SECTION 2

COAL UPGRADING AND RESEARCH

SELECTIVE OXIDATION OF COAL PYRITES IN COALS BY STEAM/AIR MIXTURES IN A FLUIDIZED BED

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ABSTRACT

Number 6 coals from two Illinois mines, and a Rosebud seam coal from Montana, were partially desulfurized by selective oxidation of the sulfur in the coals. The sulfur was reduced up to about 60 percent on a Btu basis while only losing less than about 10 percent of the heating value of the coals. The coals were treated in a fluidized bed reactor using various ratios of steam and air as the fluidizing gases. No agglomeration of the coals studied to date was observed.

The coals treated were sized to 20 x 100 mesh. Only the SO_2 content of the off gases was monitored, which was assumed to be the only important sulfur compound evolved. With the Illinois No. 6 seam coals, the sulfur was removed in about two hours. With the Rosebud coal, almost no sulfur was removed until the coal had been at treatment conditions for between two to four hours. Then significant sulfur was oxidized to sulfur dioxide in an additional two hour treatment time. Essentially complete removal of the pyritic sulfur in the Illinois coals could be achieved.

A preliminary cost estimate indicates that the cost of processing would be on the order of $5.00/ton of coal. At these levels the process would appear to be attractive for the cleaning of coal fines in general, and may be especially of interest where regulations could be met by removal of pyritic sulfur only.

INTRODUCTION

The work described in this paper was addressed to the possibility of the use of oxidation reactions to liberate the pyritic sulfur contained in steam coals and to beneficiate lower-rank coals in general. Pyritic sulfur often, if not usually, represents more than half of the sulfur in most steam coals. In view of pending regulations relating to the acid rain issue, which often propose about a 50 percent cutback in SO_2 emissions, the removal of pyritic sulfur, if it can be done inexpensively, represents an attractive control approach that should be reexamined.

The idea of oxidation of pyritic sulfur in coal is indeed old. In fact it occurs in nature and is evidenced in at least two ways. With air, the oxidation of pyritic sulfur in coal or gob piles is so exothermic that these piles often ignite spontaneously. In aqueous media, the oxidation by air (often assisted by bacteria) reacts to form highly acidic solutions which cause the well-known acid mine drainage problem that is so difficult to control.

Although interest in pyritic sulfur removal has been revived from time to time, with increasing stricter New Source Performance Standards (i.e., now at a 90 percent sulfur removal level), interest in pyritic sulfur removal, by itself, has waned over the more recent years. However, the opportunities for such a process are again attractive if lesser removal levels are possible. One approach to meet the new needs of the coal and utility industries is to remove the pyritic sulfur, i.e., about half of the sulfur in most coals, by low-cost selective-oxidation schemes such as oxidation in air-steam mixtures under conditions of good temperature control. It is probably also necessary that alkalinity in the coal ash be relatively small compared to the sulfur content, otherwise this alkalinity would tend to trap and retain the acidic sulfur dioxide formed upon oxidation.

The selective oxidation of sulfur from steam coals should not significantly change the ash properties of the fuel. Therefore, a fuel treated by the process described in this report should be usable (as determined by ash properties)

in any furnace where the untreated fuel is usable, and no new boiler problems should be encountered with the desulfurized product. Obviously, the quantity of inorganics (calcium oxide, aluminum oxide, etc.) in the ash will be increased slightly because of the loss in heating value of the fuel, and probably somewhat less sulfate will be present in the resultant ash because of the precombustion reduction in sulfur. However, sulfur in ash from commercial combustion equipment is usually small and generally has little affect on ash properties.

EXPERIMENTAL PROCEDURES

Experimental Fuels

These fuels were fairly well characterized in terms of response to a selective oxidation approach during the program--a coal from Peabody's Christian County mine in the Illinois No. 6 seam, a coal from Peabody's River King mine also in the Illinois No. 6 seam, and a coal from the Rosebud seam in Montana. The raw coals were ground and seived before use. The proximate analyses and the sulfur form analyses for these fuels are listed in Table 1.

Experimental Equipment

As may be noted in Figure 1, which is a flow diagram of the experimental equipment, fluidizing air and steam were metered into the system and then passed through a preheater furnace. This preheated fluidizing gases then passed into a reactor, where they reacted with the coal. As the fluidizing gases left the reactor, a sample was continuously extracted for monitoring the SO_2 content of the exhaust gases. The off gases were finally exhausted through a stack.

Figure 2 is a photograph of the equipment taken during early checkout runs. The large cabinet on the left is a controller for the Globar® furnace which is used to heat the fluidized-bed reactor. The Globar® furnace is located inside the slotted angle-frame support structure in the center of the photograph and the reactor can be seen extending out the top of the furnace. The inverted flask at the top of the reactor is an expanded section fused to the reactor tube to minimize particle blow-over, and it also serves as the feed charging point for coal. The fluidizing gases exhaust through the 3-inch stovepipe in front of, and roughly parallel to, the stairtreads leading to a balcony which can be seen behind the reactor.

Table 1

ANALYSES FOR SULFUR CONTENTS IN FEED COALS

Run No.	Coal	Proximate Analysis					Sulfur Forms		
		Moisture %	Ash %	Volatile %	Fixed Carbon %	Sulfur %	Pyritic %	Sulfate %	Organic %
2-8	CC	12.4	9.8	35.3	42.5	3.7	1.18	0.30	2.18
2-8	CC	11.9	9.6	36.0	42.6	3.6	1.05	0.34	2.18
2-8	CC	12.4	10.0	35.3	42.2	3.6	1.30	0.28	1.99
10	RK	7.4	22.5	33.3	36.8	4.9	2.74	0.16	1.99
11	RB	19.4	11.3	29.9	39.4	1.7	1.22	0.01	0.45
12	RB	19.6	12.0	29.8	38.6	2.2	1.93	0.02	0.21
13	RK	7.5	21.5	32.6	38.4	5.4	3.15	0.15	2.15
14	RB	18.7	10.1	38.0	33.3	1.6	1.03	0.02	0.57
23	CC	12.0	9.3	35.5	43.3	3.6	0.90	0.40	2.27

CC - Christian County RK - River King RB - Bosebud

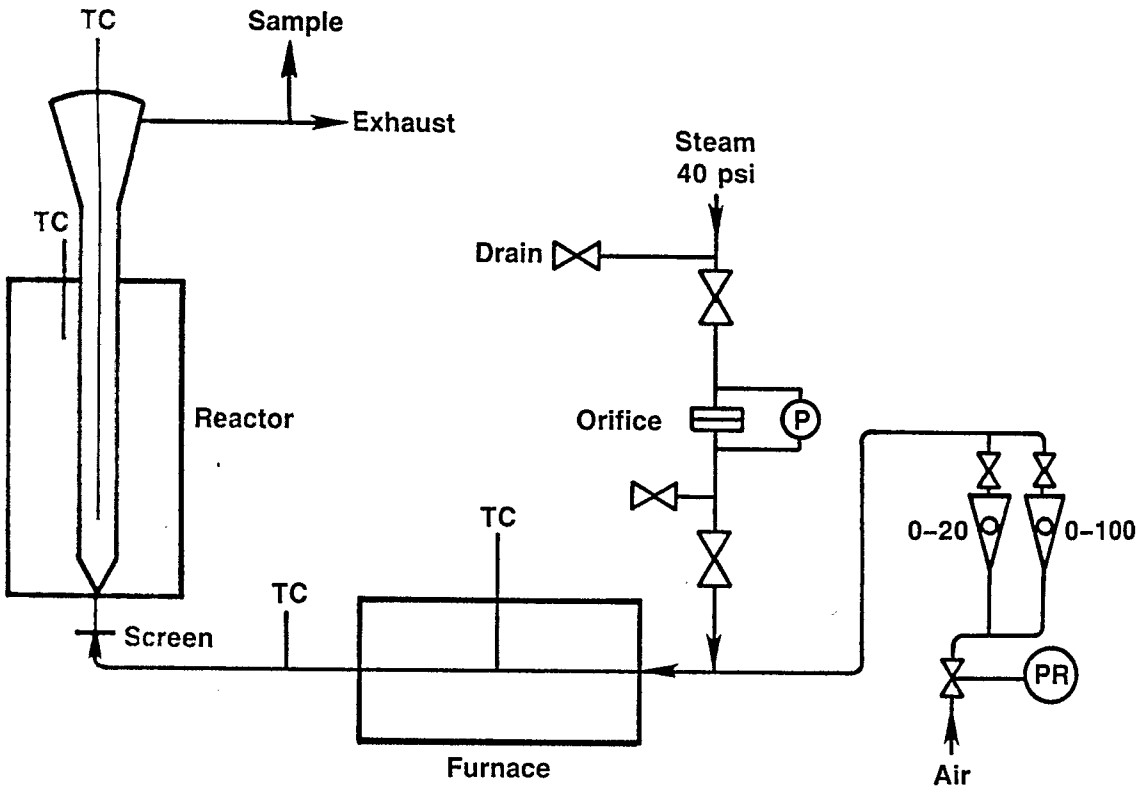

Figure 1. Flow Diagram for Experimental Equipment

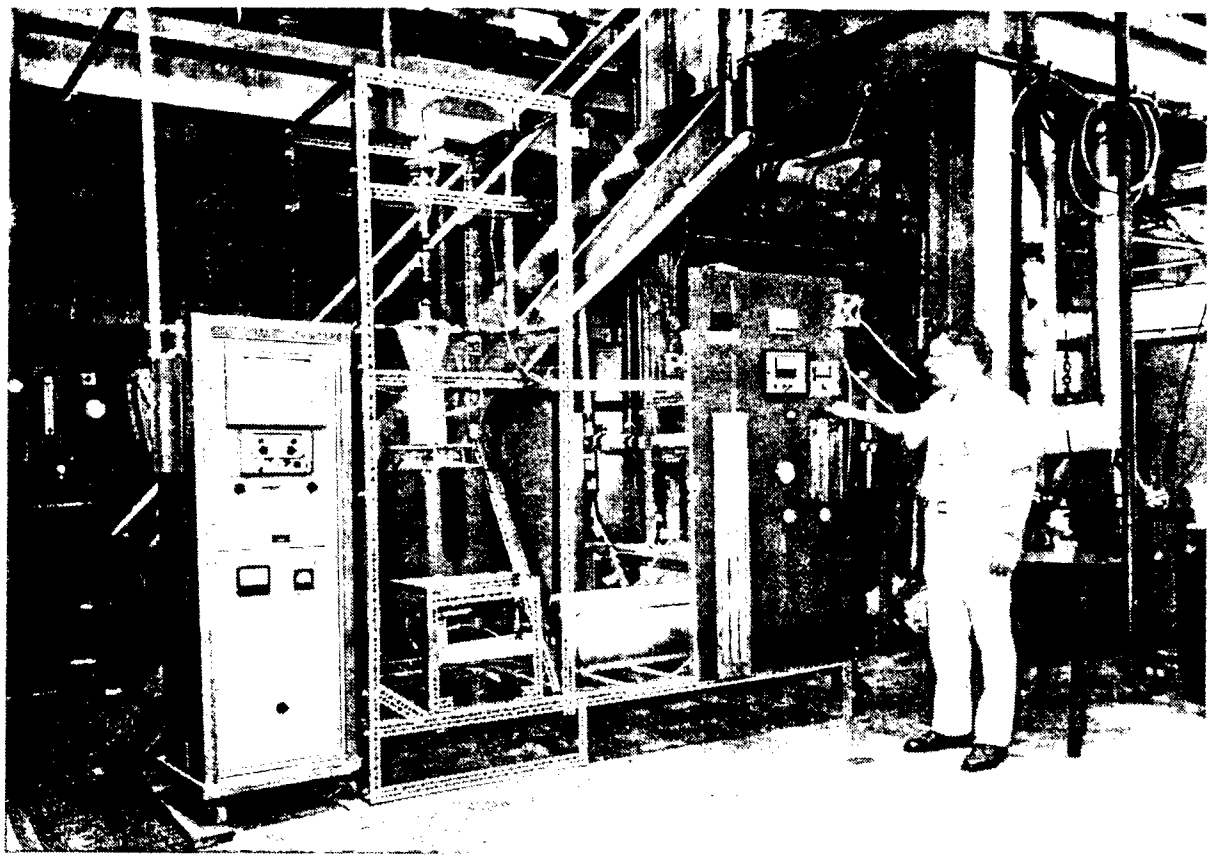

Figure 2. Photograph of the Experimental Equipment for Selective Oxidation

A furnace located within the equipment cell and shown in a horizontal position at the bottom of the photograph, preheats the fluidizing gases to the reaction temperature. The panel board has manometers to measure the pressure-drop across the bed and the pressure-drop across an orifice for total gas flow. A digital temperature gage is mounted above the manometers. The large box at the top of the panel is the SO_2 meter, and the small box is the preheater furnace control. Two rotometers measure air flow and the two gages in the center of the board are used to measure steam flow by determining the pressure drop over an orifice in the steam line.

EXPERIMENTAL RESULTS

Figure 3 shows the heating value lost to obtain a given sulfur removal for the various coals studied. The Christian County coal acts as expected. Initially, the sulfur is selectively oxidized from the coal and presumably when all of the mineral sulfur is removed, the coal oxidizes without further reduction of the sulfur on a Btu basis. Forty to fifty percent of the sulfur can be removed with little loss in heating value.

The River King coal responds differently to such treatment. Early in the experiment heating value is lost faster than sulfur. This may be due to volatilization of organic components in the coal. Later, the sulfur is removed preferentially. While not shown in the experiment plotted, if more than 60 percent of the sulfur is removed, a substantial loss in heating value is then observed. About 60 percent of the sulfur in River King coal is pyritic. These initial unfavorable burn-off phenomena were not observed with the Christian County coal, but they were consistently observed with the River King, and also the Rosebud, coals.

With Rosebud coal, analysis indicates an apparent substantial increase in sulfur content on heating to temperature. During the first few hours of a typical experiment with Rosebud coal, sulfur appears to be lost at about the same rate as the loss in heating value, with a loss of about 15 percent of each. Then, and only then, is the sulfur attacked preferentially. The experiment was somewhat arbitrarily terminated when the SO_2 content of the flue gas dropped to about 4000 ppm. At that time, sulfur was still being oxidized faster than the coal was being burned, and somewhat longer treatments may further reduce the sulfur content on a Btu basis. The amount of sulfur

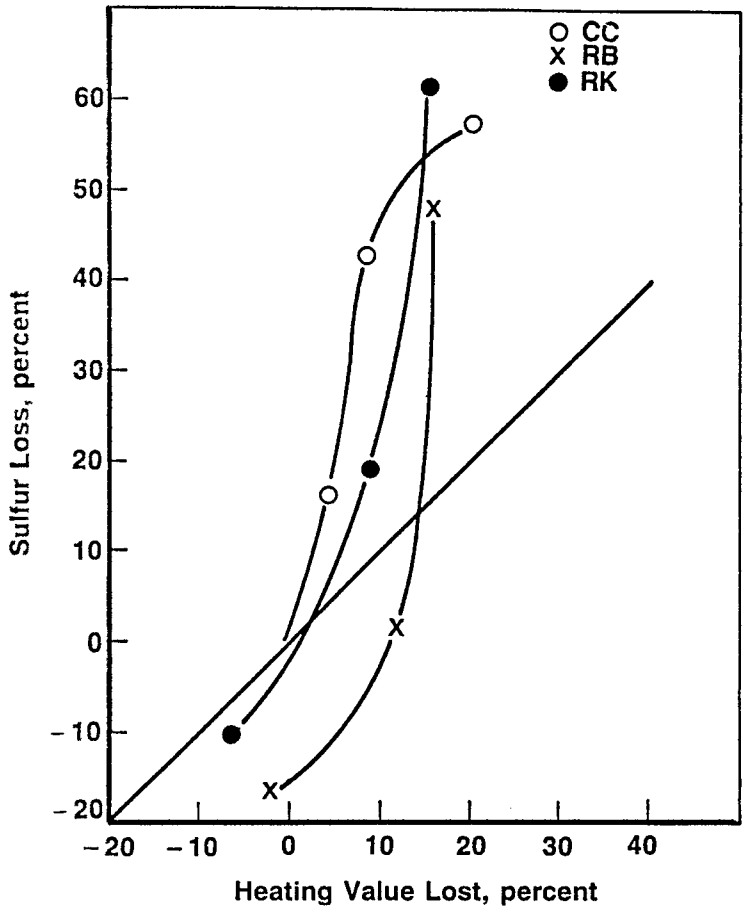

Figure 3. Comparison of Sulfur Removed and Heating Value Lost During Treatment

removed was always less than the fraction analyzed as pyritic sulfur over the range of conditions studied.

CONCLUSIONS

The results of these experiments indicate that an amount of sulfur equivalent to slightly more than the pyritic sulfur in coal can be removed from Illinois No. 6 coals with losses of heating value of less than about 10 percent. A one to two hour treatment time would be required to remove the sulfur based on batch operation.

With the Rosebud coal about 40 percent of the sulfur was removed without excessive loss of heating values. The sulfur removal was delayed from two to four hours after the coal was brought to treatment conditions, and then significant sulfur was removed in one to two hours of additional treatment time. The reason for the less favorable results with the Rosebud coal may be due to the alkaline nature of its ash.

In summary based on the work to date, it would appear that the fluidized bed selective oxidation process is attractive for the desulfurization of coal fines in general, and may be especially of interest where sulfur emission regulations could be met by removal of pyritic sulfur only.

