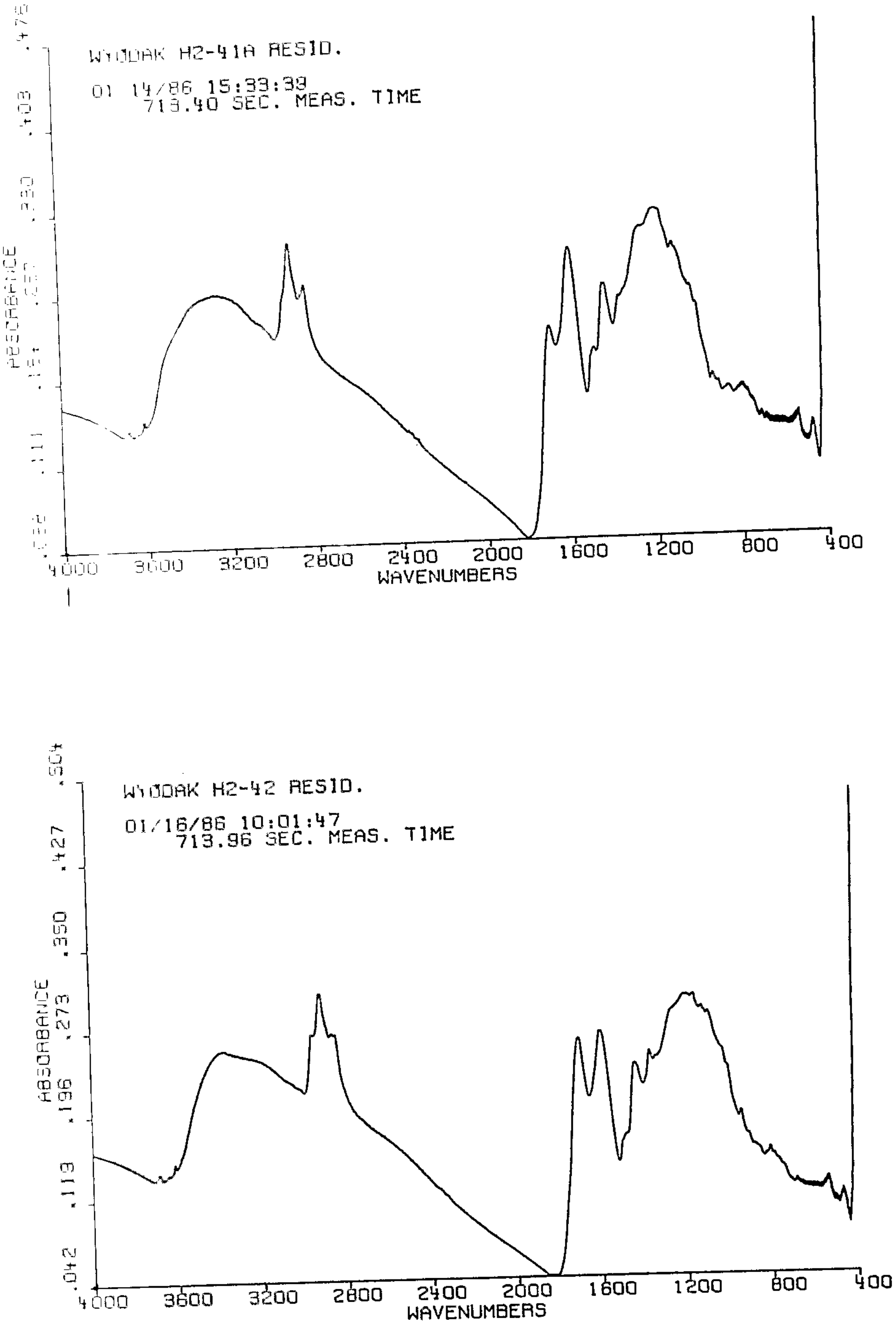


Figure 4. Continued

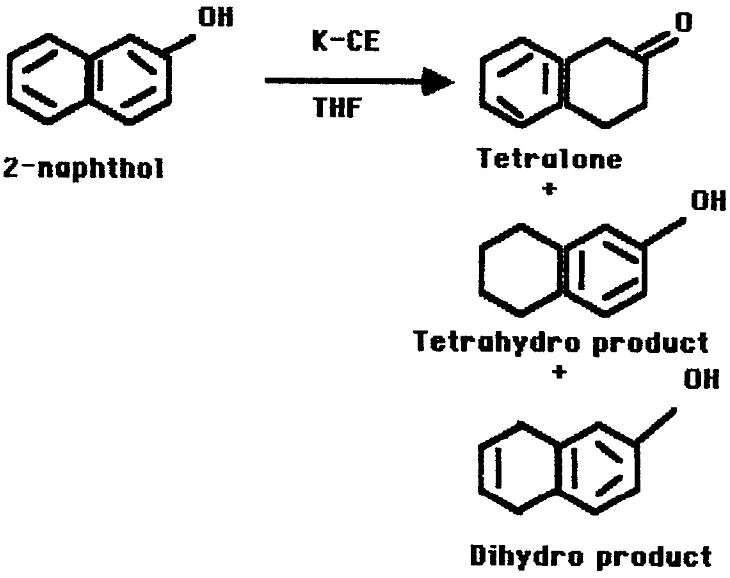


Figure 5. Model Compound Study

Table 2. Integrated Peak Intensities in the Aliphatic CH Stretch and C=0 Stretch Regions

Peak Description	Integration Region, cm^{-1}	Integrated Intensity, $Abs\text{-}cm^{-1}$ Wyodak			
		WC Wyodak Coal	WE1 Alkali Soluble	WR1 Residue 1st K-CE Reaction	WR2 Residue 2nd K-CE Reaction
Samples as Determined					
Total Aliphatic CH	2994-2790	5.3	6.5	7.5	9.3
Methyl CH	2994-2940	0.8	1.1	1.2	2.1
Total C=0 (a)	1780-1524	16 .4	29.0	22.0	22.9
Region 1 C=0	1780-1630	7.8	18.2	12.9	14.7
Region 2 C=0 (a)	1630-1524	8.6	10.8	9.1	8.2
Change (Product-Feed)					
Total Aliphatic CH	2994-2790	-	0.8	2.2	4.0
Methyl CH	2994-2940	-	0.3	0.4	1.3
Total C=0 (a)	1780-1524	-	12.6	5.6	6.5
Region 1 C=0	1780-1630	-	10.4	5.1	6.9
Region 2 C=0 (a)	1630-1524	-	2.2	0.5	-0.4

(a) Includes contributions from the aromatic C-C stretch peak at 1600 cm^{-1}.

rings is further supported by a decrease in the 1630-1524 cm^{-1} integration region corresponding to contributions from the aromatic C-C stretch peak at 1600 cm^{-1}. Thus, in WR2 which shows maximum increase in aliphatic CH, the 1630-1524 cm^{-1} integration shows a -0.4 change.

MASS SPECTROMETRY STUDIES

Field ionization mass spectrometry analysis established that the phenolic hydroxyl groups are distributed as mono and dihydroxy substituents on one, two and three ring systems (Figure 6). Evidence also indicated that dihydroxy aromatic structures were a significant constituent of the subbituminous coal. On the other hand, pyrolysis and liquefaction studies indicate that dihydroxy aromatics are not substantial constituents of the original coal. In order to validate the structural assignments based on the FIMS analysis, tandem mass spectrometry was employed. Tandem mass spectrometry is a powerful analytical tool for the unaided separation of a complex mixture into its constituent molecular ions and structural identification of the individual molecular ions. Thus, the alkali soluble coal fraction was subjected to a CI (chemical ionization) mass spectral probe using isobutane as the carrier gas. Protonated molecular ion (in CI-MS, one obtains the M+H ion and not the molecular ion M) peaks at m/z 95,109,123,137,111,125,145,159,161 are prominent in addition to a number of other molecular ion peaks. This is similar to what was obtained in the FIMS (except that FIMS gives the molecular ions M^+). These protonated molecular ions can be assigned to hydroxy and didroxyl aromatics like in the FIMS (Figure 6) based on the fragmentation pattern obtained on subjecting the protonated molecular ions to a EI (electron impact) mass spectral probe. The daughter spectra (as they are called) showed (1) loss of H_2O from the M+H ion (18 amu loss) which is typical of phenolics, (2) a fragmentation pattern typical of such structures and more importantly the fragmentation pattern matches the pattern obtained from an authentic sample! The daughter spectra of m/z 111 corresponding to the protonated molecular ion of dihydroxy benezene is shown in Figure 7 and the daughter spectra of m/z 125 corresponding to the protonated molecular ion of C1 dihydroxy benezene is shown in Figure 8 as examples.