OIL AGGLOMERATION OF LOW-RANK COALS AND DEVELOPMENT OF METHODS FOR RECOVERY OF OIL FROM AGGLOMERATES

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ABSTRACT

The process of oil agglomeration of coal fines for beneficiation and size enlargement has been studied at the Alberta Research Council (ARC) for six years. In contrast to bituminous coals, low-rank, high-oxygen subbituminous coals and lignites are hydrophilic in nature and, therefore, are considered to be unsuitable for beneficiation by oil agglomeration methods. The work carried out at ARC and supported by the Electric Power Research Institute has shown that bridging liquids, comprised mainly of bitumen or heavy oil, are very efficient in agglomeration of subbituminous coals.

This communication summarizes the results of agglomeration studies of American and Canadian coals of different ranks, and describes the results of work on:

- generation and separation of agglomerates,
- recovery of oil from agglomerates, and
- properties of agglomerates and de-oiled agglomerates

INTRODUCTION

In the past decade, there has been increasing international interest shown in the application of oil agglomeration techniques for beneficiation of low-quality and low-rank coals. The process of agglomeration is based on the principle that coal particles are naturally hydrophobic, or at least less hydrophilic, than inorganic materials, and can therefore be agglomerated and separated from mineral matter by addition of a suitable bridging liquid that wets the carbonaceous constituents.

The oil agglomeration process is very promising for:

- beneficiation of coal, especially for the extreme fines, which cannnot be treated by conventional processes,
- recovery and upgrading of coal slurries and effluents originating from conventional coal preparation plants, and
- preparation of coal that has specifically low ash and inorganic sulfur contents.

Oil agglomeration has been successfully applied to bituminous coals, but low-rank, high-oxygen content coals have been considered as less-suitable feedstocks for beneficiation by this technology.

In North America, subbituminous coals account for about 90% of total western deposits and can be mined at a very low cost. Due to high ash and moisture contents, some beneficiation appears to be necessary prior to transportation of subbituminous coals from the mine to the processing site. The potential for oil agglomeration of western American and western Canadian subbituminous coals has been investigated by the Electric Power Research Institute (EPRI) and the Alberta Research Council (ARC) over the past two years. Table 1 summarizes the results of agglomeration experiments on a number of selected subbituminous coals. Conditions for the agglomeration experiments were selected on the basis of a large number of tests performed with various subbituminous coals and were as follows: ambient pH, room temperature, particle size below 0.6 mm with mass medium diameter in the range of 0.2 to 0.3 mm, solids concentration of 30% on dry coal and agitation intensity of 1700 rpm. Bitumen or heavy oil with admixtures of diesel oil or kerosene were used as bridging liquids.

The major objective of the agglomeration experiments with Canadian coals was to decrease ash and moisture contents in order to increase their calorific value. For the low-ash American coals, the main thrust was to use the oil agglomeration technique as a means of moisture reduction. For all subbituminous coals

tested, a decrease in ash content was observed, though the extent of mineral matter removal was dependent very much on a particular coal. Reduction in ash and moisture, and addition of bridging liquid resulted in significant increases in calorific value. Combustibles recovery (organic matter of coal and bridging liquid) varied from 92% to 96% for the Canadian coals, and was close to 100% for the American coals. Detailed information regarding the procedures, equipment, and results of oil agglomeration experiments with low-rank coals is given elsewhere (1).

The work carried out at Alberta Research Council has shown that by using appropriately formulated mixtures of bitumen or heavy oil with light oils, it was possible to agglomerate subbituminous coals with success in deashing, dewatering and recovery of combustibles.

In this paper, some of the work on investigation of the properties of agglomerates generated from subbituminous coals is summarized. The results of the recovery of distillable oils from the agglomerates, and the influence of heat treatment on the properties of agglomerates and raw coals, are discussed. Preliminary results of studies on agglomeration of high-sulfur subbituminous coal and Texas lignite are also presented.

EXPERIMENTAL

Agglomeration experiments were carried out with selected American coals characterized by various rank. The coals were crushed and pulverized to a top size of 0.6 mm. Blends of bitumen, heavy oil, and coal tar with some light additives were applied as bridging liquids.

Agglomeration experiments were performed in small, stirred tanks. Some of the agglomeration tests were also done in a large, stirred tank and in a 52.0 mm-diameter pipeline loop. The major objective of the latter experiments was not only to scale-up the process, but to generate sufficiently large samples of agglomerates for further studies. Detailed information regarding the experimental procedures and the equipment used were given earlier (1,2). Agglomeration-flotation experiments with Montana subbituminous coals were performed in a standard Denver flotation machine equipped with a 2.5 litre flotation cell.

The oil recovery tests were performed in an apparatus designed and built in the ARC laboratories. Using this apparatus, it was possible to treat the agglomer-

ates and evaluate oil recovery over a wide range of temperatures, with various carrier gases. The effect of simple heat treatment and/or vacuum application for flash evaporation could also be investigated in the same apparatus. Detailed description of the unit and its operation was also given earlier (1).

Oil recovery tests were performed with agglomerates heated for 10 min at temperatures of 250, 300 and 350°C either under a slight vacuum of 800 mbar or using nitrogen or steam as carrier gas. Recovery of oils was determined by direct measurement of the condensed oil as well as through comparative analytical procedures (material balance). Standard analytical procedures were used in analysis of raw coals, agglomerates and de-oiled product.

RESULTS AND DISCUSSION

Five samples of American coals were used in this investigation and, the samples varied widely in their ranks. Proximate and ultimate compositions, of those coals are presented in Table 2.

Subbituminous Wyodak and Kemmerer coals were both characterized by low ash contents and, consequently, ash rejection during agglomeration of these coals was low (Table 3). More advanced grinding could probably increase the extent of deashing, but this would be associated with increased consumption of bridging liquid. Agglomeration of Blind Canyon coal (initial ash content 12.9%) resulted in rejection of 45% of ash forming minerals (Table 3). The test coals, as well as the agglomerates obtained therefrom (see Table 3), were analyzed for major, minor and trace elements. Furthermore, the agglomerates were subjected to oil recovery tests carried out under conditions described in Experimental.

Rejection of Major, Minor and Trace Elements

Coals contain a variety of inorganic ash-forming components, which are associated with the coal matrix in several different ways. They may be present as discrete mineral phases, as cations with the carboxylate ions of the coal structure, or bonded to either nitrogen- or oxygen-containing functional groups of the coal structure. The major minerals usually found in coals are quartz, clays, carbonates and sulfides.

The concentration of ash-forming elements (3) may range quite widely, and generally is: a) greater than 0.5% for major elements such as Al, Si, Ca and Fe; b) 0.02 to 0.5% for minor elements such as K, Na, Mg, Sr, P, Ti, etc. and

c) less than 0.02% for trace elements which include Co, Cu, Mo, V, Zn Ni etc. Oil agglomeration, as a physical cleaning method, is capable of removing only the inorganic impurities that were liberated during grinding of the coal or were present as discrete mineral phase.

For both Blind Canyon bituminous and Wyodak subbituminous coals, high removal of Si, a major contributor of mineral matter, was observed (Tables 4 and 6). The high rejection of Ca, Sr and Mg (91%, 87% and 64% respectively) from Blind Canyon coal (Table 4) suggests that these elements were present as carbonates or in the form of cations amenable to ionexchange. In low-rank Wyodak coal, most of the Ca, Sr and Mg was probably present in the form of insoluble carboxylic salts, and as such was not rejected during the agglomeration (Table 6). A decrease in trace elements contents (except for Cu and V) was observed for both coals (Table 5 and 7). An increase in V content (Table 5) was due to the presence of this element in the heavy oil, which was used as a bridging liquid. Substantial increase of Cu content in Blind Canyon agglomerates resulted from abrasion of a copper tube during pipeline agglomeration of the coal.

Oil Recovery from Agglomerates

Oil agglomeration is unique among all proven coal beneficiation processes in its ability to clean feed materials characterized by a broad range of particle sizes, and yield very high recoveries of combustible material (coal plus oil). In spite of its many advantages, oil agglomeration has not found large-scale commercial acceptance, because of the high cost of oil used in the process. Development of technically and economically feasible processes to recover and recycle oil are likely to play a crucial role in the application of oil agglomeration to produce clean coal.

For subbituminous and low-rank thermal bituminous coals, characterized by low heating values, complete recovery of bridging liquids used for agglomeration is not desirable. Bridging liquids that have been used successfully to agglomerate low-rank coals are composed mainly of bitumen and/or heavy oil with some light additives. During the thermal treatment of agglomerates at temperatures up to 350°C, only the light additives and volatile components of bitumen and heavy oil are evaporated and condensed. The heavy (least valuable) components of bridging liquids remain in the agglomerates, thus increasing the calorific value of the agglomerated product. Therefore, the main objective of the studies on oil recovery from agglomerates produced with bitumen or heavy

oil-based bridging liquids, has been to recover only the valuable, volatile components in such quantities, and under such conditions, that the calorific value of the de-oiled agglomerates would not be substantially reduced, compared with that of oil-loaded agglomerates.

Results of oil recovery experiments performed with agglomerates generated from Blind Canyon bituminous and Wyodak subbituminous coals are presented in Tables 8 and 9 respectively. Both samples of agglomerates were produced with a mixture of Mayan and diesel oils (1:1 ratio). Some of the properties of agglomerates used for recovery tests are presented in Table 3.

Experiments were carried out at temperatures of 250, 300 and 350°C under slight vacuum of 800 mbar or using nitrogen and/or steam as carrier gases with a flow rate of 1.5 litres/min. Unexpectedly large quantities of oil were recovered from agglomerates by rapid heat treatment. The amount of recovered oil was influenced by temperature, being highest at 350°C. Material balance of oils showed that, after treatment at 350°C, all the consumed diesel oil, and an additional 30% to 60% of the Mayan oil, was evaporated and condensed.

Recovery of oil was expressed on the basis of direct determination of condensed oil and, independently, by monitoring the weight loss of agglomerates during heat treatment. (Weight loss of agglomerates was corrected for weight loss of raw coal treated under identical conditions.) For experiments carried out under slight vacuum or in nitrogen atmosphere, both methods yielded comparable results. However, for the tests performed with steam at 350°C, a substantial discrepancy was observed. The raw coal samples were treated in the same manner (Table 10). Preliminary experiments (not presented in Table 10) showed that the application of nitrogen as a carrier gas yielded essentially the same results as did the use of slight vacuum. It seems that when the coals were treated under slight vacuum or in a nitrogen atmosphere, a decrease in weight was caused mainly by removal of residual moisture and evaporation of gases. These gases included free gases, as well as those from the decomposition of coal matter. It was found that heating the coal with steam at the same temperature (350°C) caused increased decomposition of coal matter, which resulted in generation of condensable hydrocarbons. When the total weight loss of coal (gases and collected hydrocarbons) was used for the calculation of oil recovery, the obtained value was substantially lower than from direct determination of condensed oil. However, when weight loss of agglomerates was corrected for only non-condensable products, better agreement was obtained. It is possible that, during heat treatment of agglomerates, evaporation of

hydrocarbons from coal was partially, or even totally, hampered by the bridging liquid on the surface of the coal. During the rapid heating of agglomerates, the volatile components of oil are evaporated from the surface of coal particles but the heavy, more viscous components become more fluid, and therefore better spread, on the coal surface. Some of the heavy components plug the pores of the coal.

An interesting finding is that, although heating agglomerates from subbituminous coals to 350°C resulted in recovering substantial amounts of the bridging liquid, this was not accompanied by reductions in calorific value of the agglomerates. A slight decrease of up to 3.5% of initial calorific value was observed, however, for agglomerates prepared from bituminous coal.

The volatile matter content of the de-oiled agglomerates decreased upon removal of the volatile components of the bridging liquid. For agglomerates produced from subbituminous Wyodak coal, the volatile matter content of the agglomerates treated up to 350°C was in the range of 39.4% to 41.5%, compared with 49.6% for untreated agglomerates (Table 9) and 42.3% for the raw coal (Table 2). This indicates that the heat treatment did not substantially reduce the volatility of the de-oiled agglomerates, and therefore, it should not have a deleterious influence on their combustion reactivity.

Energy distribution in products obtained by thermal treatment of Blind Canyon and Wyodak agglomerates at 250, 300 and 350°C is shown in Tables 11 and 12, respectively. Essentially, almost 100% of the calorific value in the feed agglomerates was recovered in the de-oiled agglomerates and condensed oil. An increase in the thermal treatment temperature normally reduces the amount of energy recovered in the solid residue and increases the heat content of the liquid phase. For experiments carried out at 350°C with steam, some inaccuracy was observed. Probably trace amounts of water were incorporated into the condensed oil, and due to the high calorific value of the oil, even a smaller error in weight could create problems in energy balance.

Another interesting finding is that oil agglomeration of subbituminous coals followed by recovery of the oil, can substantially reduce the moisture-holding capacity of the agglomerated coal. This is especially important for low-rank coals, which are characterized by high moisture content. When subbituminous coals are dried by a conventional method at over 100°C, nearly all the moisture can be removed, but re-adsorption takes place very readily when the dry coal is exposed to ambient conditions. Moreover, dried, low-rank coals are highly

reactive and very susceptible to spontaneous combustion, which causes considerable transportation and storage problems.

Oil agglomeration of subbituminous coals decreased the moisture capacity from 20.6% to 13.0% for Kemmerer coal, and from 29.3% to 20.9% for Wyodak coal; heat treatment of agglomerates caused further moisture reductions of 7.3 and 13.7, respectively. The effect of relative humidity on water sorption by de-oiled agglomerates and raw coals is presented in Fig. 1 and 2. Moisture content of de-oiled Kemmerer agglomerates was 2.6% at a relative humidity of 23%, and increased up to 7.3% at 96% relative humidity. For raw coal, an increase in moisture capacity from 5.9% to 20.6% was observed when the relative humidity increased from 23% to 96%. Similar results were obtained for Wyodak coal, but the suppression of moisture capacity was somewhat lower than for the other coal. Results of pore size distribution (not reported here) indicate that for Wyodak coal the contribution of larger pores to total surface area is large and plugging of these pores by the hydrocarbons is not efficient.

The effect of oil agglomeration followed by oil recovery on moisture capacity for coals of different rank is summarized in Figure 3. For both subbituminous coals, a substantial decrease in moisture capacity measured under standard ASTM conditions was observed. Sorption capacity of water by de-oiled agglomerates was two to three times lower compared to raw, untreated coals. Bituminous coal however, (Blind Canyon) displayed quite different behavior on agglomeration and oil recovery treatment. Moisture capacity of raw Blind Canyon coal was only 5.2%, which is typical for bituminous coals. Oil agglomeration increased slightly the sorption capacity of water, and heat treatment resulted in insignificant reduction. The results clearly indicate that oil agglomeration followed by heat treatment can be used, not only for demineralization of high-ash coals, but also for upgrading the coals with high inherent moisture contents.

Agglomeration-flotation of Montana Coal

Studies with Montana subbituminous coal were aimed at evaluating the potential for agglomeration with bitumen and heavy oil based bridging liquids for reduction of inorganic sulfur content.

There are two main forms of sulfur in coal: organic and inorganic. It is only inorganic sulfur that can be reduced by physical coal-cleaning techniques. The Montana coal used in experiments contained 4.4% sulfur, of which 64% was

inorganic and 34% was organic. Preliminary experiments with Montana coal were carried out according to a standarized procedure developed and used for subbituminous coals. Experimental conditions were as follows: ambient pH, room temperature, particle size below 0.6 mm, solids concentration 20 to 30% (on dry coal), bridging liquid addition 15 to 20% (on dry coal) and intensity of agitation 1700 rpm. Bitumen or heavy oils, with admixtures of diesel oil or kerosene, were used as bridging liquids. Agglomeration was started immediately after oil addition with very good separation of coal and mineral matter particles. It was possible to distinguish coal flocs and particles of pyrite and sand dispersed in gray mineral matter suspension. However, at that point the size of microagglomerates was still smaller than the top-size of feed coal, and it was impossible to use the screening techniques for separation. To increase the size of agglomerates, agitation time was extended to 20 min. Unfortunately, iron pyrites, the major part of inorganic sulfur, exhibit similar agglomerating characteristics to coal. As a result, well-liberated particles of pyrite were incorporated into the agglomerates.

Similar results of poor desulfurization of coals, using oil agglomeration techniques, have been reported by other researchers (3,4). Application of classical pyrite depressants did not cause any improvement in reduction of sulfur. In the presence of pyrite depressants some delay in the start of the process was observed. On the basis of oil agglomeration experiments with Montana coal, an important observation was made that the effective method of separation of coal flocs at very early stages of the process could improve the efficiency of pyrite removal. A series of experiments were, therefore, carried out using combined agglomeration-flotation (AGLOFLOAT) process. The description of experimental procedures and the results are presented in Table 13. Experiments were performed with an addition of 15% bridging liquid which was typical of standard oil agglomeration tests. A classical pyrite depressant was also used. The best results, in terms of deashing were obtained when column flotation was used for separation of microagglomerates. The effect of bridging liquid addition on deashing and desulfurization of coal is presented in Table 14. Agglomeration experiments were conducted in the flotation cell and were followed by flotation in the flotation machine. Inversion time increased with a decrease in oil consumption, reaching 11 min at 5% oil addition. The best results showed about a 50% reduction in ash content and a 62% reduction in total sulfur content. About 94% of inorganic sulfur was removed by the AGLOFLOAT process.

Results of the experiments described above indicate that the combined agglom-

eration-flotation process seems to be a very promising method for deashing and desulfurization of subbituminous coals.

Oil Agglomeration of Texas Lignite

A major effort was made to evaluate the potential of oil agglomeration for beneficiation of lignite. It has been widely acknowledged that the selectivity of oil agglomeration decreases with decreasing rank of coal. The oxygen content of coal, as well as the distribution of oxygen among the functional groups (such as hydroxyl, carboxyl, carbonyl or methoxyl), determine the rank of coal and its behavior. Carboxyl groups may account for nearly 25% of total oxygen in lignite and subbituminous coals, but their content in bituminous coals is negligible. As a rule, the hydrophobicity of coal is directly related to its oxygen content, and oxygen functionality. With an increase in oxygen content, the surface of coal becomes increasingly more hydrophilic. Beneficiation of coal by oil agglomeration is based on the hydrophobic properties of coal and the hydrophilic character of mineral matter. Bituminous and subbituminous coals can be successfully agglomerated when suitable oils or mixtures of heavy oils are used as bridging liquids.