It was thus established that dihydroxy one, two, and three ring aromatics are major structural units in the coal. The question that then arose was whether the

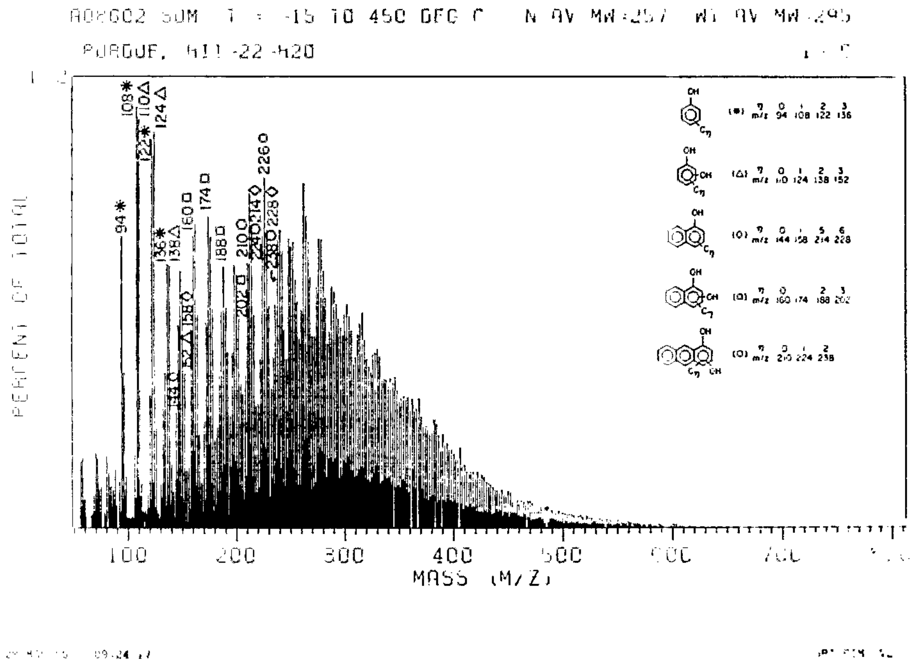


Figure 6. Field Ionization Mass Spectrogram

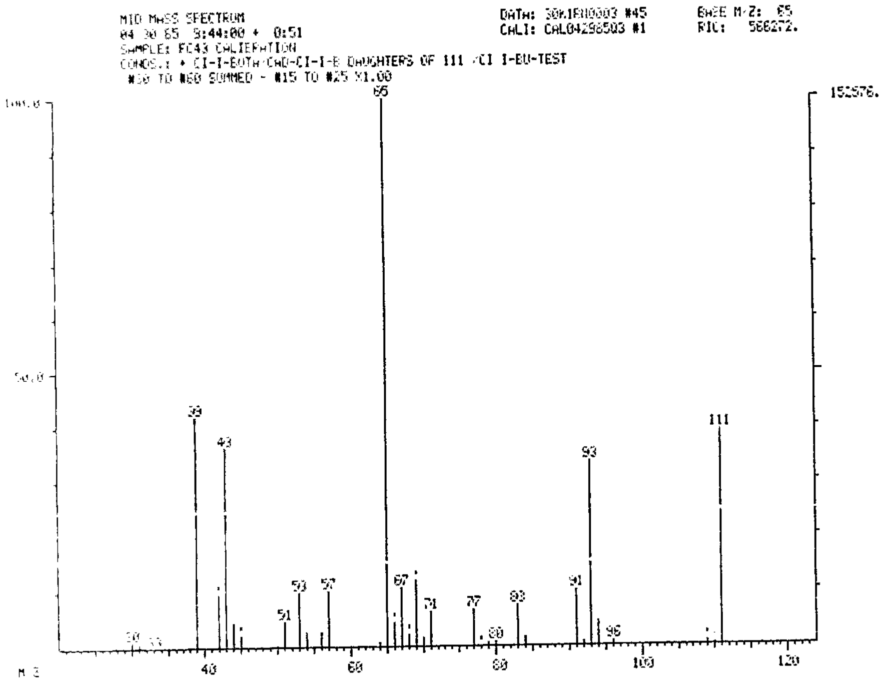


Figure 7. MS/MS-Daughter Spectra of m/z 111

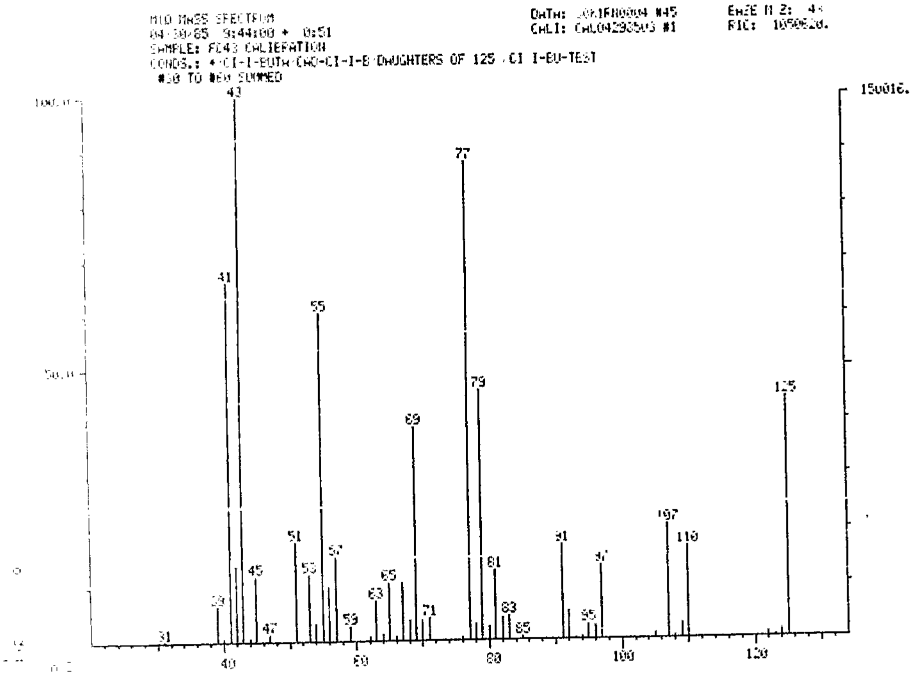


Figure 8. MS/MS-Daughter Spectra of m/z 125

potassium-crown ether reagent was cleaving the coal macromolecular structure down to the monomer dihydroxy or monohydroxy aromatic units for detection by FIMS. The selective room temperature and atmospheric pressure chemistry of the potassium-crown ether reagent should preclude any drastic cleavage of the macromolecular structure down to the hydroxy and dihydroxy monomers. It would, thus, appear that the hydroxy and dihydroxy one, two, and three ring aromatics with its alkyl substituted site chain analogs that are detected by FIMS analysis are produced by thermal rupture of the large coal oligomer fragments. The thermal cleavage could occur at the linkage between a coal cluster and the dihydroxy or monohydroxy aromatic ring system which may or may not contain alkyl substituents on it (Figure 9). It is also conceivable that some of these alkali site chains on the hydroxy aromatics arise by thermal cleavage of a long chain aliphatic bridging group as shown in Figure 10.