Agglomeration experiments with lignite showed that its agglomerating properties are extremely poor. Bridging liquids, which have been very efficient in the agglomeration of subbituminous and low-rank, bituminous coals, did not work with lignite. A water emulsion of coal tar and anthracene oil was found to be a suitable bridging liquid for lignite. Addition of anthracene oil tends to improve adhesion between tar and fine lignite particles (5). Small amount of anthracene oil was also necessary to generate a stable emulsion.

The results of oil agglomeration of Texas lignite are presented in Table 15. Two tests (No. 1 and 2) were conducted with tar derived from bituminous coal, and one (No. 3) with tar generated from subbituminous coal. Agglomerates were separated in the flotation column, and the middlings were retained on a screen. The recovery of combustible material in floats was dependent on the bridging liquid addition, and reached 81% to 90%. About 6-7% of the combustible material was collected in the middlings. Ash content in the tailings was dependent on oil concentration. For higher oil addition, cleaner tailings were obtained. Table 16 presents the properties of lignite agglomerates. The efficiency of oil agglomeration of Texas lignite in terms of deashing was poor; only a 20% reduction in ash was observed. Of interest was the finding that oil agglomeration resulted in lowering the sorption capacity of water. Moisture

capacity of Texas lignite was 25.5%; oil agglomeration reduced this value to about 18%. Heat treatment of lignite agglomerates caused a further decrease in moisture capacity to 9.4%. Reduction in ash content and addition of bridging liquid resulted in a substantial increase in the calorific value of agglomerated lignite.

To increase the selectivity of oil agglomeration of lignite, special additives were introduced to modify the surface of the lignite. Results are quite promising, and further study in this area is recommended.

CONCLUSIONS

The results of studies on oil agglomeration of low-rank coals, carried out at the Alberta Research Council lead to the following conclusions:

1. Subbituminous coals can be efficiently agglomerated, using bridging liquids comprised mainly of bitumen and/or heavy oil with some light oils. The process results in:
   - High recovery of combustible material (95-100%).
   - Good deashing (up to 50%).
   - Reduction in moisture capacity of about 30%.
2. Results of tests on oil recovery from agglomerates produced from hv-bituminous and subbituminous coals show that:
   - Higher quantities of oil (up to 80%) were recovered than would be expected from bridging liquid compositions.
   - Moisture capacity of the de-oiled agglomerates was reduced by about 65%, compared to raw coals.
   - The energy balances for oil recovery process are close to 100%.
3. The AGLOFLOAT process, used to clean high sulfur subbituminous coal, result in:
   - Very low bridging liquid addition (5%).
   - Reduction in mineral matter by about 50%.
   - Reduction in total sulfur content from 4.5% to 1.7%.
   - Removal of about 94% of inorganic sulphur.
4. Lignite can be agglomerated, using coal-derived hydrocarbons as a bridging liquid, but the efficiency of the process in terms of deashing is poor.

   Better results are obtained in terms of moisture capacity suppression. Oil agglomeration reduces the moisture capacity from 25.5% to about 18%, and a

further decrease to 9.4% can be obtained by heat treatment of lignite agglomerates. Agglomeration experiments with some specific additives that modified the surface properties of coal or mineral matter particles show some potential for improvement in the selectivity of the process.

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Table 1

AGGLOMERATION TESTS WITH CANADIAN AND AMERICAN SUBBITUMINOUS COALS

Origin and Type of Coal	Bridging Lig.	Feed Coal		Agglomerates		
	Quantity (wt %)	Moisture[a] (%)	Ash[c] (%)	Moisture[b] (%)	Ash[c] (%)	Recovery of Comb. (%)
Canadian (C)	16.9	16.9	22.5	9.2	11.2	92.3
Canadian (B)	13.7	10.9	13.2	8.9	7.0	95.0
Canadian (B)	17.4	19.7	10.1	8.3	7.0	96.0
American (B)	14.9	21.2	7.1	3.9	5.4	100
American (B)	20.8	17.7	5.4	4.5	3.3	99

[a] As received
[b] Air dry
[c] Dry basis

Table 2

PROPERTIES OF TEST COALS

Sample	Proximate Analysis				Moisture Capacity (%)	Calorific Value[a] (BTU/lb)
	Moisture[a] (%)	Ash[b] (%)	Volatile Matter[b] (%)	Fixed Carbon[b] (%)		
Kemmerer Subbituminous	17.7	5.4	41.6	53.0	20.6	10,260
Wyodak Subbituminous	21.2	7.1	42.3	50.6	29.3	9,320
Montana Subbituminous	7.2	17.8	36.2	46.0	19.7	10,000
Texas Lignite	21.4	25.3	39.6	35.1	25.5	7,260
Blind Canyon Bituminous	3.0	12.9	40.6	46.5	5.2	11,800

[a] As received
[b] Dry basis

Table 3

PROPERTIES OF AGGLOMERATES* PRODUCED FROM COALS OF DIFFERENT RANK

Type of Coal	Oil Content[a] (%)	Ash Content[a]			Ash rejected (%)
		Raw Coal	Agglomerates	Oil-Free Agglomerates	
Kemmerer Subbituminous	14.2	5.4	3.6	4.3	20.4
Wyodak Subbituminous	13.8	7.1	5.3	6.1	14.1
Blind Canyon Bituminous	10.1	12.9	5.9	7.1	45.0

* Bridging liquid-mixture of Mayan crude and Diesel in ratio 1:1

[a] Dry basis

Table 4

MAJOR AND MINOR ELEMENTS FOR BLIND CANYON COAL AND AGGLOMERATES PRODUCED FROM THIS COAL

Element	Concentrations[a], µg/g		% Element rejected
	Feed Coal	Agglomerates (oil-free)	
Al	13,965	8,415	39.7
Ba	80	27	66.3
Ca	29,925	2,572	91.4
Fe	3,444	3,636	5.6[b]
K	917	464	49.4
Mg	997	361	63.8
Mn	39	8	79.5
Na	2,500	1,854	25.8
P	186	183	1.6
S	2,167	1,681	22.4
Si	36,348	15,937	56.2
Sr	1,317	169	87.2
Ti	891	839	5.8

[a] Dry basis
[b] Indicates increase

Table 5

TRACE ELEMENTS FOR BLIND CANYON COAL
AND AGGLOMERATES PRODUCED FROM THIS COAL

Element	Concentrations[a], ppm	
	Feed Coal	Agglomerates (oil-free)
Co	10.6	3.0
Cu	10.1	121.2
Mo	10.6	8.5
Ni	10.6	7.2
V	10.1	20.8
W	10.1	1.4
Zn	10.1	7.1

[a] Dry basis

Table 6

MAJOR AND MINOR ELEMENTS FOR WYODAK COAL AND AGGLOMERATES PRODUCED FROM THIS COAL

Element	Concentrations[a], µg/g		% Element rejected
	Feed Coal	Agglomerates (oil-free)	
Al	5,186	4,251	18.0
Ba	604	332	45.0
Ca	13,018	12,189	6.4
Fe	3,258	2,723	16.4
K	120	103	1.4
Mg	2,751	2,683	2.5
Mn	22	6	72.7
Na	1,156	550	52.4
P	506	432	14.6
S	4,483	4,479	0.1
Si	11,574	6,153	46.8
Sr	317	314	1.0
Ti	385	188	51.2

[a] Dry basis

Table 7

TRACE ELEMENTS FOR WYODAK COAL AND AGGLOMERATES PRODUCED FROM THIS COAL

Element	Concentrations[a], ppm	
	Feed Coal	Agglomerates (oil-free)
Co	6.0	1.6
Cu	12.3	7.0
Mo	6.0	4.1
Ni	12.3	8.6
V	6.0	20.0
W	12.3	1.1
Zn	6.0	4.6

[a] Dry basis

Table 8

RECOVERY OF OILS FROM BLIND CANYON AGGLOMERATES

	Temp.(°C)	Oil Recovery (%)		De-oiled Agglomerates				
		Weight Loss of Aggl.[a]	Direct Determ. of Condensed Oil	Ash[b] (%)	Volatile Matter[b] (%)	Fixed Carbon[b] (%)	Moisture Capacity (%)	Calorific Value[b] (BTU/lb)
	--	--	--	6.2	46.0	47.7	5.9	14,070
Reduced Pressure	250	14.9	14.9	6.2	44.9	49.0	4.0	13,850
	300	39.5	39.5	6.5	43.0	50.5	2.8	13,550
	350	51.6	45.3	6.5	42.6	50.8	2.5	13,620
Nitrogen	250	35.6	34.9	6.4	43.8	49.8	3.9	13,690
	300	52.5	49.9	6.7	42.3	51.0	3.5	13,600
	350	61.5	65.0	6.7	41.1	52.3	2.9	13,610
Steam	250	31.2	35.0	6.3	43.4	50.3	3.6	13,670
	300	47.1	51.2	6.6	42.4	51.0	3.4	13,490
	350	--	83.0	6.6	40.6	52.8	2.8	13,560

[a] Corrected for weight loss of coal under identical conditions of thermal treatment
[b] Dry basis

Table 9

RECOVERY OF OILS FROM WYODAK AGGLOMERATES

	Temp.(°C)	Oil Recovery (%)		De-oiled Agglomerates				
		Weight Loss of Aggl.[a]	Direct Determ. of Condensed Oil	Ash[b] (%)	Volatile Matter[b] (%)	Fixed Carbon[b] (%)	Moisture Capacity (%)	Calorific Value[b] (BTU/lb)
	--	--	--	5.0	49.6	45.4	20.9	12,410
Reduced Pressure	250	38.4	33.5	5.7	45.1	49.2	15.4	12,280
	300	43.1	38.3	5.8	44.1	50.1	14.4	12,340
	350	78.3	63.9	6.1	39.4	54.5	12.7	12,400
Nitrogen	250	36.3	32.6	5.7	45.4	48.9	16.4	12,220
	300	52.2	47.0	5.9	43.5	50.6	15.0	12,220
	350	65.2	59.4	6.0	40.9	53.1	13.7	12,350
Steam	250	28.8	35.3	5.9	46.1	48.0	16.1	12,120
	300	51.7	53.5	6.2	43.5	50.3	14.6	12,200
	350	76.9	77.4	6.3	41.5	52.2	13.8	12,260

[a] Corrected for weight loss of coal under identical conditions of thermal treatment
[b] Dry basis

Table 10

HEAT TREATMENT OF RAW COALS AT 350°C

	Weight Loss of Coal (%)	Condensed Hydrocarbons (%)	Volatile Matter (%)	Fixed Carbon[a] (%)
Kemmerer				
Raw coal	-	-	44.0	56.0
Reduced Pressure	3.3	0.0	40.5	59.5
Steam	5.4	0.8	39.0	61.0
Wyodak				
Raw coal	-	-	45.4	54.6
Reduced Pressure	5.4	0.0	43.0	57.0
Steam	11.7	7.2	38.9	61.1
Blind Canyon				
Raw coal	-	-	46.6	53.4
Reduced Pressure	2.2	0.0	43.7	56.3
Steam	6.7	5.6	40.7	59.2

[a] Dry ash free

Table 11

ENERGY BALANCE FOR PRODUCTS FROM THERMAL TREATMENT OF AGGLOMERATES FROM BLIND CANYON COAL

Process Conditions		Energy Distribution (%)		
	Temp. (%)	De-oiled Agglomerates	Recovered Oil	Unaccounted For
Reduced Pressure	250	97.4	2.0	0.6
	300	92.5	5.1	2.4
	350	92.2	6.1	1.7
Nitrogen	250	93.6	4.7	1.7
	300	91.0	6.7	2.3
	350	89.3	8.8	1.9
Steam	250	94.0	4.7	1.3
	300	92.8	6.9	0.3
	350	89.1	11.2	0.1[a]

[a] Indicates increase

Table 12

ENERGY BALANCE FOR PRODUCTS FROM THERMAL TREATMENT OF AGGLOMERATES FROM WYODAK COAL

Process Conditions		Energy Distribution (%)		
	Temp. (%)	De-oiled Agglomerates	Recovered Oil	Unaccounted For
Reduced Pressure	250	91.9	7.0	1.1
	300	90.6	8.0	1.4
	350	84.6	13.3	2.1
Nitrogen	250	91.6	6.8	1.6
	300	88.5	9.8	1.7
	350	86.1	12.3	1.6
Steam	250	92.2	7.3	0.5
	300	88.6	11.1	0.3
	350	85.6	16.4	2.0[a]

[a] Indicates increase

Table 13

AGGLOMERATION-FLOTATION OF MONTANA SUBBITUMINOUS COAL

Experimental Procedure	Inversion Time (min)	Ash (% dry, basis)
Feed coal	-	17.7
Cell agglomeration, Cell flotation	3	10.0
Cell agglomeration, Column flotation	3	9.1
Vessel agglomeration Column flotation	15	8.7

Table 14

AGGLOMERATION-FLOTATION OF MONTANA SUBBITUMINOUS COAL

Oil Addition (%, on dry coal)	Inversion Time (min)	Ash (%, dry basis)	Total Sulfur (%, dry basis)
Feed Coal	-	17.7	4.4
15.3	3	10.0	-
10.0	5	8.2	1.6
5.0	11	9.1	1.8

Table 15

AGGLOMERATION OF TEXAS LIGNITE WITH TAR EMULSION

Bridging Liq. Concentration (% on dry coal)	Floats		Middlings		Tailings Ash[a] (%)
	Ash[a] (%)	Combustible Recovery (%)	Ash[a] (%)	Combustible Recovery (%)	
13.6	18.5	81.3	24.5	6.5	53.6
17.4	18.5	89.7	22.1	6.0	73.7
17.0	17.9	87.3	22.5	7.1	72.5

[a]Dry Basis

Table 16

AGGLOMERATION OF TEXAS LIGNITE - PROPERTIES OF FLOATS

Bridging Liquid Concentration (% on dry ash)	Ash[a] (%)	Volatile Matter[a] (%)	Capacity Moisture (%)	Calorific Value[a] (BTU/lb)
Feed coal	25.3	39.6	25.5	9,230
13.6	18.5	48.2	19.0	10,670
17.4	18.5	49.4	13.3	10,850
17.0	17.9	50.1	18.0	10,980

[a]Dry Basis

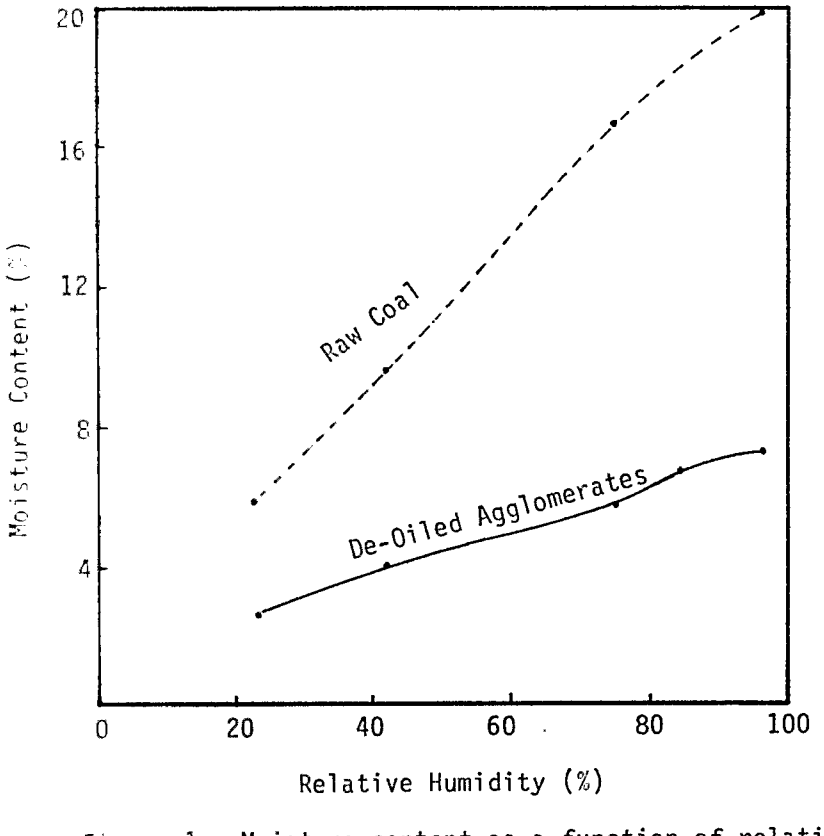

Figure 1: Moisture content as a function of relative humidity at 30°C for raw Kemmerer coal and de-oiled agglomerates produced from this coal.