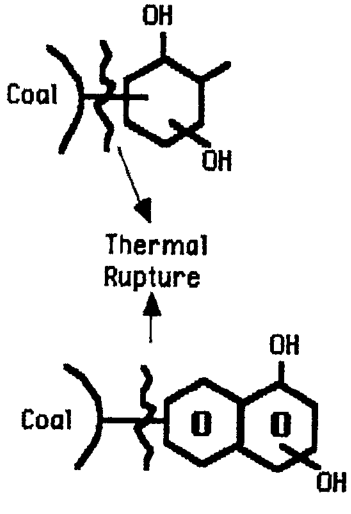


Figure 9

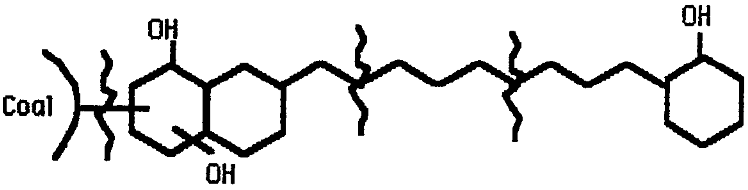


Figure 10

This was confirmed by the FIMS thermal evolution profiles. Figure 11 shows the thermal evolution profile of the molecular ions m/z 110,124,138 corresponding to the dihydroxy benezene and its C1 and C2 analogs. Similarly, Figure 12 shows the thermal evolution profiles of molecular ions m/z 160,174,188 corresponding to the dihydroxy naphthelene and its C-1 and C-2 analogs. The figures clearly show that these volatile dihydroxy aromatics do not evolve until a temperature of 350°C is reached. Thus, the coal oligomer fragments generated by the potassium-crown

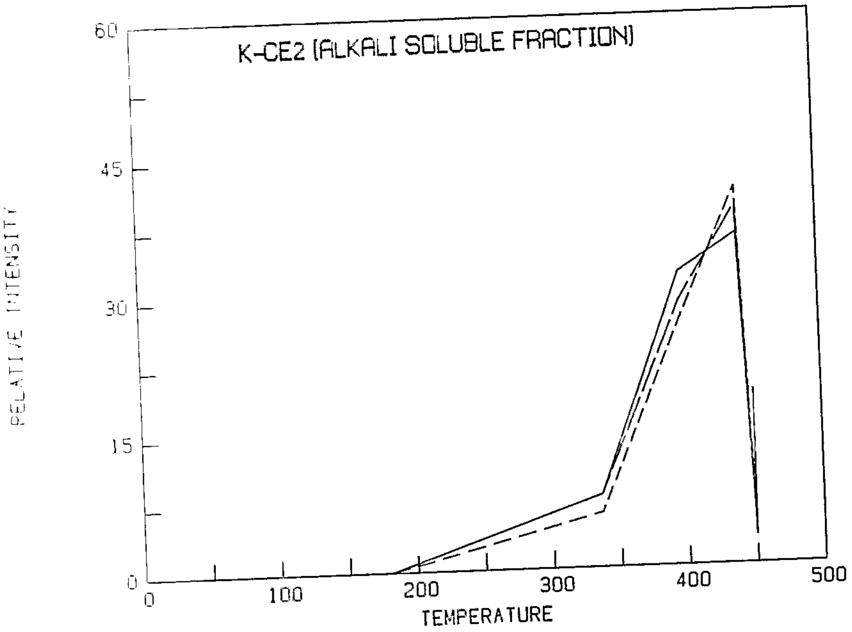


Figure 11. FIMS-Thermal Evolution Profile, m/z 110, 124, 138

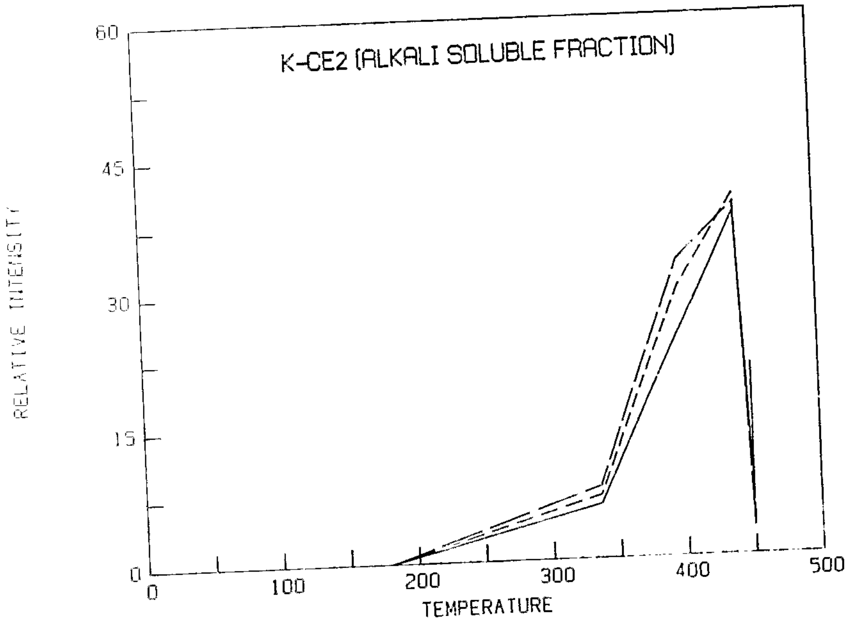


Figure 12. FIMS-Thermal Evolution Profile, m/z 160, 174, 188

ether reagent has been further thermally cleaved to generate these hydroxy aromatics and the alkyl substituted hydroxy aromatics prior to detection by FIMS.

MOLECULAR WEIGHT DISTRIBUTION OF THE COAL OLIGOMER FRAGMENTS IN THE ALKALI SOLUBLE FRACTION

Size exclusion chromatography (SEC) using a continuous viscosity detector combined with a refractive index concentration detector was used for the determination of molecular weight and molecular weight distribution. This method provides quantitative absolute molecular weight distribution using the universal calibration plot. It would appear that the alkali soluble coal oligomer fragments generated by the potassium-crown ether reaction with the coal macromolecule has a bimodal molecular weight distribution. Low molecular weight components with a number average molecular weight of only 632 and a weight average molecular weight of 5839 predominate in the THF soluble methylated alkali coal of the first K-CE reaction (Figure 13). A small hump corresponding to the higher molecular weight fraction is also seen. The SEC chromatogram of the second K-CE reaction also reveals a similar bimodal molecular weight distribution (Figure 14). Again, lower molecular weight components predominate although the values are slightly higher than after the first K-CE reaction. A slightly larger fraction of the higher molecular weights are obtained in the second K-CE reaction as seen in the figure.

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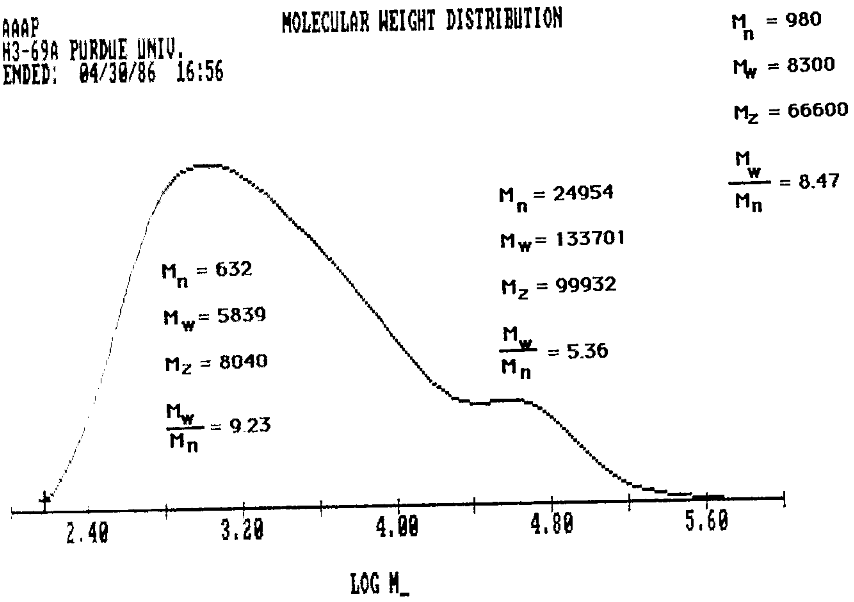