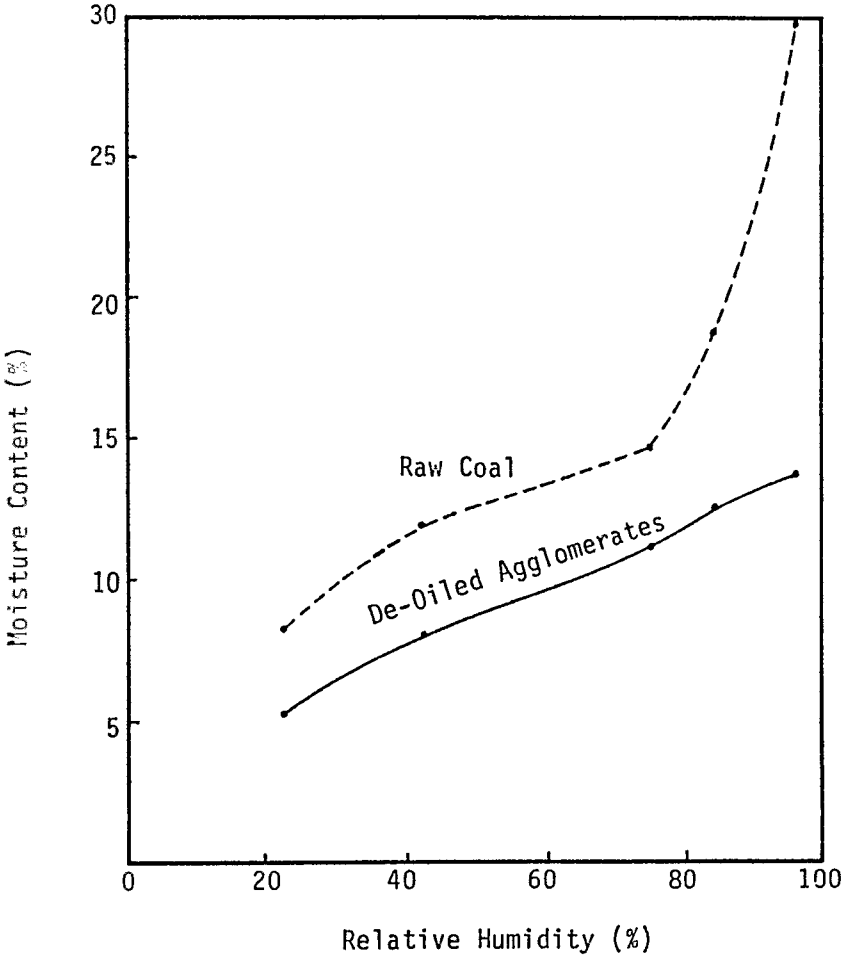

Figure 2: Moisture content as a function of relative humidity at 30°C for raw Wyodak coal and de-oiled agglomerates produced from this coal.

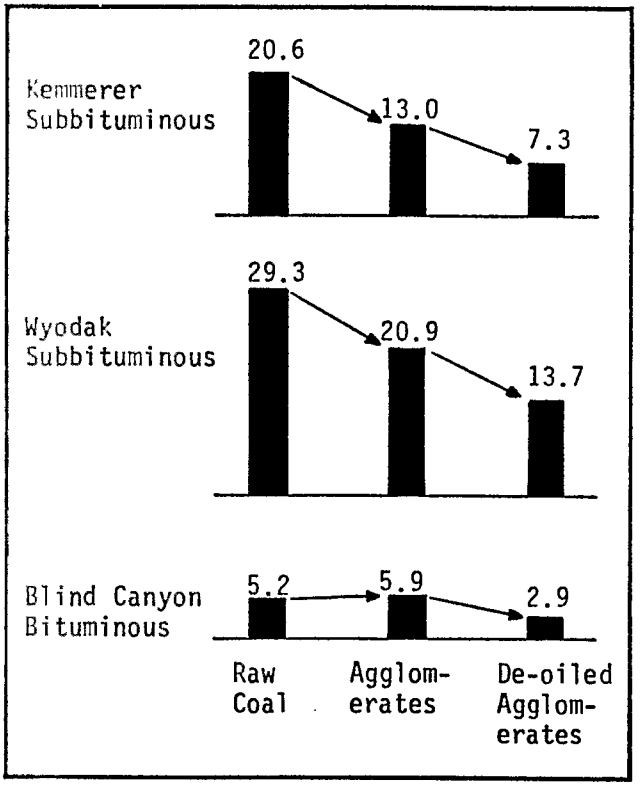

Figure 3: Moisture capacities measured at 30°C and relative humidity of 96% for different rank of coals, agglomerates and de-oiled agglomerates produced from these coals.

MICROBIAL BENEFICIATION OF LOW-RANK COALS

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ABSTRACT

At least three strains of fungi have now been shown to convert lignite coal into a water-soluble fuel product. Bioconversion reactions have been carried out on petri dishes at apparently high (but not accurately determined) conversion, and in small scale bioreactors at conversions of between 4 and 5%. Bioconversion has also been demonstrated using a cell free preparation of laccase enzyme isolated from P. versicolor.

Chemical analyses show that the bioconverted products, compared to feed coals, are higher in hydrogen and oxygen content, and appear to be lower in aliphatic hydrogen (as determined by proton NMR and IR). Product materials appear to have increased molecular weight, as determined by ultrafiltration, compared to lignite fractions prepared by high temperature hydrolysis of covalent oxygen linkages. The bioconverted materials are highly polar and exhibit a wide range in apparent molecular weight, with most material in excess of 10,000 daltons at acidic pH, as determined by ultrafiltration experiments. Calorimetric measurements on samples of the freeze-dried extract show that it retains 94 to 97% of the heating value in the feed coal.

INTRODUCTION

Biological conversion of low rank coals by bacteria or fungi, or by preparations of the enzymes that they produce, is currently of some interest. Because these processes occur at essentially ambient temperatures and pressures, their use may generate potential cost savings in the processing of certain coals and lignite. Work in this area has been reported by Cohen and Gabrielle (1982) using lignite, and with German coal by Fukaussa (1981). Literature in the area of bioconversion of coals and relevant work on lignin has recently been reviewed by Pyne and Wilson (1986).

At the EPRI Contractors Review Meeting in 1985, we reported initial results from experiments in a project to confirm that low rank coals could serve as substrates for bioconversion processes, and to study the mechanisms involved. Over the past year, the Battelle group has also been working closely with Dr. Cohen and his associates at the University of Hartford. This report contains data from products obtained in both laboratories.

Tasks over the last year at Battelle Northwest have been oriented toward understanding the biochemical processes occurring in this conversion and have therefore focused in five main areas, namely; product characterization, enzyme isolation and characterization, nutrition, and coal substrate screening. Small scale bioreactor studies have also been carried out in an attempt to provide larger quantities of the materials for study. Complimentary work on coal pretreatment and screening of additional candidate microbial strains has been carried out at University of Hartford.

OVERVIEW OF PROGRESS BY TASK AREA

SAMPLE DESCRIPTION

Samples discussed here were obtained from the action of Polyporus versicolor on a North Dakota lignite coal obtained from American Colloid Co. in Skokee, Illinois. American Colloid has recently confirmed that this lignite sample could also be classified as Leonardite. Samples were stored in air; hence, substantial oxidation is assumed to have occurred. Elemental composition of the "as used" lignite, unoxidized lignite and on the bioconverted product are shown in Table 1.

Table 1

	C	H	O	N
N.D. Lignite (Beulah South)	100	62	32	1.5
N.D. Leonardite	100	78	41	1
U. of H. Bioextract	100	98	50	8

Samples designated as "U. of H. bioextract" were prepared as described by Cohen et. al. elsewhere in these proceedings. Designated as "BNW bioextract" were obtained from a bioreactor as described below. The water soluble products obtained from the reactor of a cell free enzyme preparation with lignite has not yet been characterized.

ENZYME ISOLATION STUDIES AND THE MECHANISMS OF LIGNITE CONVERSION

The white rot fungi Phanerochaete chrysosporium is a well characterized strain that may be used as a model for studying the biochemical reactions involved in lignite degradation. This fungus produces several enzymes which act cooperatively to accomplish degradation in the case of lignin as shown in Figure 1.

The enzyme thought to be the key to lignin degradation by Phanerochaete chrysosporium is called ligninase or lignin peroxidase. This enzyme catalyzes cleavage of aliphatic chains connecting aromatic rings at a carbon adjacent to the ring.

Another enzyme which is thought to be involved in lignin degradation by white rot fungi is laccase, which is a polyphenol oxidase. Evidence for the involvement of laccase in lignin degradation is genetic, and a chemical role for this enzyme in lignin degradation is presently unclear. A third enzyme thought to be involved is lignin degradation is cellobiose quinone oxidoreductase (CBQ). This enzyme reduces quinones to diphenols which can be used by the cell for growth.

We have looked for the enyzmes ligninase, CBQ, and laccase in cultures of the lignite degrading Polyporus versicolor. Of the three, only laccase has been detected to date. This enzyme occurs in several fungal strains. Isolated and

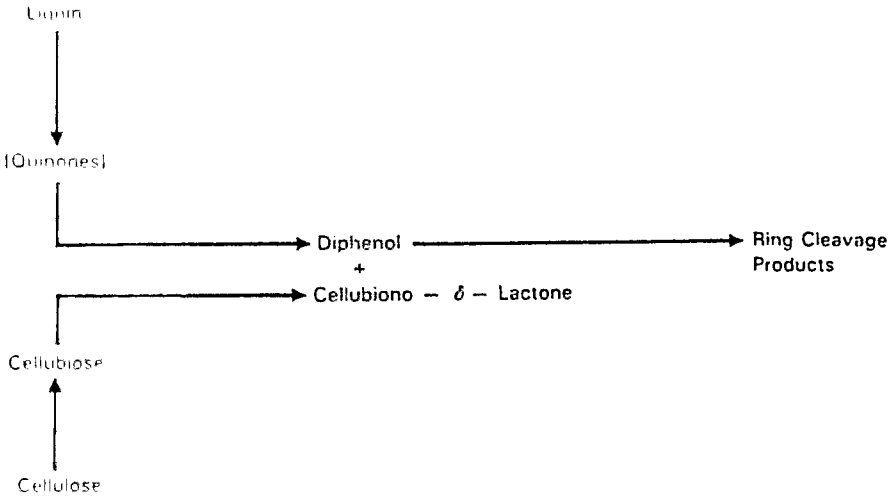

Figure 1. Involvement of Cellulose in Lignin Degradation

partially purified laccase from Polyporus versicolor, ATCC 12679. This strain has also been studied relative to the bioconversion of lignite as described by Cohen, and Grabrielle (1982).

The laccase preparation used here isolated and partially purified from a 1 L culture which had been induced to form laccase with xylidine (2,5-dimethylaniline) (Figure 2). A purification procedure described by Wood (1980) through the DE-52 cellulose ion-exchange step was used. Laccase activity was measured spectrophotometrically at 525 mm using syringaldazine as a substrate. One unit (I.U.) of the enzyme was defined as that amount which at the conversion of 1.0 μmole of substrate min^{-1} of substrate a reaction mixture composed of 0.7 ml of 0.1 m citrate phosphate buffer (pH 5.2), 0.06 ml of 0.1 mM syringaldazine in ethanol (24°C) and 0.02 ml enzyme preparation. Results of the laccase purification procedure are summarized in Table 2.

Experiments were conducted to determine if this partially purified laccase preparation would degrade a subbituminous coal and a North Dakota Leonardite supplied by American Colloid. An undiluted laccase preparation, a 1:10 dilution of this preparation were tested with 100 mg amounts of both coal types. All samples were tested in 1 ml aliquots of the laccase preparation. After 6 days of incubation, there was no evidence of bioconversion with the subbituminous coal (i.e., darkening of the liquid as compared to a blank). However, degradation of the Leonardite coal began to occur after overnight exposure to the laccase. Both the undiluted and diluted laccase had evidence of bioconversion.

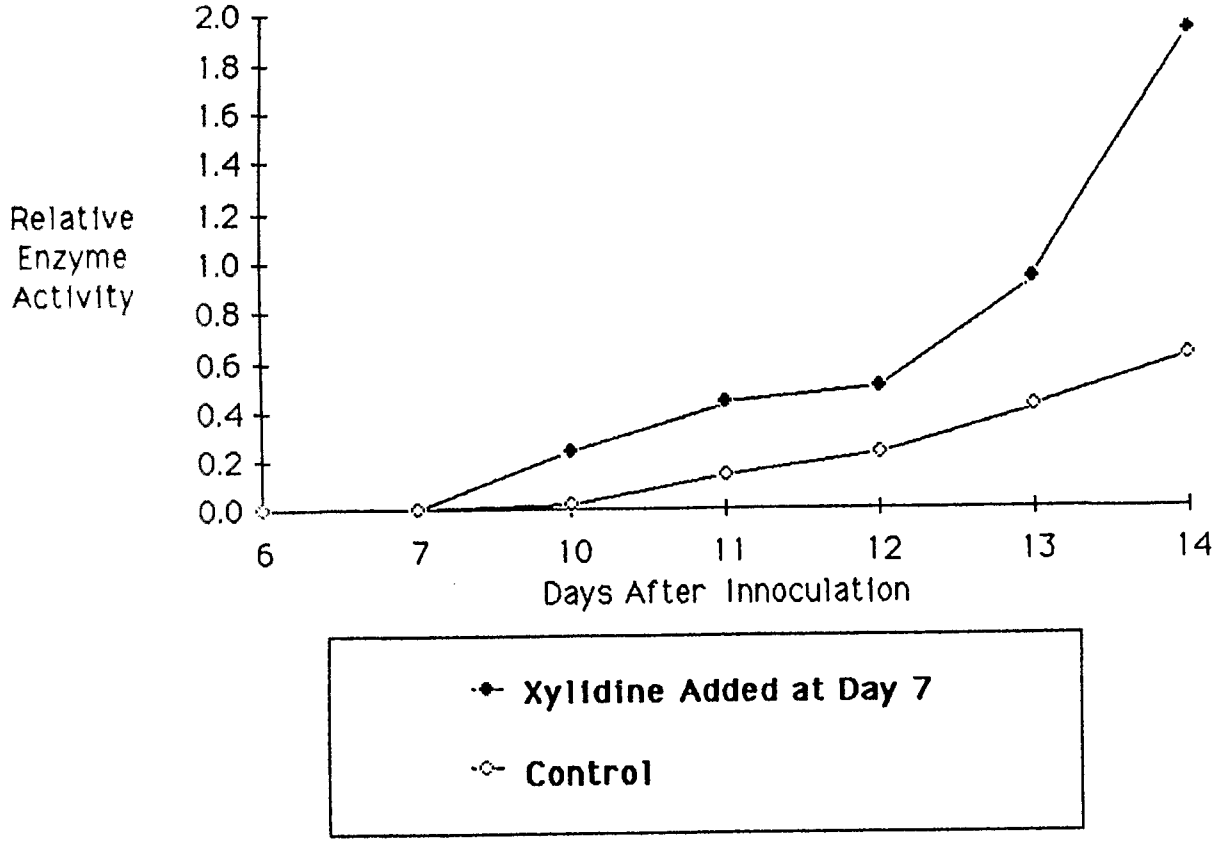

Figure 2. Appearance of Laccase in Liquid Culture

NUTRIENT REQUIREMENTS AND COAL SUBSTRATE SCREENING

Initial studies in this task area have been focused on culturing the fungi Polyporus versicolor on a chemically defined growth medium in order to expedite future carbon balance studies and chemical analyses. The results indicated that Polyporus will grow on glucose, succinate, and maltose as carbon sources. Irradiation and autoclaving were examined as methods of sterilizing coal as well as to determine what effects the two treatments would have on bioconversion. Lignite samples were autoclaved for 30 min once, or twice on two consecutive days, or were exposed to 1 Mrad or 4 Mrad of gamma radiation. The lignite was then added to Sabouraud maltose broth cultures of Polyporus and to sterile controls. After 6 weeks no microbiol growth was evident in the sterile controls indicating that all methods were effective in sterilizing lignite.

Table 2

PURIFICATION OF EXTRACELLULAR LACCASE FROM Polyporus versicolor

Fractionation Step	Volume (ml)	Total Activity (I.U.[a] x 10^{-3})	% Recovery[a]
Culture Supernatent	800	523	100
Ultrafiltration Concentrate (Amicon PM10 Membrane	132	224	43
Ultrafiltration Filtrate	668	34.3	7
Ammonium Sulphate Precipitation	--	--	--
DEAE-52 Cellulose Ion-Exchange Chromatography	6 ml	40.1	8

(a) I.U. = International unit; μmoles/min of enzyme activity.

In a separate study, four sources of lignite substrate were assessed for potential biodegradation by Polyporus versicolor cultured on Sabouraud maltose agar for six days before addition of the autoclaved lignites. Of the four lignites examined, only with the North Dakota Leonardite obtained from American Colloid was there evidence of degradation, even after three weeks incubation. Leonardite showed evidence of coal liquefaction within 24 hr after the lignite was added to the cultures. The three coals showing no degradation (Texas lignite, North Dakota Beulah #3 and the North Dakota Beulah Zap) were stored under nitrogen prior to autoclaving and addition to Polyporus cultures, allowing little opportunity for oxidation. Current investigations are focusing on the effect of lignite pretreatment, including oxidation and/or irradiation on rates of lignite degradation by Polyporus versicolor.

Illinois #6 coal (bituminous) coal was treated with 17% perchloric acid and stirred for 48 hrs. After 7 days incubation with Polyporus, some conversion was apparent. Similar results were obtained after 2 mo. incubation with Aspergillus. The resulting block liquid has not yet been characterized.

LABORATORY-SCALE BIOREACTOR STUDIES

The near term goal of developing a small bioreactor system was to produce the lignite product in sufficient quantities to support analytical chemistry studies. Several possible bioreactor types were tested. The most straightforward and reproducible system would be that of simply add a cell-free enzyme preparation to the coal and then incubate for short period of time.

In an initial experiment, North Dakota lignite (Beulah Zap #3) was mixed with the spent broth in which the white rot fungus Polyporus versicolor had been cultivated. Sabouraud maltose broth was used as the growth medium and was filtered through a 0.45 μm filter to remove mycelia after cultivation was finished. In growing the Polyporus versicolor for this experiment, the broth was maintained in a static state with a broth depth of about 1.5 cm. Limited agitation is thought to be important in enhancing lignin degradation by white rot fungi. Samples of the medium were removed at several time periods during the growth cycle of the fungus. No degradation of lignite samples was observed even after two weeks of incubation.

The type of bioreactor used in the next studies was a packed bed of lignite. The lignite particles although irregularly shaped has an average diameter of from 5 to 10 mm. This particle size was large enough to easily allow retention of the particles in the reactor. A schematic of the reactor used is shown in Figure 3. This reactor configuration was used in hopes of simulating the Petri dish system used by the U. of H. group. (Several experimental runs were also made with liquid medium.) Aeration was achieved by direct injection of air into the column or by circulating medium through an aerated recycle vessel. Media was circulated upflow or downflow in different experiments using Sabouraud broth. In all cases the column eventually became plugged due to growth of the fungus across coal particles and filling in the interstitial spaces between particles. When the minimal media of Jager, et al. (1986) and Fahraeus and Reinhammer (1967) were used plugging did not occur.

After the termination of these runs the lignite and attached mycelia were removed from the column and Soxlet extracted with distilled water. Color production was used as a test of product formation. The results are summarized in Table 3. All runs shown in Table 3 used Sabourand Maltose broth medium. Only in one case was any significant conversion observed. Run #1 showed considerably greater light absorbing material than in other runs. The main difference between Run #1 and the others is that a Leonardite sample obtained from American Colloid was used whereas in the

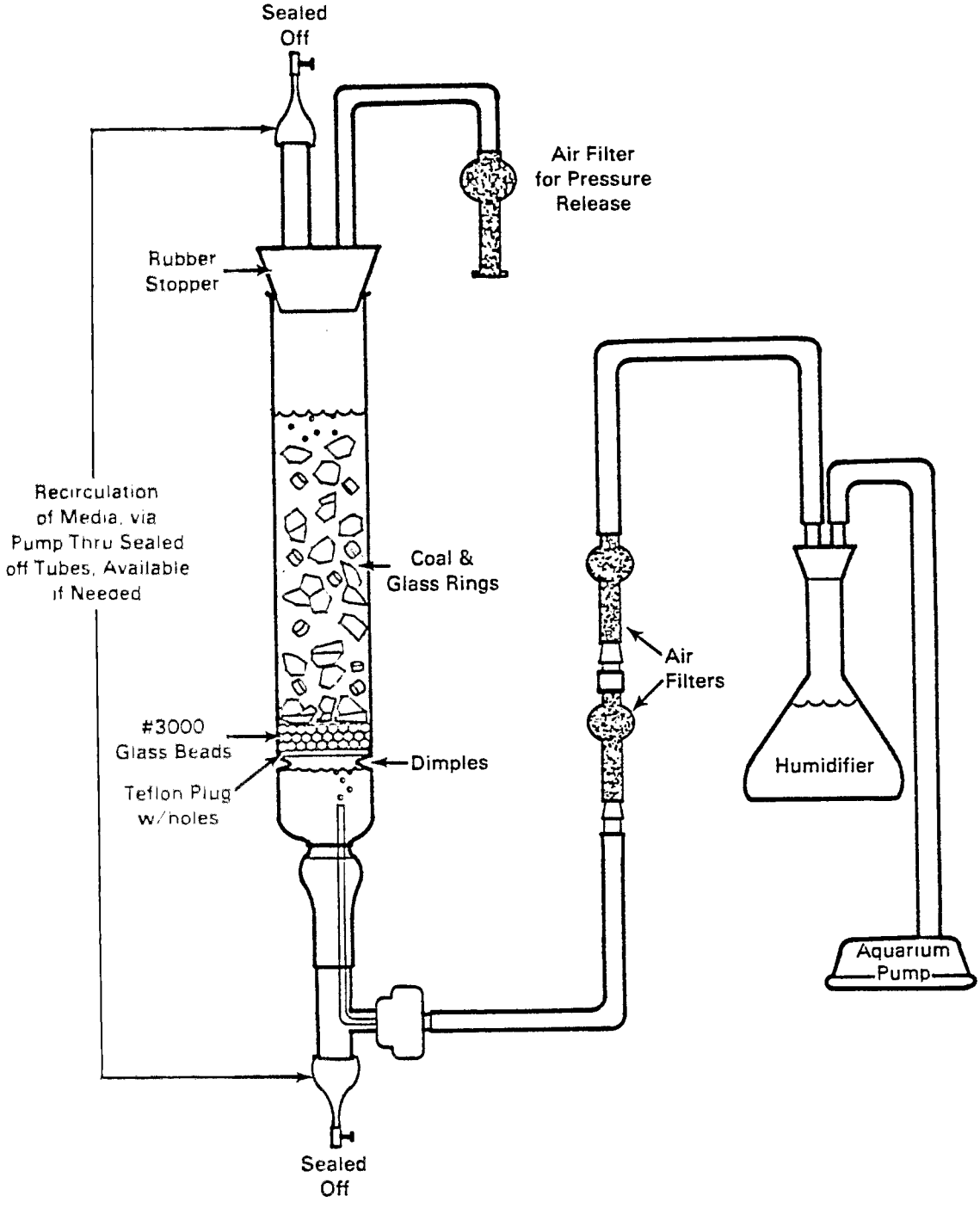

Figure 3. Schematic of Coal Bioreactor

Table 3

RESULTS FROM PACKED BED REACTORS

Trial Number	$A_{600NM}/g.cm^{-1}$*	$A_{260NM}/g.cm^{-1}$*
1	28	409
2	0.13	3.6
3	0.28	2.7
5	0.08	0.01
Plate Assay (minimal)	2.59	12

* Equal to total mls of sample times the absorption at the particular wavelength divided by the number of grams of coal extracted.

others Beuhla Zap was used. The conversion on Leonardite was about 4% to 5% on a weight basis. The low conversion is presumably caused by stoppage of aeration due to plugging of the column by fungal growth.

CHEMICAL CHARACTERIZATION

Elemental compositions as determined by combustion (%C,H,O,N,S) analysis for the feed coal and U. of H. bioextract is shown in Table 4. Note the high oxygen content of the North Dakota lignite (Leonardite) "as used" compared to typical North Dakota lignite (Beulah south) which has been stored in an oxygen free environment. Results

Table 4

ELEMENTAL ANALYSIS (%)

Microbial Product		Lignite	
C	46.09 ± 0.11	C	54.95 ± 0.08
H	3.80 ± 0.03	H	3.60 ± 0.08
N	4.34 ± 0.15	N	0.80 ± 0.10
O	30.87 ± 0.11	O	30.24 ± 0.50
S	1.03 ± 0.01	S	1.06 ± 0.02
P	0.51 ± 0.01	P	<0.005
Ash	7.27 ± 0.28	Ash	8.32 ± 0.05
		(Water	42.76)

Bioproduct ($C_{10}H_{9.8}N_8O_5S_{0.09}P_{0.04}$)

Lignite ($C_{10}H_{7.8}N_{0.1}O_{4.1}S_{0.07}$)

from x-ray fluorescence determinations for trace metals in the U. of H. bioextract and the feed Leonardite are shown in Table 5. Combustion ash data for the samples of interest were as follows: North Dakota Leonardite; 8.32%, raw bioextract (filtered); 7.27 acid precipitated bioextract; 3.48%.

The molecular weight range of the U. of H. bioextract was estimated by vapor pressure osmometry. The VPO measurements gave a value for U. of H. material of 342±18 daltous. This apparently low value is likely due to the contribution of low molecular weight counterions such as sodium and potassium as well as ammonium. Microanalytical determination showed that approximately 50% of the nitrogen in the U. of H. material was in the form of ammonium counterions.

Both the U. of H. and BNW samples were fractionated according to molecular weight range by ultrafiltration. Figure 4 shows a comparison of these results as obtained at approximately pH 6.4. Adjustment of pH altered the apparent molecular weight of the U. of H. materials as determined by this method. Results from determinations at pH 3.0, 6.4, and pH 10.4 are shown in Figure 5. This shift to lower apparent molecular weight at higher pH is consistent with the NMR data (see below) showing a large amount of exchangeable hydrogen, and suggests that the apparent molecular weight of the material may be altered by hydrogen bonding at lower pH.

Proton NMR spectra of the both materials in deuterium oxide showed that approximately 70 to 75% of the hydrogen was exchangeable, and therefore in the form of carboxylic acids or exchangeable protons on hydroxyl groups. Less than 10% of the protons have no aromatic character, as demonstrated by the NMR spectrum of the U. of H. material (Figure 7a). The BNW material from the bioreactor (at low conversion), on the other hand, shows substantial feature in the aromatic shift region (Figure 7b). (Some of the features in the aliphatic shift region may be due to media contamiantion.)

Table 5

X-RAY FLUORESCENCE ANALYSIS %

	Na	K	Mg	Ca	Si	Al	Cl	Fe	S
Lignite	--	-/-2	--	0.41	0.47	0.15	ND	0.38	0.69
Biodegraded	2.77	0.55	0.35	0.47	ND	0.43	0.34	1.45	1.04

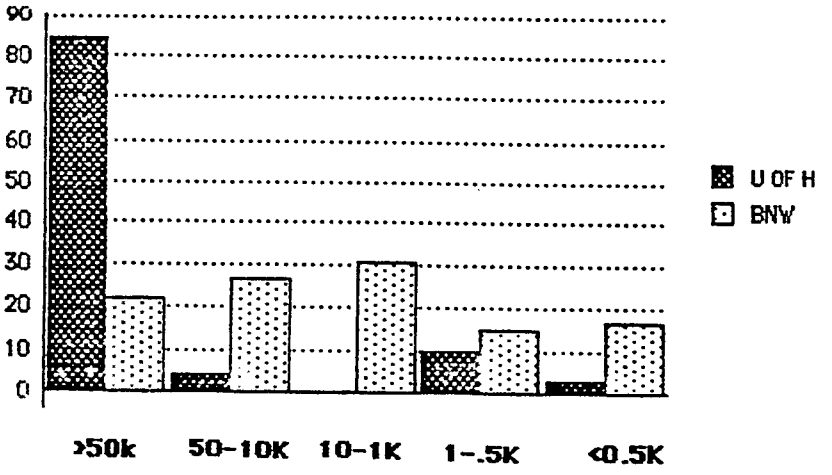

Figure 4. % Molecular Wt. Distribution of Biodegraded Coals

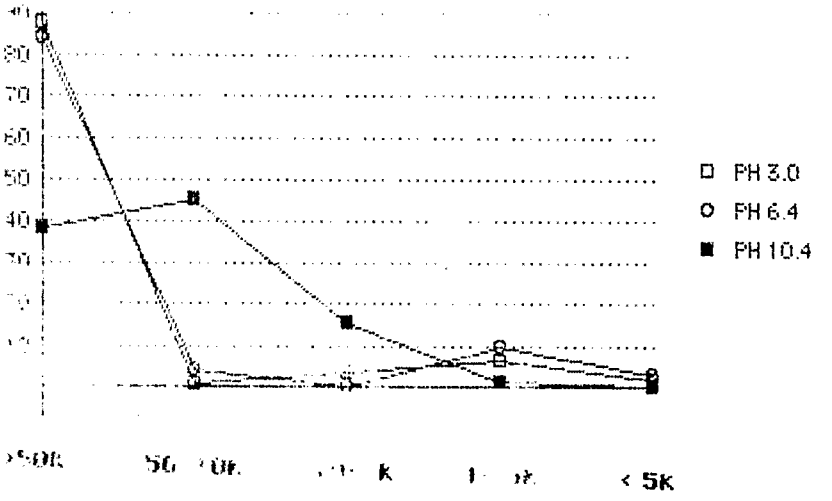

Figure 5. % Molecular Wt Distribution of Hartford Product with pH

IR spectra of the feed lignite and U. of H. bioextracts are shown in Figure 7a, 7b. The main difference in these spectra appears to be the loss of the aliphatic (CH_2) stretching peaks in the bioconverted material (Figure 7b). This apparent loss is consistent with proton NMR data.

The U. of H. freeze dried extract yielded no useful spectra from ^{13}C solid NMR analysis when run under those conditions used to analyze solid coal samples. We postulate that failure to detect the ^{13}C signal was due to interference from paramagnetic (iron containing) components in the extract. Similarly, gas chromatographic and electron impact mass spectral analyses yielded little useful data. Field desorption mass spectral analyses of this material yielded no clear ion

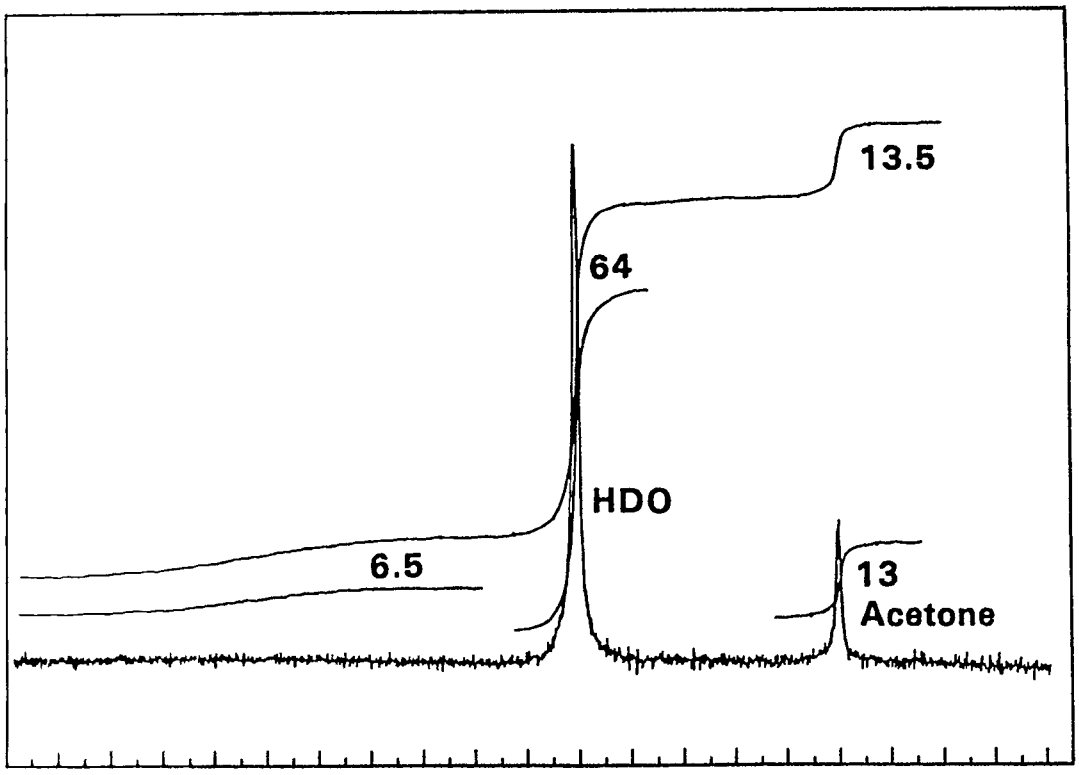

Figure 6a. NMR Scan of Cohen Microbial Product
(Acetone added as internal standard)

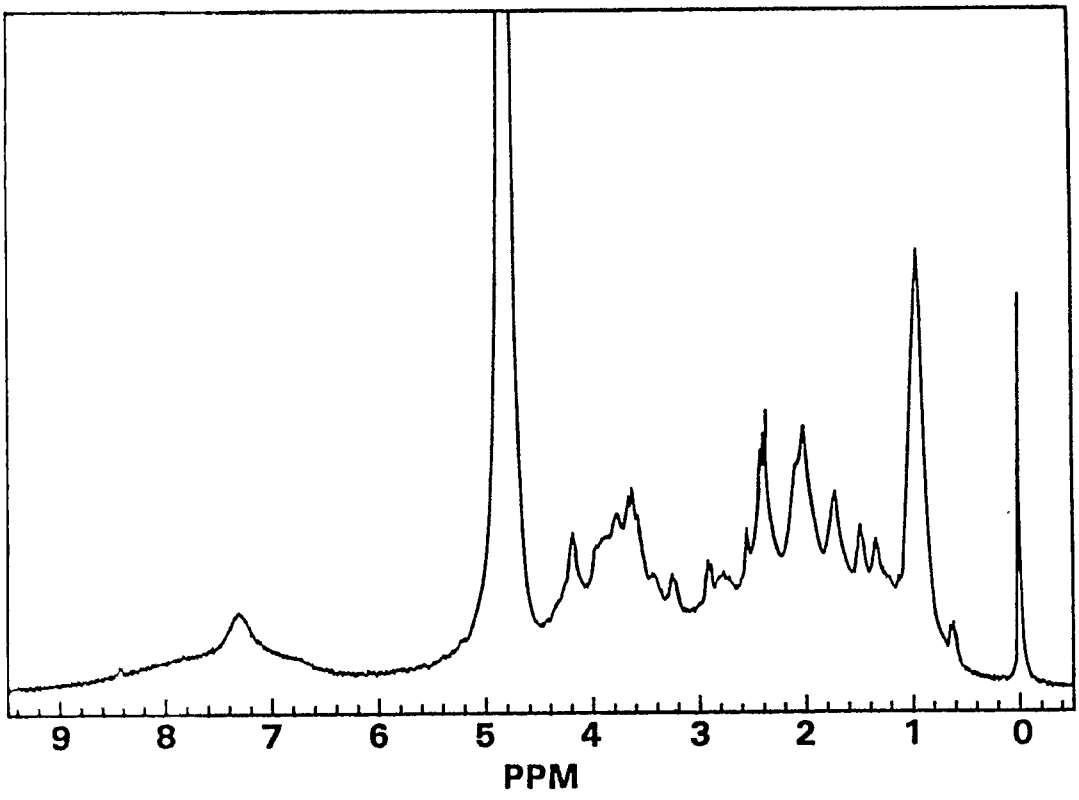

Figure 6b. NMR Scan of BNW Microbial Product

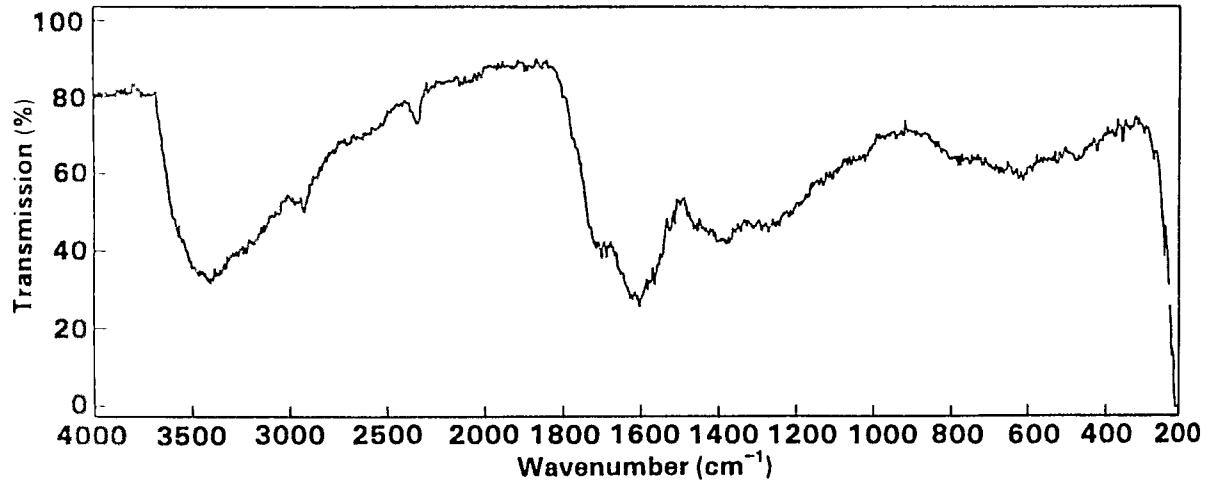

Figure 7a. Infrared Scan of Lignite (K Br pellet)