Figure 13. Molecular Weight Distribution of 1st K-CE Reaction

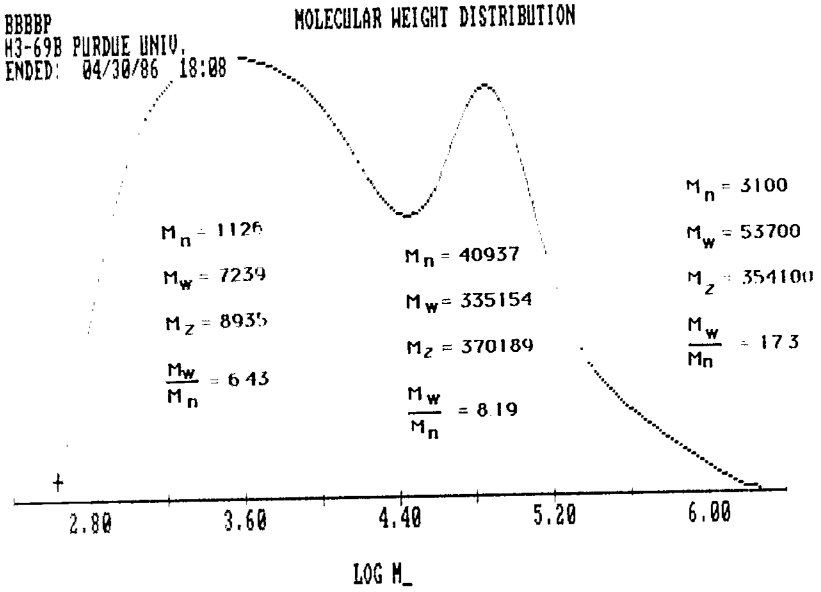


Figure 14. Molecular Weight Distribution of 2nd K-CE Reaction

DIFFERING REACTIVITY OF OXYGENATED MODEL-COAL STRUCTURES IN HYDROGEN-DONOR AND COH^{2}O SYSTEM

D. F. McMillen, R. Malholtra, S. E. Nigenda, T. C. Min and D. S. Ross

SRI International

ABSTRACT

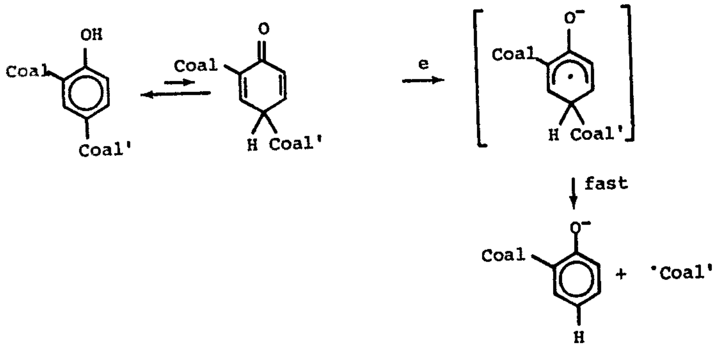
This paper describes the results of initial studies designed to test this suggestion that the effectiveness of CO/water/base systems in coal conversion can be attributed to the susceptibility of the keto-forms of phenolic coal structures to reaction with hydride- and electron-transfer reagents. The dealkylation, deoxygenation, and coupling or retrograde reactions of p-benzylphenol, 9-phenanthrol, o,o'-biphenol, 2-methyl-1-naphthol, and veratrole (1,2-dimethoxybenzene) have been studied as representative of classes important in coal conversion. Experiments were conducted in fused silica ampoules and stainless steel microautoclaves using at least two different donor solvents (typically tetralin and tetralin/THQ) and in $CO/H_2O/KOH$ systems. Comparison of the conversion rates in the organic and aqueous systems leads to the conclusions summarized below.

- Both dealkylation and deoxygenations can be faster in $CO/H_2O/KOH$ systems.
- Dealkylation rate appears to correlate with the amount of base, possibly due to nucleophilic displacement.
- Deoxygenation is not accelerated when dealkylation is a viable alternative.
- H_2O/Base can substantially accelerate coupling reactions. This tendency is moderated by CO.
- Alkylated polyoxygenated structures undergo rapid Ar-O cleavage.

Since both bond cleavage and retrogressive reactions are accelerated in aqueous/base systems, the net benefit clearly depends upon the balance between the two effects. The susceptibility of even mono-oxygenated structures to conversion in aqueous systems and the high inherent reactivity of di- and tri-oxygenated structures in low-donor solvents strongly suggests that bond cleavage and facile oxygen loss in low-rank coals may be due to alkylated di- and trihydroxy structures. The results of our study suggest that the increased pyrolysis yields reported on methylation of low-rank coals are due not only to protection of hydroxyls from coupling reactions but are also due to enhanced cleavage of the strong Ar-O bonds. These results suggest that the facile dissolution of subbituminous coals in alcoholic KOH media could well be due to reactions of partially alkylated polyphenolic structures rather than to hydrolysis of esters as has been previously asserted.

INTRODUCTION

Carbon monoxide/water/base systems have been known for many years to be effective media for coal liquefaction, and have recently received increased attention (1-3). Yet, the chemical mechanisms by which they depolymerize and defunctionalize the coal structure are largely unknown. Appell and co-workers demonstrated a number of years ago that CO/H_2O systems are effective reducing agents for carbonyl compounds, presumably via a hydride-transfer mechanism (4). However, coals are generally considered to contain very few carbonyl groups. In the absence of carbonyl structures as such, phenols may also serve as sites for possible coal structure degradation. In their keto forms, phenols can potentially act as hydride and/or electron acceptors. The intermediates produced can readily undergo cleavage as shown below:



In this paper we describe the results of initial studies designed to test this suggestion. Model compounds chosen for this study represent structures likely to be prominent in coals and which encompass the general classes of reactions known to be important in coal conversion: dealkylation, deoxygenation, and coupling or retrograde reactions. Specifically, we studied the conversion of p-benzylphenol, 9-phenanthrol, o,o'-biphenol, and 2-methyl-1-naphthol in organic donor solvents and in aqueous systems. We also examined the reactions of a dioxygenated substrate, veratrole (1,2-dimethoxybenzene). However this substrate has been studied only in an organic donor solvent, dihydrophenanthrene.

We will show that in many cases tautomerization of the phenol to the keto structure opens up avenues of reactivity not available to the phenolic structure. It should be remembered that the keto form of the phenols is present in increasing abundance in polycyclic aromatic structures; the favored tautomer of 9-hydroxyanthracene is anthrone. The presence of oxygen functions makes ionic pathways accessible and play a determining role in the overall reactivity of these systems.

EXPERIMENTAL

Experiments with donor solvents, tetralin, tetralin/20% tetrahydroquinoline (THQ), and dihydrophenanthrene were conducted in fused silica ampoules. Relative amounts of the substrate and solvent were generally on the order of 20% and 80% respectively. Runs with $CO/H_2O/KOH$ systems were conducted in stainless steel microautoclaves. The initial pH of the alkaline solution was 13 and the molar ratio of KOH to the substrate was between 0.2 and 2. The reactors were charged with 500 psi cold of CO, or in some cases with N_2. Unless otherwise indicated, all reactions were conducted at 400°C for varying periods such that total substrate conversions generally ranged from 5% to 30%. Reaction products were characterized and determined by GC and GC/MS. The results are arbitrarily reported as defined first-order rate constants, since rates were generally not determined as a function of time or initial concentration. A first-order rate constant of 10^{-6} s^{-1} corresponds to a half-life of 200 h.