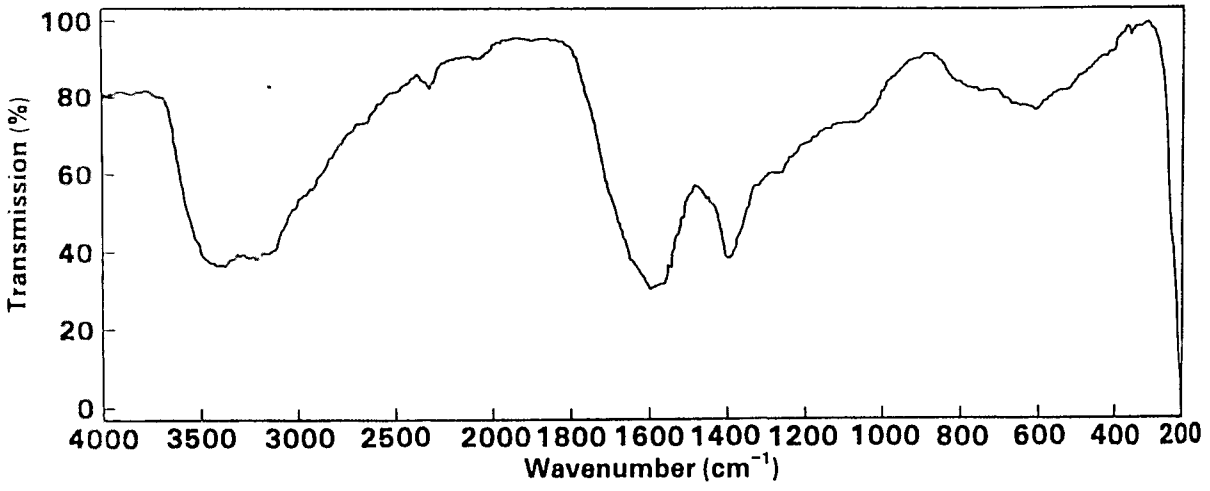

Figure 7b. Infrared Scan of Microbial Product (K Br pellet)

signals between approximately 100 and 3400 daltons. Failure to detect molecular ions in this mass range is consistant with the molecular weight estimates derived from ultrafiltration.

Figure 8 shows an model average structure for the bioconverted material based on the data obtained to date. It has been adapted from the structure of lignite and takes into account known reactions catalyzed by fungal enzyme systems. This model is not consistant with the loss of CH_2 as indicated in the IR data. This model unit structure will be further refined as new data become available.

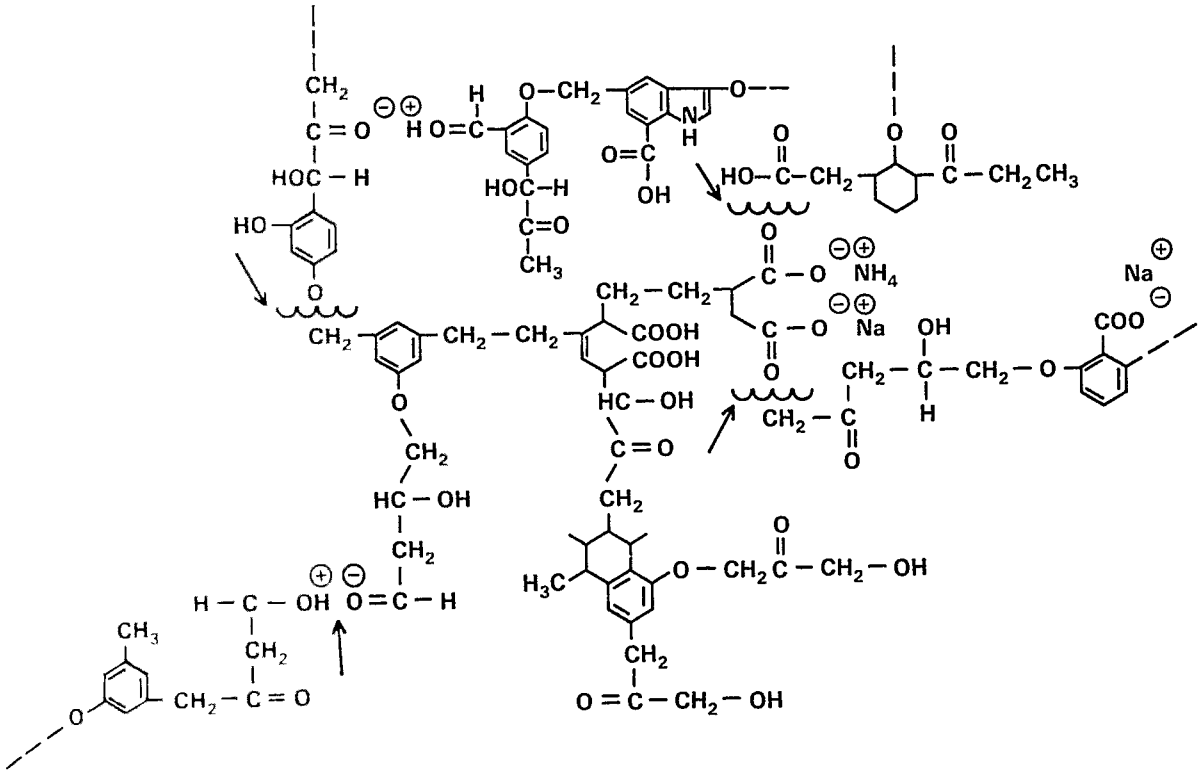

Figure 8. Possible Model Structure for Water Soluble Lignite Product

CONCLUSIONS

There have been several rather important advances in coal bioconversion in the last 12 months. These include characterization of additional strains capable of lignite conversion, limited conversions in liquid media bioreactors, and limited conversion of bituminous coal. (Limited conversion of subbituminous coal was reported by our group at the 1985 EPRI meeting.) However, demonstration of degradation by a laccase enriched enzyme preparation, probably has the most important implications for the eventual development of a conversion process based on bio-technology.

We have demonstrated the exchange of counterions in these materials by acid precipitation, and suggest that such exchange may allow flexibility with regard to solubility and other characteristics. For example, a more "soapy" material may be obtained by increases in the sodium counterion concentration. These soapy materials may be useful as energy-rich surfactants to enhance the quality of coal/water slurries. Ion exhange results also indicate that unwanted trace metals may be exchangeable for less bothersome counterions.

The bioconverted materials are more analogous in structure to the feed coals than are thermochemically-derived materials. Structure of the bioproduct appears to be very dependent on process conditions. Thus, the bioreactor products appear quite different from the Petri dish materials. No chemical analyses are yet available on the enzyme catalyzed conversion products.

As obtained to date, these products are of lower quality than many thermochemically-derived coal conversion materials. However, it is also likely that they may eventually be much less expensive to produce. Further research will be required to determine if there is a place in the energy market for such "bargain basement" liquid fuels.

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MICROBIAL DEGRADATION OF COAL BY POLYPORUS VERSICOLOR: METABOLISM AND PRODUCT CHARACTERIZATION

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Abstract

Stock cultures of Polyporus versicolor were grown in solid and liquid clutures at 30°C, 84-98% RH, and pH = 5.8. The growth of Polyporus was stimulated by the addition to the growth medium of 2,5-dimethylanaline at 2×10^{-4} M. Lignite coal has been degraded to liquid products (the bioextract) in sufficient amounts to permit various methods of analysis. The bioextract was collected with a pipette, freeze-dried, and stored dessicated at room temperature. The bioextract was soluble in solvents of high polarity such as water and ethanol and insoluble in hexane and similar solvents. The bioextract was analyzed by UV spectrophotometry, titrimetry, and electrophoresis. The enegy content was determined by calorimetry. Taken together, these analyses showed that the bioextract contains polar, water soluble species containing strong bases highly resistant to titration up to pH = 12. As the alkalinity of the bioextract was increased, the overall negative charge of the molecules also increased. The bioextract contained 95.7% of the energy content of the lignite from which it was produced.

Introduction

The United States has large untapped deposits of lignite and bituminous coal which have been considered as an energy source that might replace imported oil. However, many problems are associated with the various technologies which have been developed to use coal as a major energy source. These problems have been reviewed elsewhere (1). Some of the technical problems result from the fact that coal is an organic rock which contains both organic and mineral materials in different proportions and embedded in different physical structures. This variability affects the completeness of coal combustion, amounts of catalyst poisons present, the amounts and types of desirable hydrocarbon products that are formed, and the nature and amounts of slag and ash resulting from combustion. The current methodologies of physical and chemical coal conversions require high temperature and pressure, and produce particulate pollution products which are difficult or impossible to remove.

Although coal conversion technology has been studied since 1780 (1), little attention has been directed towards biological degradation. This may have resulted from the presence of few reports of coal degrading organisms in the scientific literature. In 1982, Cohen and Gabriele published the first report that fungi could grow directly on and metabolize naturally occurring coal as a substrate (2). Since that time, Cohen, Aronson, and Gray (3) have reported that, in their system, lignite coals are reliably degraded to a black, viscous liquid which has been partially characterized. Bailey Ward (4) has reported the isolation of lignite-degrading fungi from a weathered coal outcrop and Scott and Strandberg (5) have reported that seven different fungi (three of which have been identified) have degraded different lignites to variously colored liquid products. Wilson, et al. (6) have reported that the liquid products resulting from lignite biodegradation are water soluble, highly oxygenated, structurally heterogeneous, with a wide range of molecular weights and containing no detectable polycyclic aromatic hydrocarbons.

Materials and Methods

Metabolism. Stock cultures of Polyporus versicolor are routinely maintained in both solid Sabouraud maltose agar and Sabouraud maltose broth cultures. All cultures are incubated at 30°C, 84-98% RH, and pH = 5.8. Experimental cultures are also incubated as described above with the exception of the experiments involving specific additions to the media. Solid cultures are inoculated with a hyphal suspension and allowed to incubate for approximately 12 days to produce a continuous fungal mat. Sterile lignite pieces (approximately 5 mm^3) were placed directly on the hyphal mat.

The compound 2,5-dimethylanaline, a known inducer of the fungal enzyme laccase (7) was added to agar media to determine its effect on fungal metabolism and lignite degradation.

Solubility Tests. In order to determine the solubility characteristics of the bioextract, it was first lyophilized. Twenty five mL of the neat bioextract was freeze-dried using a Bellco cold finger. Temperature of the cold finger was maintained at approximately -70°C using a dry ice-acetone slurry. The residue that remained following freeze drying was weighed and the concentration of the neat bioextract was calculated to be 60 mg of solids per mL of neat bioextract. The dry product is a brown, flake-like solid with the ability to hold a static charge. The solubility of the freeze-dried (FD) bioextract was tested by dissolving the FD particles to saturation in various solvents of different polarities. The solutions were then dried and the solutes were weighed to determine solubilities expressed as grams of FD bioextract per mL of solvent.

UV Spectrophotometry. The coal extract was prepared by drying powdered lignite coal at 100°C for 24 hours. The dry powder was then extracted overnight with methanol/water (50/50 by volume) using a Soxhlet apparatus. Products from the extraction were stored at 4°C. Samples for the UV-VIS spectrophotometry were taken from the coal extract and from the FD bioextract described above. Both samples were standardized to a concentration of 5 mg of solids per mL of distilled and deionized (D+D) water or 50/50 methanol/water as appropriate. Both samples were diluted 1:20 with the appropriate solvent and then scanned from 800 to 190nm using quartz cuvettes (1cm path length) in a Varian MS90 spectrophotomenter.

Titration Experiments. A 0.07516 gm sample of FD coal was diluted with water to 100 mL. A 15.00 mL aliquot was titrated with 0.1832 M carbonate-free NaOH. The NaOh was delivered from a digital syringe driven by a stepper motor. The stepper motor was controlled by a Z-80 based microcomputer, which also recorded the pH directly from an Orion model 701A pH meter. The pH meter was initially standardised with standard buffers at pH = 6.685 and pH = 4.008. Since ionic strength was not controlled throughout the titration, a pK_w of 14.0 was used to calculate the free $[OH^-]$ at any pH.

Electrophoresis. Polyacrylamide gel electrophoresis was carried out as described by Brewer (8) except for the following modifications. Sample preparation involved used tube gels at a concentration of 15%. Recrystallized acrylamide was degassed and polymerized using N,N,N',N'-Tetramethyl-ethylenediamine (temed), and 2 mL of 0.03 g/10 mL ammonium persulfate.

Calorimetry. Powdered coal samples, FD bioextract, benzoic acid, and naphthalene were each pressed into pellets weighing approximately 1 gram. The benzoic acid was used to calibrate the calorimeter and the naphthalene was used to check the accuracy of the calculations. Each pellet was burned in an nonodiabatic bomb calorimeter. Temperature was measured with a thermister interfaced to a computer for data collection. The accuracy of the thermister is +/- 0.001°C.

Results

Coal Liquification. Samples of lignite coal have been digested to a black viscous liquid. Polyporus secretes drops of a clear yellowish liquid. When these drops appear, liquification of lignite occurs and the color of the secretion drops become darker, eventually becoming opaque (black).

Liquification of the coal is visually apparent within 24 hours after the coal is added to the cultures and is not restricted to coal pieces in contact with the secreted drops. When the yellowish drops were removed from the cultures and placed in a test tube with small pieces of coal, no degradation was apparent.

The process of coal liquification by Polyporus continued with the amount of black liquid product continuously increasing until the lignite is completely liquified or the growth of the fungi ceases, possibly due to the effects of toxic products produced during the process of liquification. Liquified coal (the bioextract) was removed from the top of the mycelium and/or coal pieces with a pasteur pipette, freeze-dried, and stored dessicated at room temperature. The bioextract contains no particulate matter that can be observed at a magnification of 400X using a compound microscope.

Metabolism. Addition of the compound 2,5-dimethylanaline resulted in a stimulation of fungal growth as compared to growth on sabouraud maltose agar (Figure 1). At each measurement, growth of treated cultures paralleled that of the controls. After 7 days of treatment, the diameter of the mycelium of treated cultures was 9% greater than that of the controls.

UV Spectrophotometry. The absorbance of the FD bioextract (b) at 200 nm is only about half that of the coal extract (a) and the absorbance remains less than that of the coal extract until about 400 nm at which point the absorbance of the FD bioextract becomes greater than that of the coal extract (Figure 2). There are two likely explanations for these results. First, the absorbance of the FD bioextract at 200 nm might be lower than that of the coal extract because the FD bioextract contains the same distribution but fewer chromophores than the coal extract. Second, the FD bioextract may contain the same number of chromophores as the coal extract with each chromophore having a lower absorbance. This second

explanation is more likely and can be supported by the following arguments. A change from pi to pi^* transitions which are characteristic of benzene, naphthalene, and other aromatic ring structures to more n to pi^* transitions would result in a decrease in UV absorbance as seen in figure 2. Such a change in transitions would be brought about by addition of heteroatoms like oxygen, nitrogen, or sulfur across double bonds of an aromatic ring structure. Such additions would also result in an increase in polarity of the molecules. Our results show that the FD bioextract contains polar functional groups which are completely water soluble and insoluble in hexane. The increased absorbance of the FD bioextract as compared to the coal extracts which starts at about 400 nm would also result from the addition of heteroatoms across the double bonds of aromatic ring structures. This would destroy chromophores of high epsilons and create new chromophores with n to pi^* transitions, low epsilons, and absorbance at longer wavelengths as seen in figure 2.

Solubility Tests. When the FD bioextract was mixed with solvents having polarity indices less than 4 such as hexane (0), methylene chloride (3.4), and 1-butanol (3.9), the solvents appeared to have little if any effect onthe FD solid (Figure 3). Mixing the FD bioextract with solvents having polarity indices between 4 and 6.2 such as THF (4.2), 1-propanol (4.3), and ethanol (5.2), resulted in formation of a light yellowish-brown solution. This indicates an increase in solubility of the FD solid as compared with the solvents of lower polarity mentioned above. The FD bioextract was most soluble in methanol or water (polarity indices 6.6 and 9.0 respectively), resulting in an opaque, black, solution.

Titration Results. The results of the titration of the FD coal sample are presented in Figure 4. Curve a, the acutual titration, actually has 200 data points, with the solid line drawn for ease of reading. Using these data points, the free $[OH^-]$ in the solution was subtracted from the total number mmoles of OH^- added to give the number of mmoles of OH^- which reacted with the coal species (Curve b). There is clearly no endpoint, but it should be noted that at pH = 12, the remaining "acidic" sights have conjugate bases equal in strength to a 0.01 M solution of NaOH. Thus, approximately five millimoles of OH^- are reasonably titratable in one gram of the FD coal sample, or an equivalent weight of approximately 200 grams per equivalent for titratable hydrogen.

Electrophoresis. The dyes were well separated (Figure 5). Two of them, phenol red and bromcresol green, have low molecular weights of 354 and 698 respectively. At pH = 7.5, these dyes migrated with the greatest RF values of any samples or standards run. Blue dextran, with a molecular weight of 2×10^6, migrated with an RF=0.052.

The neat sample of bioextract in tube 2 separated into 5 banding regions. Two of these bands are distinct and are referred to as bands d (RF=0.73) and e (RF=0.79). In dissolved samples of the bioextract, these bands appear consistently. In the neat bioextract (tube 2), bands d and e are less dense than the corresponding bands in tubes 3 and 4 where the pH has been adjusted to highly alkaline values. The bulk of the bioextract in tube 2 has remained near the top of the gel. The other 3 bands are less well defined than bands d and e. Band c is a light, thin band which migrated about half way down the gel (RF=0.57). Bands a and b contain the bulk of the material from this sample. Band a has an approximate RF value of 0.73. No RF value could be assigned to band b because the material did not separate into distinct bands.

Tube 3 contains an acid precipitated and base dissolved sample of the bioextract at a pH = 9. In this sample, all of the components migrated into two discrete bands (RF = 0.76 and 0.81) which correspond to bands d and e of the neat bioextract.

Tube 4 contained the bioextract treated as in tube 3 but had the final pH adjusted to equal 13. The sample migrated into three discrete bands two of which correspond to bands d and e (RF = 0.75 and 0.78) with a third band appearing above them with an RF=0.65.

Tube 5 contains an acid precipitated sample of the bioextract (pH = 4) which was not dissolved in base. This sample did not migrate through the gel.

Calorimetry. The average energy content of the lignite coal sample was 4.394 Kgcal/gram or 7,378 BTU/pound. The average energy content for the FD bioextract was 4.208 Kgcal/gram. This indicates that the FD bioextract still contained 95.7% of the original energy content of the lignite on a gram for gram basis. It should be noted that one gram of coal yields less than one gram of liquified coal. Measurement of the energy content of naphthalene showed that the maximum error of these measurements was 1.2%.

Discussion

The single, most important key to a successful analysis of the action of Polyporus on coal is the ability to produce enough of the degradation product to feed the arsenal of tests which might be performed. Analytical tests previously reported (3) such as NMR, infrared spectroscopy, and HPLC required little of the coal solution produced by Polyporus. However, procedures such as calorimetry require much more sample, and the sample is much easier to work with and quantify if it is a solid. In response to this need, the production of the water-soluble coal product was increased to meet the demands of the analytical methodology. Approximately

50 mL per month have been produced in the last six months, which has yielded a freeze-dried product in sufficient quantity to satisfy the needs of our, and other, laboratories.

In an attempt to hasten the process of identifying the optimum conditions for the liquification of coal by Polyporus, a laccase inducer (2,5-dimethylanaline) was added to the agar media. The increase in overall growth is sufficiently encouraging to warrant the introduction of coal samples in order to observe the effect of the rate and capacity of liquification of the coal. While an increase in the thickness of the mycelium in treated cultures was obvious, this difference is not reflected in the diameter of the cultures.

In the continuing attempt to characterize the water-soluble liquification product, electrophoresis and titrimetry were performed using the FD product. The electrophoretic results show a clear pH effect, with the almost bandless result at pH = 7 which tighten into observable bands at higher pH. The titration curve in Figure 4 (with the free $[OH^-]$ subtracted) shows a virtually featureless titration curve, which is typical of polybasic moieties. That is, in aqueous solution, there appears to be approximately five milliequivalents of titratable proton on a series of strong bases (notice the high initial pH) whose pK_a's range in a region of 8 and higher, providing continued buffering throughout the titration. Thus, as the electrophoretic solutions are made ever more basic, the soluble coal species become ever more negative, and thus migrate toward the positive gradient. The one exception seems to be at pH = 13, but under the influence 0.1 M NaOH, it would be unreasonable to assume that nothing more than proton neutralization is occurring. Even so, the solution is still clearly banded. Note that five milliequivalents per gram implies an equivalent weight of 200 in terms of titratable protons.

The titration curve itself is of interest. It should be noted that it is not unreasonable for the pH of a solution of the FD coal to be approximately equal to that of the agar medium since Polyporus is living at the pH and since there is probably some small amount of medium in the coal solution produced by Polyporus. The freeze-drying process will produce a solid which should reproduce the original solution conditions when rehydrated. Given that, there is still a titratable sight (below pH = 12) for every 200 grams of the FD solid. Since there is little evidence for a large amount of nitrogen and sulfur, one must conclude that there are a large number of alcohols, in various environments, giving rise to the bulk of the titratable protons. This is in agreement with the large percentage of exchangable protons seen in nmr spectra of the liquification product (3).

The UV-Visible spectroscopy tends to also support these ideas. The spectra of the extracted coal and the FD product are different in the distribution of the absorbance bands. The FD product has a higher percentage of its absorbance at longer wavelength. Although not definitive, this shift is consistant with a diminishing of the number of C-C pi bonds, such as those in benzenoid moieties which generally give rise to pi to pi^* transitions in the 200 nm to 350 nm range, and an increasing number of heteroatoms, which would tend to display their n to pi^* transitions at longer wavelengths and much lower oscillator strengths. Coupled with the relatively large molecular weights implied in the electrophoretic experiments and the high polarity of the FD product as seen in the solubility studies, the implication that the major function of the action of Polyporus on coal is to add water or hydrogen peroxide, or both, across C-C double bonds and other sights of unsaturation continues to be supported.

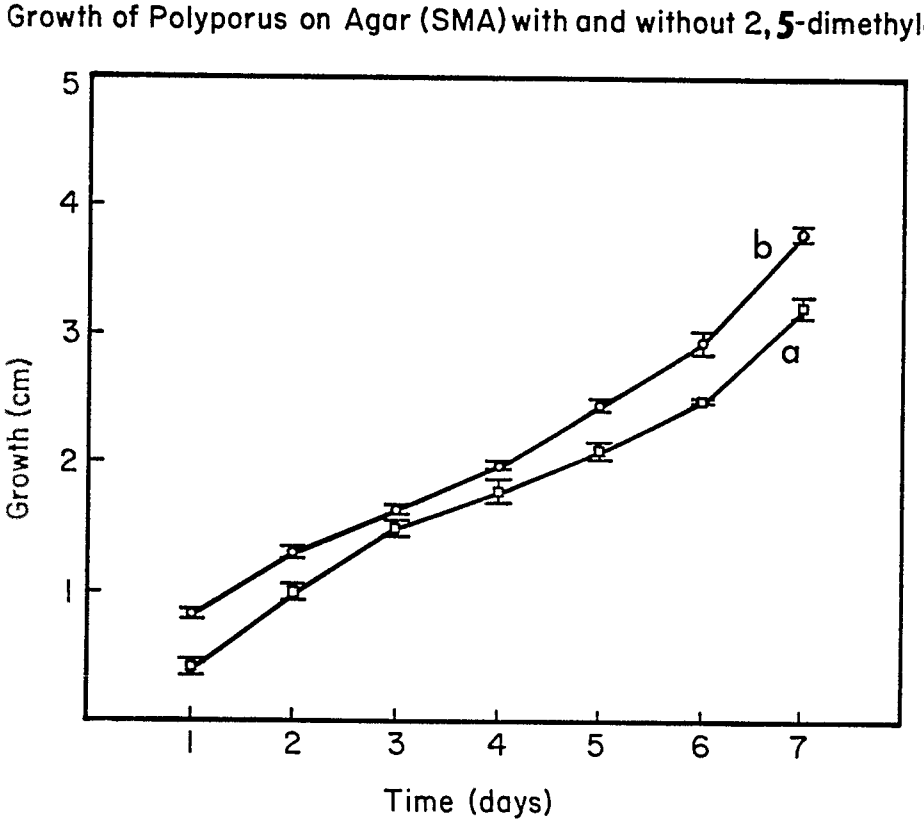

Figure 1. Growth of Polyporus with (b) and without (a) the laccase inducer 2,5-dimethylanaline ($2x10^{-4}$M).

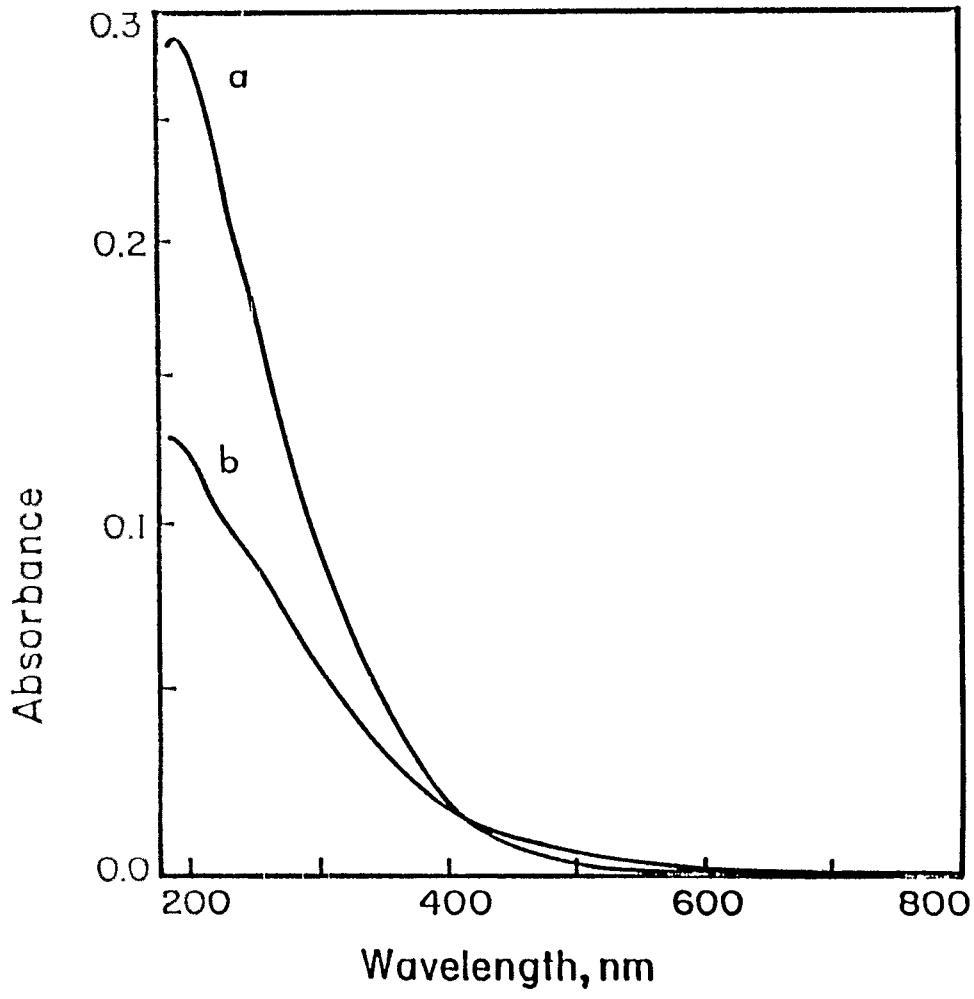

Figure 2. UV-Vis spectra of the neat bioextract (a) and a methanol-water (50/50 v/v) extract of lignite (b). Each sample was standardized at a concentration of 5 mg of solids per ml of D+D water or 50/50 methanol water as appropriate.

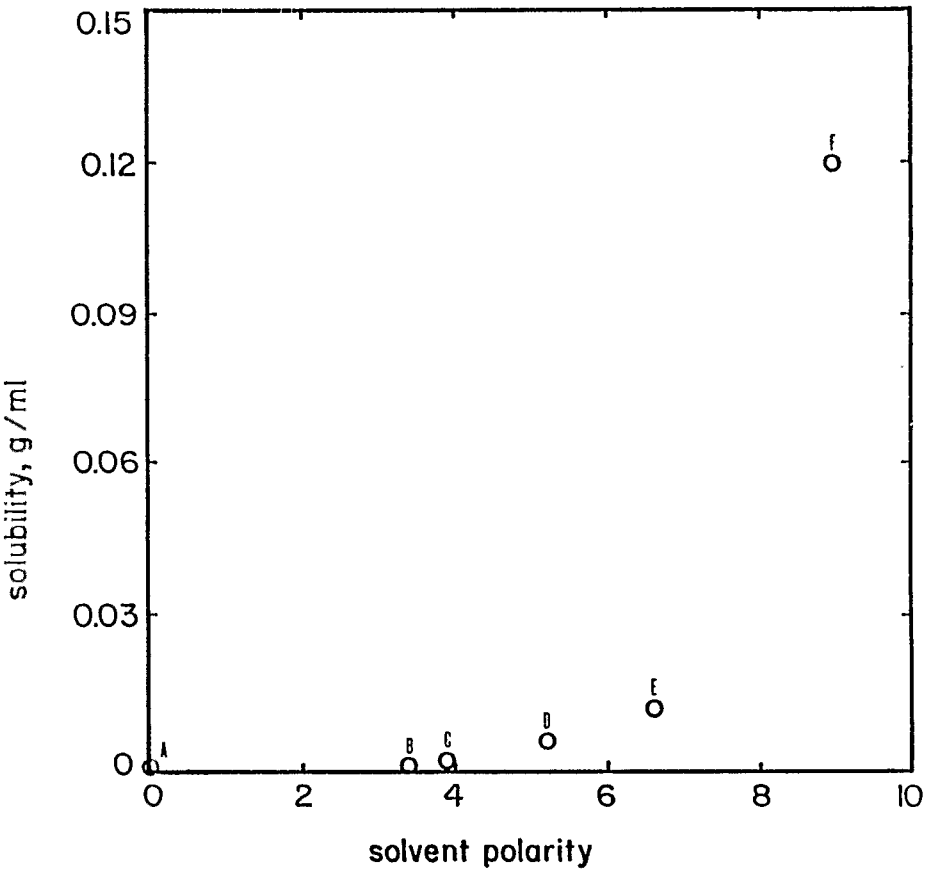

Figure 3. Solubiity of the freeze-dried bioextract in various solvents of different polarities (debye units). The solvents were hexane (A), methylene choloride (B), butanol (C), ethanol (D), acetonitrile (E), and water (F).

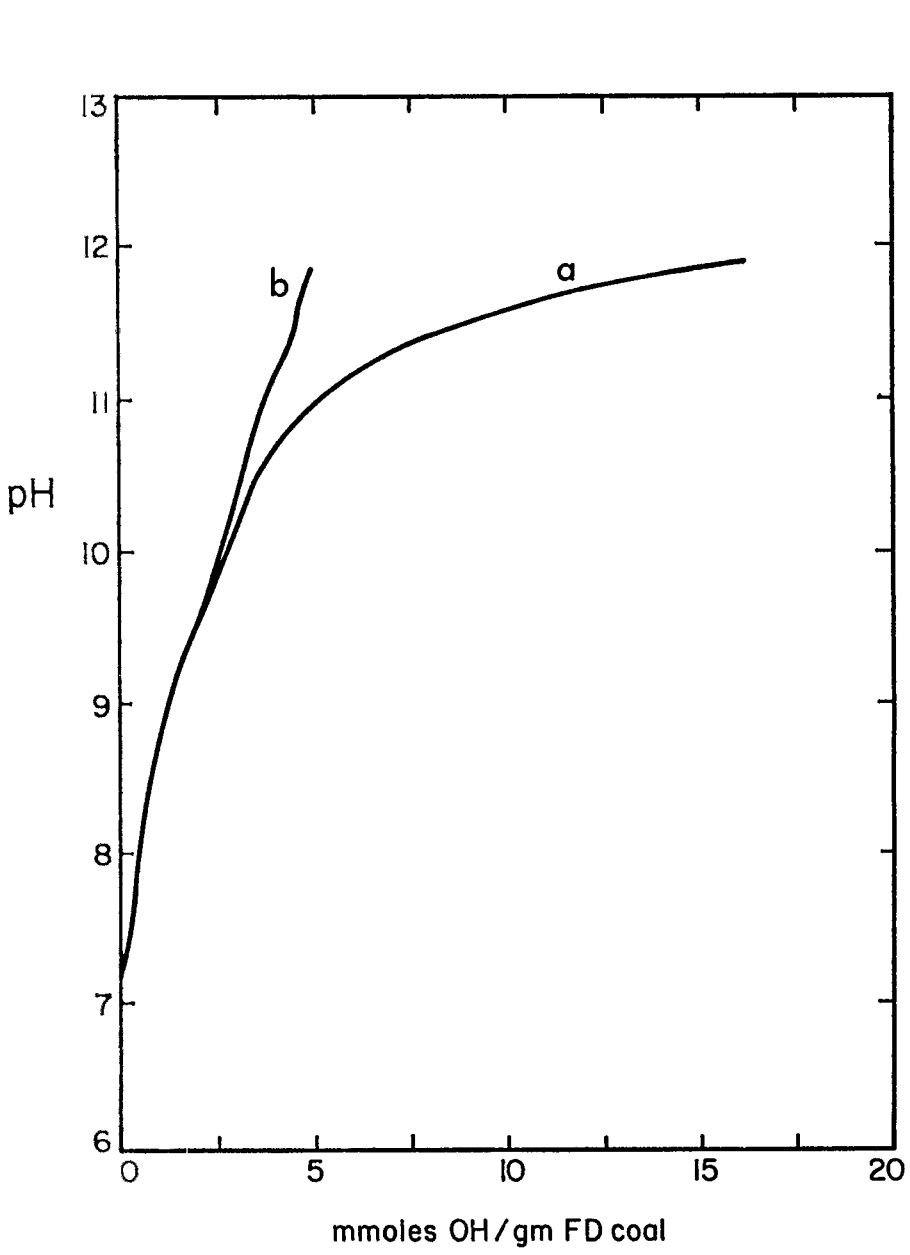

Figure 4. Titration of the freeze-dried bioextract showing free (a) and reacted (b) OH^-. At pH = 12, only about 5 mm of OH^- has reacted with the bioextract.