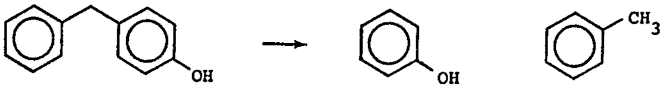
RESULTS AND DISCUSSION

p-Benzylphenol Dealkylation

We have previously reported on the decomposition of p-benzylphenol in tetralin and other donor-solvent systems (5). The rate constants for the cleavage in organic and aqueous systems are given in Table 1.

Table 1

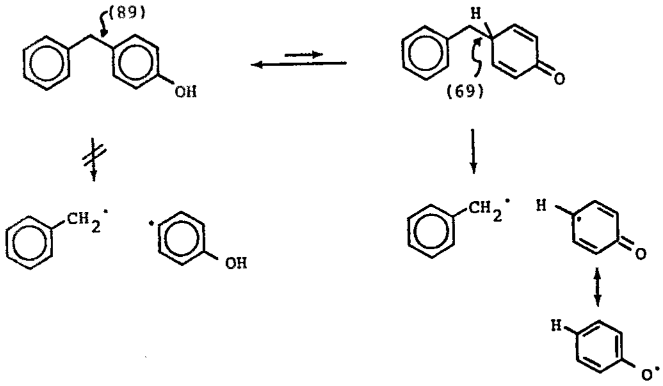
RATES OF DEALKYLATION OF p-BENZYLPHENOL



Solvent System	k_{dealk} (10^{-6} s^{-1})
TETRALIN	8.5
TETRALIN/20% THQ	6.4
$CO/H_2O/KOH$	140.
$N_2/H_2O/KOH$	250.

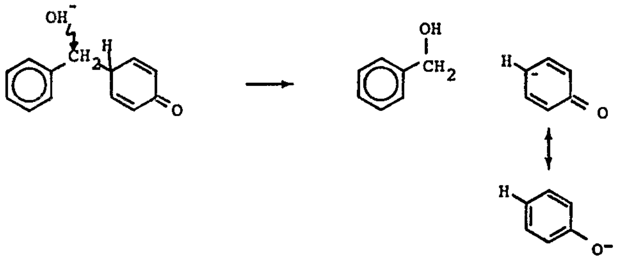
In donor solvents, toluene and phenol are formed in near-stoichiometric quantitites and no deoxygenation to diphenylmethane was observed (see below). The cleavage in tetralin proceeds with a defined first order rate constant of about 8 x 10^{-6} s^{-1}. The rate is too high for a simple thermolysis of the CH_2-Ar bond, which is approximately 89 kcal/mol strong. Based on this bond strength and a reasonable A-factor of

$10^{15.5}$, the calculated rate constant for thermolysis is on the order of 10^{-13} s^{-1}, in other words about seven orders of magnitude too slow. As discussed in our previous publication, the reaction proceeds in tetralin by first tautomerization of the phenol into a keto form (5). This tatutomerization is accompanied by a weakening of the CH_2-Ar bond by about 20 kcal/mol. The predicted rate for the cleavage of this bond is in accord with the observed values.



If the decomposition was limited by the rate at which the phenol tautomerized to the keto form, we could expect addition of a base such as tetrahydroquinoline (THQ) to increase the overall rate, since keto-enol tautomerizations are catalyzed by acids and bases. However, the rate of p-benzylphenol cleavage did not increase upon addition of 20% THQ to the solvent tetralin. Thus, in this case tautomerization is not rate limiting. As reported by us earlier, this result is in contrast with the case of phenoxyphenol where tautomerization was rate limiting and the cleavage was accelerated by THQ and piperidine by factors as large as 1000 at 400°C (6).

In the $CO/H_2O/KOH$ system, the decomposition rate of p-benzylphenol increased twenty fold. As mentioned above, the increase cannot be attributed to an increased rate of tautomerization. Nor is the increase a result of the greater reducing power of the $CO/H_2O/KOH$ system because replacing CO with N_2 produced a further increase in the decomposition rate. Another indicator that the mode of accelerated cleavage in the aqueous systems does not involve tautomerization/homolysis is the fact that the yield of toluene was only about 1/5 the yield of phenol. Were the keto-form simply to undergo homolysis, the yields of phenol and toluene should be very similar (as they are in donor solvents). In other words, when benzyl radical is produced, nearly all of it can be accounted for by the toluene formed. Therefore, we surmise that in these aqueous systems substantial amount of cleavage is resulting from another pathway, possibly the direct displacement of phenolate ion in the keto form by the hydroxide:



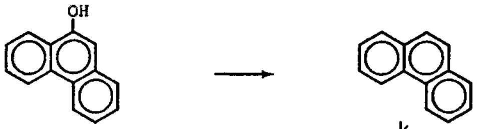
Toluene is not produced in this reaction, and the benzyl alcohol formed probably undergoes further reactions. This suggestion is by no means proven, but is consistent with the observed higher rate when CO is replaced by N_2, in that in the former case basicity of the medium is reduced by the production of CO_2 by the water gas shift reaction. With N_2 there is no such attenuation of the basicity and base promoted reactions are expected to be faster.

9-Phenanthrol Deoxygenation

Table 2 gives the rate constants for the deoxygenation of 9-phenanthrol. Phenanthrene was formed in these cases in greater than 95% yield.

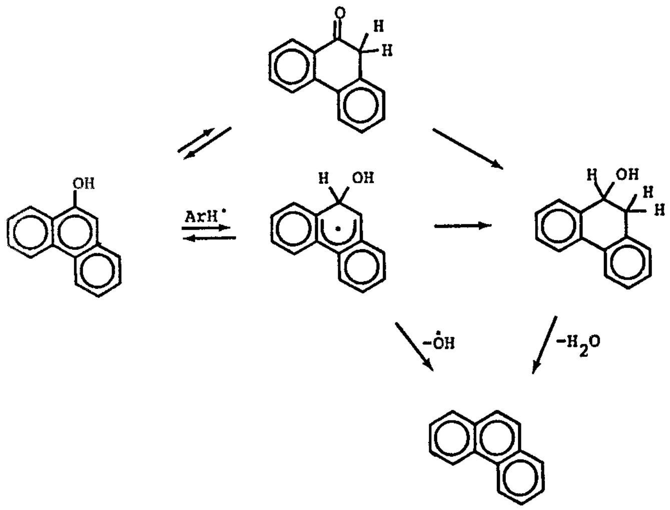
Table 2

RATES OF 9-PHENANTHROL DEOXYGENATION



Solvent Ssystem	k_{deox} $(10^{-6}\ s^{-1})$
TETRALIN	17.
TETRALIN 20%/THQ	76.
$CO/H_2O/KOH$	170.

This deoxygenation is another reaction that cannot take place by simple thermolysis of the Ar-O bond. In organic systems it is most likely engendered by the transfer of a hydrogen atom to the ipso position by a solvent radical. This type of H-transfer has been termed as radical hydrogen transfer, RHT, by us and we have demonstrated its operation in several model systems (7,8). Following RHT, there is a competition between the loss of OH and transfer of another hydrogen to produce the reduced product, which in turn can lose water to give phenanthrene:



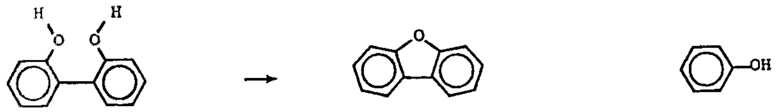
In our studies on the RHT reaction we have observed that THQ is a more effective in transferring hydrogen than tetralin. The four-fold increase in the deoxygenation rate in the presence of THQ is consistent with the reaction proceeding by RHT, since similar rate increases with THQ are seen for other reactions where the mechanism is known to involve cleavage induced by RHT. Furthermore, the lack of deoxygenation in p-benzylphenol can also be rationalized, since RHT to a benzene ring is much more difficult than to a polycyclic system. In aqueous systems the reduction of 9-phenanthrol to the dihydro derivative may proceed via hydridic reduction of the keto form. [RHT processes in CO/H_2O systems could conceivably take place through the intermediacy of the HCOO· (or ·COOH) species, but its unimolecular elimination of H· is nearly thermoneutral and its anticipated lifetime at 400°C ($< 10^{-10}$ s) would be much too short for any bimolecular transfer processes to compete (9,10).]

o,o'-Biphenol Coupling

In the previous two cases we saw examples of two major modes of bond cleavage being accelerated by the aqueous systems. However, in order to help understand the impact of $CO/H_2O/KOH$ system on coal liquefaction, we must also consider bond forming or retrogressive reactions. Coupling of o,o'-biphenol to give a very refractory material, dibenzofuran, can be taken as representative of such retrogressive reactions. We studied the reaction of o,o'-biphenol in organic and aqueous systems. In all cases dibenzofuran was the major product. Cleavage of the substrate to give phenol was observed only in the case of tetralin containing 20% THQ. The rate constants for dibenzofuran and phenol formation are given in Table 3.

Table 3

RATES OF RING CLOSURE AND BOND SCISSION OF o,o'-BIPHENOL



Solvent System	k_{DBF} (10^{-6} s^{-1})	k_{Phenol} (10^{-6} s^{-1})
TETRALIN	2	.05
TETRALIN/20% THQ	7	1.6
$CO/H_2O/KOH$	520	.05
$N_2/H_2O/KOH$	1600	.05

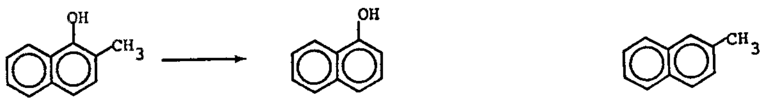
As can be seen in Table 3, the aqueous systems strongly promote the coupling reaction. This tendency is somewhat ameliorated, but not eliminated, in the reducing environment provided by CO. Thus the net benefit of CO/H_2O systems is severely limited by the retrogressive reactions. If means could be found to suppress retrogressive reactions in aqueous systems even greater benefits may be reaped.

2-Methyl-1-Naphthol Dealkylation and Deoxygenation

2-Methyl-1-naphthol exhibits both dealkylation and deoxygenation reactions and is a convenient substrate to examine these reactions in a single molecule. In organic donor-solvents dealkylation and deoxygenation reactions are observed with the former occuring two to four times faster. The rate data are summarized in Table 4.

Table 4

DEALKYLATION AND DEOXYGENATION RATES OF 2-METHYL-1-NAPHTHOL



Solvent System	k_{dealk} (10^{-6} s^{-1})	k_{deox} (10^{-6} s^{-1})
TETRALIN	3.8	1.9
TETRALIN/20% THQ	28.4	6.5
$CO/H_2O/KOH$	2.4	1.4
$N_2/H_2O/KOH$	200.	1.5

Unlike the case of p-benzylphenol, here the predicted rate constant for dealkylation by thermolysis of the keto form is roughly three orders of magnitude too low. Dealkylation in donor solvents, like deoxygenation, is most likely taking place via RHT. Again, the increased rates of dealkylation and deoxygenation in the presence of THQ are consistent with the RHT pathway.

The rates of dealkylation and deoxygenation in CO/H_2O/KOH were almost identical to those in tetralin. Upon replacing CO by N_2 the dealkylation rate increased almost one hundred times but the deoxygenation rate remained the same. We noticed in these reactions that the ratio of dealkylation to deoxygenation (reduction) changed with the stoichiometric amount of the base. In general, dealkylation increased with increasing ratio of base to substrate. The trend can be seen in the data given in Table 5.

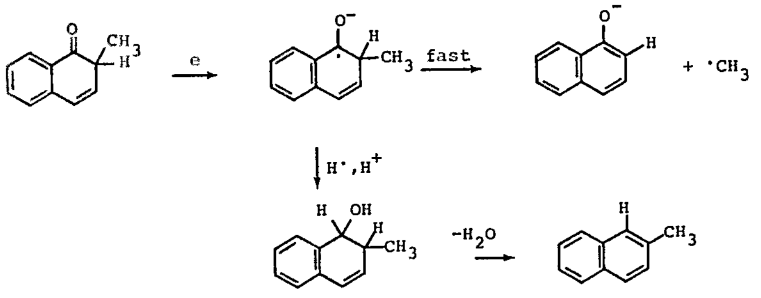
Table 5

EFFECT OF CHANGING KOH/SUBSTRATE RATIO ON PRODUCT DISTRIBUTION FOR CONVERSION OF 2-METHYL-1-NAPHTHOL

KOH/ 2-MeNOH	1-Naphthol/ 2-MeN	Cleaved Products/ Reduced Products
1.96*	140	60
1.13	29	3.4
0.85	1.9	0.48
0.60	6.4	0.99
0.22	2.2	3.2

*With N_2 instead of CO.

As with p-benzylphenol, we surmise that a significant portion of the dealkylation is proceeding by a nucleophilic displacement by OH^-, however, we cannot be certain of this. Deoxygenation is most likely taking place by first reduction of the naphthol to the dihydro derivative followed by loss of water. This pathway explains why dealkylation of this alkylated substrate, but not deoxygenation, is subject to promotion in aqueous systems. The first step in hydridic reduction of carbonyls is considered to be electron transfer (11,12). In order to give the reduced product, the radical anion intermediate has to accept an H-atom and a proton. However, in a competing process the intermediate produced in the case of 2-methyl-1-naphthol can unimolecularly lose the methyl radical giving the naphtholate anion:



Veratrole Decomposition

All the other model compounds reported in this study were monooxygenated. Given the abundance of oxygen in coals, particularly in low rank coals, structures bearing more than one oxygen atom on one benzene ring would be significant even if they were distributed in a purely statistical manner. Beyond this, the fact that lignin contains an abundance of polyphenolic structures, makes it even more likely that such structures are more important than the statistical expectation in lignites and subbituminous coals. In previous years we have reported on coupling reactions of dihydroxyaromatics, however, we also noted rapid deoxygenations in certain substrates (13,14). In continuation of the investigations of bond scission reactions in polyoxygenated structures, we recently began a study of veratrole (1,2-dimethoxybenzene), as the simplest and probably least reactive representative of the methylated poilyphenolic lignin structures.

Decomposition of veratrole was investigated as a 50 m% solution in 9,10- dihydrophenanthrene at 300 and 400°C. The overall conversion at 300°C/1 h was 25 ± 5% and at 400°C/3 h was 95 ± 5. The distribution of products at the two temperatures is very different. For example, at 400°C 50% of the product is catechol, whereas at 300°C, we did not detect any catechol. Other products include anisole, phenol, guaiacol, and cresols. The distribution of the products at the two temperatures is shown in Figure 1. Clearly, cleavage of both ArO-Me and the stronger Ar-OMe bonds is taking place. Even the cleavage of the weaker O-Me bond at 300°C is surprising in view of its bond strength (~ 60 kcal/mol), as shown by the estimated and observed decomposition rate constants shown in Table 6.

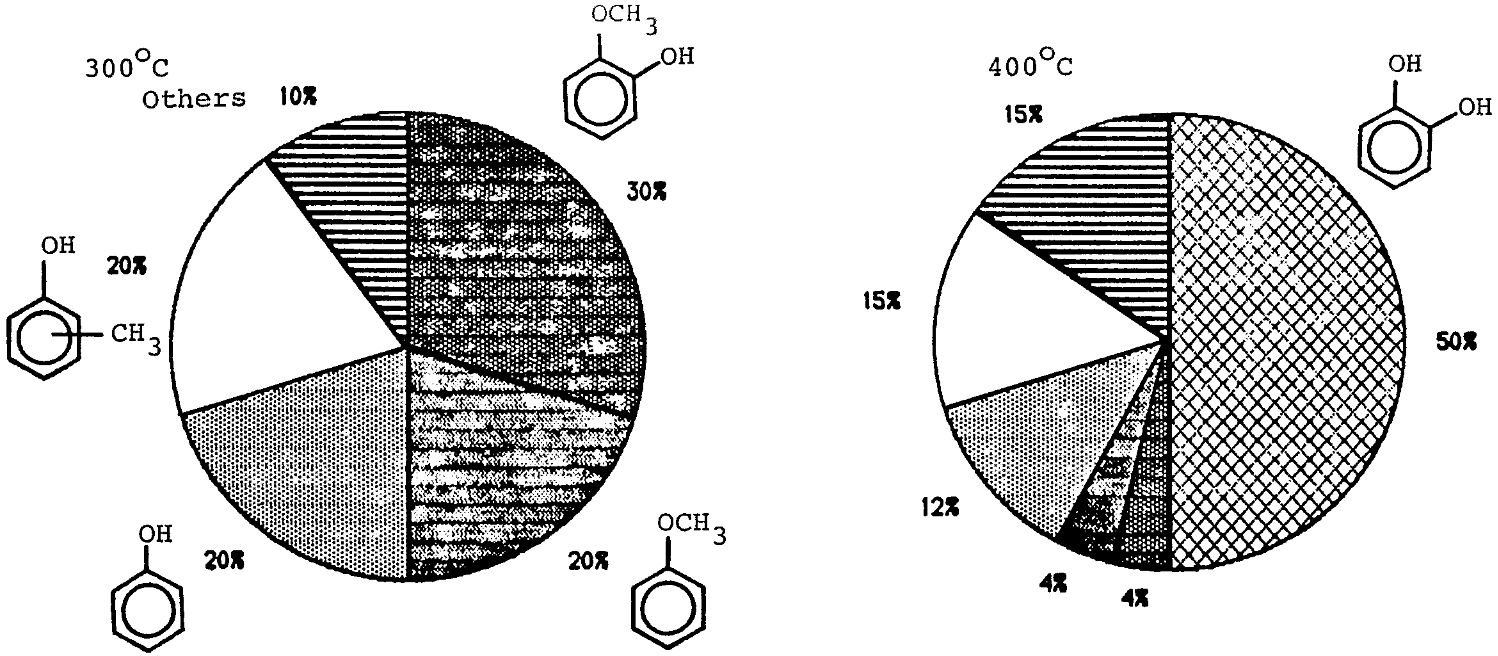


Figure 1. Product Distribution of Veratrale Decomposition in Dihydrophenanthrene at 300° C and 400 ° C.

Table 6

ESTIMATED AND OBSERVED O-CH_3 BOND HOMOLYSIS RATE CONSTANTS IN ANISOLE AND VERATROLE

Substrate	Bond Strength	Estimated Homolysis Rate Constant s^{-1} (°C)	Observed Reaction Rate Constant s^{-1} (°C)
$C_6H_5O\text{-}CH_3$	64	5×10^{-6} (400)	5×10^{-4} (400)
o-$CH_6H_4(O\text{-}CH_3)_2$	$\sim$60	1×10^{-4} (400)	3×10^{-3} (400)
"		4×10^{-8} (300)	2×10^{-5} (300)

While the exact agreement between estimated and observed rates for the monofunctional ether is in part fortuitous, the contrast with the case for veratrole clearly indicates another pathway besides homolysis has been opened up in the case of veratrole.

The ratio of the products of Ar$\nmid$OMe cleavage to ArO$\nmid$Me cleavage decreases from about 1.0 to 0.5 in going from 300 to 400°C; in other words the temperature dependence of the reaction leading to the cleavage of the stronger bond is lower. The temperature dependence of veratrole decomposition (all losses) is shown in Figure 2 and is much too low to correspond to homolysis. The filled circles are the data from the present study. Bredenberg and Ceylan have also studied the decomposition of several aromatic ethers including veratrole and guaiacol (2-methoxyphenol) (15,16). They also observed the cleavage of Ar-O links in these cases. Interestingly, decomposition of guaiacol produces phenol and cresols but no anisole. Thus, it appears that methylation is involved in some way in inducing this cleavage. One suggestion is the initial formation of Ar-OCH_2• radical, which then loses CH_2O and produces an Ar• radical. The latter, being very reactive, can abstract a hydrogen from the starting material and continue the chain process. However, estimated rates for this process in the donor-solvent dihydropheanthrene, which will rapidly scavenge the phenyl radicals, are roughly three orders of magnitude too low.

Some of Bredenberg's results are also plotted in Figure 2. The data for veratrole and guaiacol lie close to the line connecting data points from our study. The monooxygenated systems have much lower rates of decomposition (present study).

Additional suggestions as to the nature of Ar-O bond cleavage can be obtained by examining the fate of dihydrophenanthrene and analyzing the gas make. By itself, dihydrophenanthrene undergoes little transformation under the reaction conditions

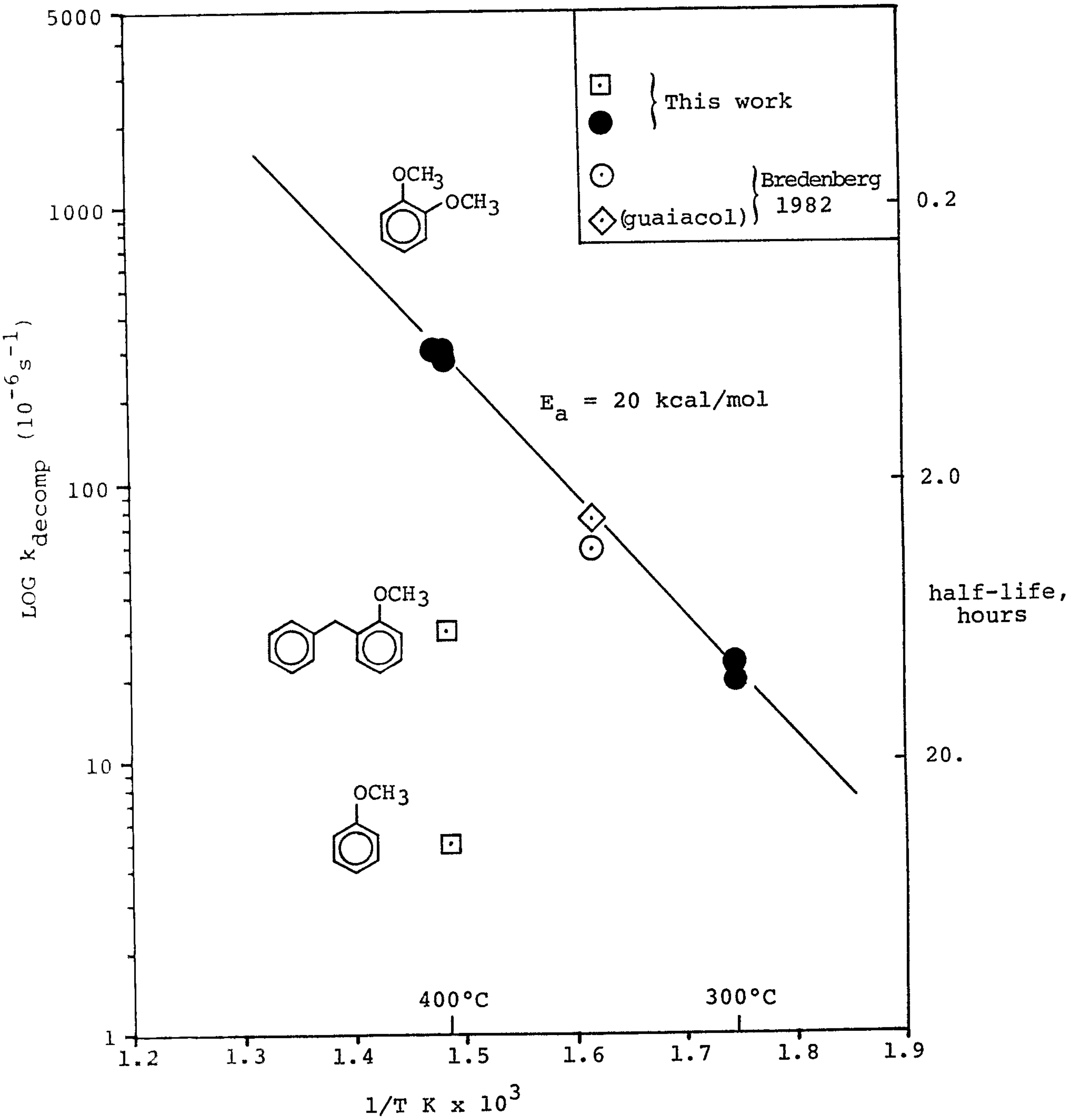


Figure 2. Temperature Dependence of Veratrale Decomposition in Dihydrophenanthrene

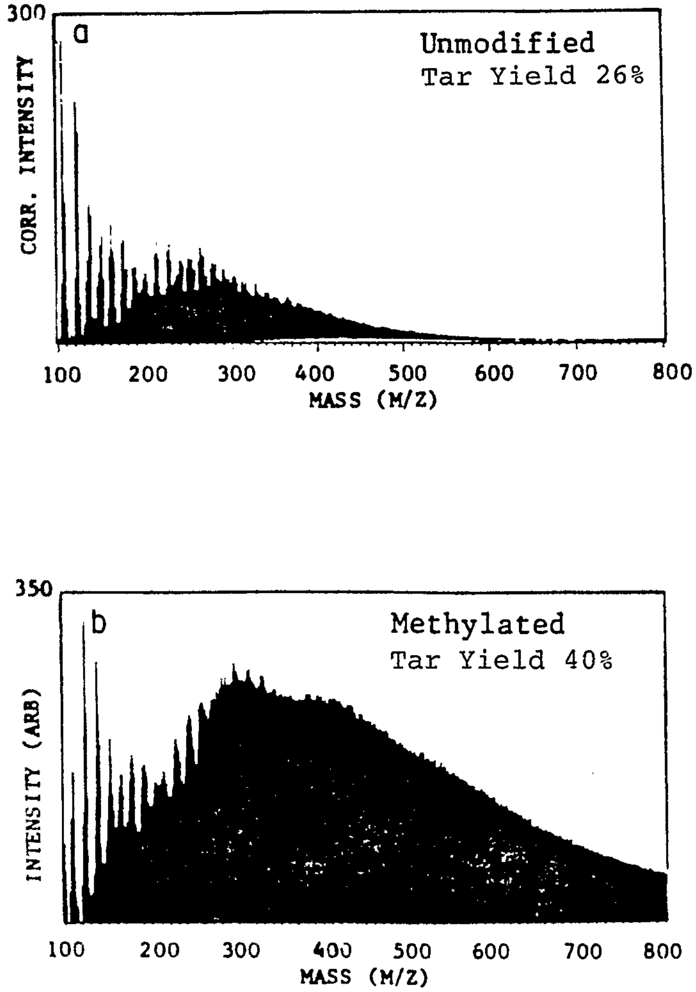
(400°C/3 h). However, with veratrole present in equimolar amounts, dihydrophenanthrene is completely converted into phenanthrene. Among the gaseous products, H_2 is the most abundant with CH_4, CO, and CO_2 being roughly 1/10 the level of hydrogen. At present, the results are best explained in terms of a chain process with the cleavage of Ar-O bonds resulting from RHT by 9-hydrophenanthryl radicals:

$$
\begin{aligned}
\mathrm{ArOMe} + \mathrm{9PhH}\cdot &\rightarrow \mathrm{ArH} + \cdot\mathrm{OMe} + \mathrm{Ph} \\
\cdot\mathrm{OMe} &\rightarrow \mathrm{H}\cdot + \mathrm{CH_2O} \\
\mathrm{H}\cdot + \mathrm{Ph} &\rightarrow \mathrm{9PhH}\cdot \\
\mathrm{H}\cdot + \mathrm{PhH_2} &\rightarrow \mathrm{H_2} + \mathrm{9PhH}\cdot \\
\cdot\mathrm{OMe} + \mathrm{ArOMe} &\not\rightarrow \mathrm{CH_2O} + \mathrm{ArHOMe}\cdot
\end{aligned}
$$

The methoxyl radicals could also provide hydrogen for cleavage, either via RHT or as free H-atoms. RHT processes will result in cleavage but not in H_2 formation, however, if the methoxyl radical unimolecularly eliminates a hydrogen, the resulting fre H-atom could end up as H_2 by abstracting a hydrogen from a donor. The very strong bond of H_2 (104 kcal/mol) makes its production a "waste" of active hydrogen as we discussed previously (8). The unimolecular elimination of H-atoms is more endothermic than RHT and hence is favored by higher temperatures. At 400°C, we estimate (9) elimination of H from methoxyl to be two orders of magnitude faster than transfer by RHT to phenanthrene (1 M). Consistent with this estimation, we observe the most of the hydrogen from cleaved methoxyls wind up as H_2 at 400°C, but a substantially smaller portion does so at 300°C.

The above consistency notwithstanding, the cleavage of Ar-O bonds is not fully reconcilable with all the facts. Thus, the loss of OMe, but not OH, from guaiacol, and the relative stability of anisole cannot be rationalized strictly in terms of intermolecular hydrogen transfer. Further, the reported near-first-order behavior of guaiacol decomposition (15) would also seem to demand another explanation.

While we cannot at this point suggest a mechanism that is consistent with all the observations of the decomposition of polyphenols and their methyl ethers, the impact of methylation on coal conversion can be substantial. For instance, Solomon has reported on the pyrolysis/FIMS of unmodified and methylated Texas Big Brown lignite (17). The tar yields increased from 26 to 40% upon methylation. The molecular weight profile of the evolved tars is also substantially different in the two cases as shown in Figure 3. The increase in the tar yield has been attributed to the protection of the phenolic groups from undergoing retrogressive reactions. Our study suggests that besides this protective effect, methylation may also be inducing cleavage reactions.



Solomon, 1985

Figure 3. Pyrolysis/FI-Mass Spectra of Unmodified and Methylated Big Brown Texas Lignite

Although we have not yet examined veratrole and similar coal-like structures in aqueous systems, the susceptibility of even mono-oxygenated substrates in aqueous systems and the high inherent reactivity di- and trioxygenated structures in donor solvents strongly suggests that bond cleavage and facile oxygen loss loss in low rank coals may be due to alkylated polyphenolic structures. In fact, the reported dissolution of subbituminous coals in alcoholic KOH media could well be due to reactions of polyoxygenated non-ester structures rather than merely to the hydrolysis of esters as has been previously asserted (18).

SUMMARY

- Both dealkylation and deoxygenations can be faster in $CO/H_2O/KOH$ systems.
- Dealkylation rate appears to correlate with the amount of base, possibly due to nucleophilic displacement.
- Deoxygenation is not accelerated when dealkylation is a viable alternative.
- H_2O/Base can substantially accelerate coupling reactions. This tendency is moderated by CO.
- Alkylated polyoxygenated structures undergo rapid Ar-O cleavage.

Since both bond cleavage and retrogressive reactions are accelerated in aqueous/base systems, the net benefit clearly depends upon the balance between the two effects. The susceptibity of even mono-oxygenated structures to conversion in aqueous systems and the high inherent reactivity of di- and tri-oxygenated structures in donor solvents strongly suggests that bond cleavage and facile oxygen loss in low-rank coals may be due to alkylated di- and tri-hydroxy structures. Solomon and coworkers have shown that methylation of a lignite resulted in increased tar yield upon pyrolysis. The results of our study suggest that the increased yield is due not only to protection of hydroxyls from coupling reactions but also due to enhanced cleavage of the strong Ar-O bonds. The mechanism of this latter cleavage is not yet clear, but it cannot simply be attributed to chain reactions involving the decomposition of phenoxy radicals.

ACKNOWLEDGEMENT

We gratefully acknowledge financial support for this work by the Electric Power Research Institute, Contract No. RP 2147-5, and the U.S. Department of Energy, Pittsburgh Energy Technology Center, Contract No. DE-FG22-84PC70811.

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