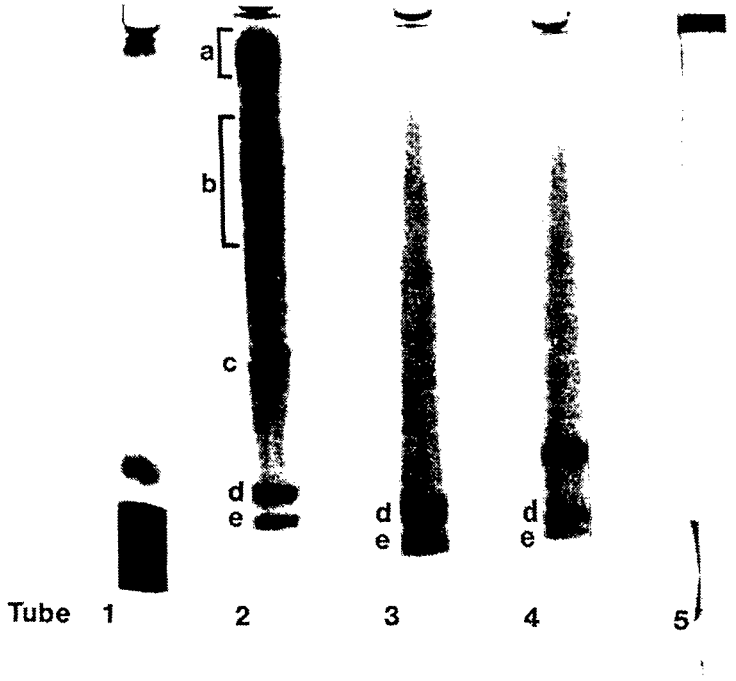

Figure 5. Electrophoretic separation of the freeze-dried bioextract. Tube 1 contains 3 tracking dyes (blue dextran, phenol red, and bromocresol green) at pH = 7.5. Tube 2 contains the neat bioextract at pH = 7.5. In tube 3, the bioextract was precipitated in acid and then dissolved in base and run at pH = 9.Ø. In tube 4, the bioextract was treated as in tube 3 but run at a pH = 13.Ø. Tube 5 contains an acid precipitated sample of the bioextract run at pH = 4.Ø.

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CHEMICAL STRUCTURAL DIFFERENCES BETWEEN TWO LOW-RANK COALS

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ABSTRACT

Chemical structural characteristics of a Wyoming subbituminous coal and a Texas lignite were determined by controlled solubilization of each coal, solvent fractionation of the product, and detailed analyses of the product fractions to obtain average molecular structural parameters. The controlled solubilization was carried out in reactions with NaOH/ethanol/H_2O at temperatures between 200 and 300°C. Material and elemental balances revealed that the oxygen functional groups of each coal were attacked selectively in the solubilization process, resulting in an orderly, definable dimunution of the complex coal structure.

Structural information obtained on each coal includes the distribution and arrangement of oxygen functional groups, aromatic clusters, linkages between the clusters, and side chains on the clusters. The structural characteristics were used to construct molecular structural models specific to the coals examined. Also, the structural data were related to their hydroliquefaction yields such as potential products, their distribution and hydrogen consumption.

The arrangements of aromatic clusters and functional groups were similar in both the coals. Two to four aromatic clusters of a similar size are linked to each other by alkyl C-C bonds, making a chain of aromatic clusters. Two or more of these chains are connected to each other by ester and ether groups. The size of aromatic clusters ranges from single ring to five-fused ring clusters.

The two coals are different in the distributions of aromatic clusters and oxygen functional groups. The lignite contains fewer large aromatic clusters than the subbituminous coal, although they contain similar amounts of single ring and two-fused ring aromatic clusters. Hydroxyl and ether groups contain more of the oxygen in lignite than the ester and carbonyl groups. However, the ester and carbonyl groups contain more of the oxygen than hydroxyl and ether groups in the subbituminous coal.

These structural data were used to predict the product distribution in the hydroliquefaction of each coal. The predicted distribution from the subbituminous coal agreed well with experimental values. The potential yield of distillable product from the lignite is 15% higher than that from the subbituminous coal. The amount of hydrogen to be consumed in cleaving alkyl linkages is 0.3% of feed in both the coals.

1. INTRODUCTION

Elucidation of the coal structure has been hindered by two major obstacles: the complex composition of a coal, and its low solubility in known solvents. A promising approach to overcome these difficulties is to "depolymerize" a coal and analyze the product, although earlier investigations did not approch the expected potential. In a recent study, we re-examined this approach based on the current understanding of coal structure, and devised a methodology for molecular structural characterization of coal, which was applied to a Utah coal.

In this presentation, we describe a refined methodology for chemical structural characterization of a coal, and examine experimental data to define major structural features of a Wyoming subbituminous coal and a Texas lignite. The Wyoming subbituminous coal and Texas lignite are significantly different from each other in major structural features.

2. METHODOLOGY FOR THE COMPOSITIONAL AND STRUCTURAL CHARACTERIZATION OF COAL

Complex composition and low solubility of a coal in known solvents have been major obstacles to the quantitative determination of chemical structural features of the coal. An effective way to elucidate the chemical nature of a given coal is the examination of carefully prepared coal-derived liquids. The coal needs to be degraded or depolymerized in a controlled manner so that (1) the coal-derived products retain the major structural features of the coal, (2) the products are amenable to analysis on a molecular level, and (3) the chemical process involved in the dissolution is known or determinable. Nevertheless, coal-derived products are still a complex mixture of numerous components with different functional groups. Thus, their examination requires a systematic approach which includes fractionation, organization of appropriate analytical means, and proper treatment of the experimental data.

With the goal of characterizing coal via analyzing its products, we have developed a unique, practical methodology for a detailed characterization of coal-derived material. This characterization, in turn, leads to the characterization of a specific coal in molecular terms (1-3). We have found that the solubilization reaction of NaOH/ethanol with Utah bituminous coal caused an orderly and readily definable diminution of the complex coal structure at temperatures of 300°C and 320°C. To obtain valuable information, an effective fractionation of the solubilization product by a unique solvent extraction was also found to be essential. When each fraction was analyzed in detail on a molecular level and represented by average molecular structural parameters, it was distinctly different from other fractions, revealing compositional and structural characteristics of the coal.

In this investigation of the characterization of a Wyoming coal and a Texas lignite, the same methodology has been applied and improved to obtain more detailed information on oxygen functional groups and linkages as well as the distribution of aromatic/hydroaromatic clusters in the coal. The reaction temperatures for the solubilization reactions were lowered to 215°, 260° and 300°C. Evolution of CO_2 to form Na_2CO_3 was observed during the reaction, and its determination was found to be important in evaluating the experimental data.

With these improvements, a comprehensive chemical characterization methodology has been formulated as shown in Fig. 1. The chemical structure of a given coal is represented by aromatic clusters of different sizes, joined by various linkages. The coal is solubilized by selective bond cleavages in reactions with NaOH/ethanol/H_2O. The information on bond cleavages is obtained from gaseous products, elemental balances, product distribution, molecular weight and functional groups of the solubilized product. The soluble product is separated into chemically different fractions by an effective solvent extraction, and each fraction is analyzed in detail to obtain average structural parameters. The structural data on the solubilized product fractions are combined with the information on the selective bond cleavages to describe the original chemical structural features of the sample coal.

The characterization methodology provides a comprehensive description of the chemical structural characteristics of a coal. The structural data are quantitative on a molecular level, and thus they can be related to the chemical behavior of the coal under combustion, gasification, liquefaction and upgrading conditions. The methodology is versatile, and when necessary, it can be adapted or modified to obtain more detailed information on specific structural features of a coal.

3. EXPERIMENTAL

A subbituminous coal sample from the Rawhide mine in northeastern Wyoming and a lignite sample from the Big Brown mine in northeastern Texas were investigated. Each sample was ground in a ball mill with water. After removing the excess water, the moist coal samples were used in the experiments. The moisture contents of the samples were typically 50%. The Wyoming coal, after drying at 110°C, had the following composition: C, 64.9%; H, 4.2%; N, 0.6%; O and S, 24.8% by difference; and ash, 5.5%. The composition of a dried Texas lignite sample was: C, 59.7%; H, 4.2%; N, 1.2%; O and S, 22.6% by difference; and ash, 12.3%.

For each coal sample, three reactions with NaOH and ethanol were carried out at 215°C, 260°C and 300°C. Subbituminous coal reactions were denoted by Sub-215, Sub-260 and Sub-300. Lignite reactions were denoted by Lig-215, Lig-260 and Lig-300. In each reaction, a weighed portion of 50 g of a moist coal sample was mixed with 40 g of ground NaOH and the mixture was placed in a 1-liter autoclave, followed by the addition of 120 g of ethanol. The reactor was heated to the desired temperature, the reaction was continued for 1 h, and then the reactor was cooled to ambient temperature. The gaseous product was examined by IR and GC. The condensed product was collected in water and the solution was centrifuged. The solid material from the centrifugation was called "Basic Solution Insoluble" or BaI. The amount of CO_2 evolved during the reaction was determined by a forward/backward titration method using an aliquot of the supernatant solution. The rest of the supernatant was acidified to pH 2.7 to obtain precipitates, which were collected and called "Basic Solution Soluble" or BaS. These two fractions were further separated, as shown in Fig. 2. Acetone extraction was performed only on BaI-HI obtained in the reaction at 300°C. Pyridine extraction was performed at room temperature with the solvent/sample ratio of 10. H_2O-soluble material was recovered from the water washes of BaS and BaI by chloroform extraction.

Most of condensed-phase product fractions were analyzed for elemental composition, ash content, average molecular weight, hydrogen distribution and functional group contents. Elemental composition was determined with a Perkin-Elmer Model 240B analyzer. The ash content was determined by heating at 750°C in a ventilated furnace. Hydrogen distribution and functional group contents were determined by H^1-NMR and IR spectroscopies using a JOEL FX-60-Q NMR spectrometer and a Nicolet

MX-1 Fourier transform IR spectrometer. Average molecular weight was determined by vapor phase osmometry using a Corona Model 232A apparatus (Wescan Instruments, Inc.). The experimental procedure and conditions were carefully chosen to ensure the correct determination of molecular weight.[4]

4. RESULTS AND DISCUSSION

The chemical characteristics of the solubilization products depend on the solubilization reaction employed, as well as the feed coal. Thus, the correct understanding of the solubilization reaction will help determine the characteristics of the products, as well as those of the starting material. We will discuss the solubilization reaction first based on the results from the Wyoming coal experiments, and then examine the structural characteristics of the solubilization products, followed by the description of the coal structure and its relationship to liquefaction behavior. The results from the Texas lignite will be examined in a similar manner, pointing out major differences from the Wyoming coal.

FORMATION OFTHE SOLUBILIZATION PRODUCTS FROM THE WYOMING COAL

Recently the base/alcohol reaction of coal has been investigated by several groups,[1-3,5-7] but there has been no consistent interpretation of the chemistry involved. During this investigation, we observed the evolution of CO_2 on the acidification of the product solutions; this observation has not been reported in the literature. The amount of CO_2 evolved was 19.4% in Sub-260. Only a trace of CO_2 was detected in the gaseous products by IR. According to a blank test by Makabe et al,[7] NaOH and ethanol produced only a minute amount of CO_2, 0.011% based on carbon in ethanol at 300°C. Our observation of CO_2 evolution is extremely significant to understand properly the chemistry of the feed coal.

The product distribution and molecular weights of condensed-phase products from the three reactions of the Wyoming coal are compared in Table 1. The yield of CO_2 was significant in Sub-215, and it increased by more than a factor of four at 260°C and remained constant at 300°C. Nevertheless, the recovered H_2O-soluble and the lost H_2O-soluble increased with reaction temperature, by a factor of three between 260° and 300°C. The trends of CO_2 and the H_2O-soluble yields reveal that dissimilar reactions took place at the different temperatures.

The distribution of the condensed-phase products also reflects the different reactions that have taken place. Even at 215°C, 70% of the feed coal was converted to the soluble and gaseous products. Furthermore, 51% was soluble in basic

solution. This high solubility indicates a high content of polar functional groups in the products.

At 260°C, the conversion increased to 94%, and the condensed product distribution was altered drastically. The substantially higher yields of BaS-HI and BaI-PS came from BaS-HS and BaI-PI in Sub-215, respectively. Still the yield of BaS-HI and BaS-HS is 50% of the feed, and the high solubility in basic solution indicates a large content of polar functional groups in these fractions as well. Obviously, decarboxylation was responsible for the change as indicated by the large amount of CO_2 evolved, but hydrolysis and other reactions may have contributed. The yield of the H_2O-soluble (recovered and lost) is significant. The average molecular weights of soluble fractions ranged from 1140 to 1400.

At 300°C, the conversion, 95%, remained almost the same as at 260°C, but the product distribution changed from that found at 260°C. Since the CO_2 evolution was not altered from that at 260°C, the larger yield of the H_2O-soluble material is characteristic to the reaction which took place at 300°C. Thus, the reaction above 260°C seems to be hydrolysis involving functional groups other than ester groups. The molecular weights of the soluble fractions ranged from 590 to 2100, which were approximately 34% less than those in Sub-260. BaI-AS is a unique fraction which had the lowest molecular weight (Table 1), but it was mixed with BaI-AI-PS, which had potentially the highest molecular weight among the soluble fractions in Sub-300. The elemental composition reveals that BaI-AS had the lowest oxygen content but the highest H/C ratio: thus, it was not soluble in the basic solution or H_2O. The much larger molecular weight of the BaI-PS fraction in Sub-300 than in Sub-260 reveals that (1) the fraction from Sub-260 consisted of at least two subfractions which greatly differ in molecular weight and functionality, and (2) the BaI-PS fraction obtained from Sub-300 was changed little, even though the reaction temperature was increased by 40°C.

In addition to the product distribution, element balances provide important information. In Sub-215, the total carbon recovery was 97% as shown in Table 2, which indicates that the product collection and its analysis were dependable. However, hydrogen and oxygen recoveries were 110% and 117%, respectively. The high hydrogen recovery and CO_2 evolution resulted in significantly higher H/C ratios of the product fractions, BaS-HI, BaS-HS, BaI-HI and BaI-HS, than that of the feed coal.

Similar trends were observed with Sub-260 fractions, as shown in Table 3. The total product yield was more than 100%, although the ash recovery was only 31%. The unrecovered ash material was assumed to be lost in the aqueous solution during alkali and acid treatments. The CO_2 evolution increased substantially, more than four times the amount in Sub-215; the oxygen recovery increased to 130%, and the

hydrogen recovery increased to 112%. The higher CO_2 evolution in this reaction resulted in a greater average H/C ratio of the condensed products than that of Sub-215 products.

The yield and composition of Sub-300 products, Table 4, showed variations from the trends observed in Sub-260 and Sub-215. The amount of CO_2 evolved remained the same as in Sub-260, while the amount of the H_2O-soluble increased by a factor of three. The total product yield, carbon recovery and oxygen recovery decreased substantially, indicating some product was not recovered. The large amount of the H_2O-soluble suggests that the unrecovered material was water soluble species of small molecular size. The average H/C ratio of the condensed product was increased beyond that of Sub-260 product. The increased H/C ratio seems to be due to the lost material, which had a high O/C ratio, at least 1.3, based on the carbon and oxygen recoveries.

Results from the three reactions showed that hydrogen incorporation in the products accompanied the oxygen incorporation. Apparently, most of the hydrogen and oxygen incorporation took place in Sub-215 and it increased slightly in Sub-260. However, further incorporation in Sub-260 and Sub-300 might not have been detected due to the H_2O-soluble lost material.

The experimental data presented so far indicate that three major reactions have taken place at three different reaction temperatures. The hydrolysis of ester and carboxyl groups was the predominant reaction at 215°C. Decarboxylation was a major process at 260°C. Another hydrolysis which produced the H_2O-soluble material was a major reaction at 300°C. This progressive reaction path illustrates the complexity of coal chemistry and the need for carefully controlled liquefaction experiments. The identification of different reactions which took place revealed that different oxygen-functional groups were selectively attacked.

Table 5 shows how the composition and yield of the condensed-phase products changed as a result of the oxygen-related reaction steps. The composition and yield were calculated based on 100 carbon atoms of the feed. The differences among the coal and the products at the different reaction temperatures reveal that most hydrogen, 10% of the hydrogen in the feed, was added to the coal at 215°C, while substantial amounts of carbon and oxygen were removed between 260 and 300°C. Consequently, the Sub-300 product had a much higher atomic H/C ratio than the feed, 1.1 vs 0.78, contained 60% less oxygen, and was analyzable in detail. Since the solubilization reaction involves the hydrolysis of different oxygen functional groups, this observation reveals that the Wyoming coal can be hydrogenated with H_2O instead of H_2 or hydrogen-donor solvents as in current liquefaction processes.

IR spectra of the feed coal and some product fractions are shown in Fig. 3. Unlike the coal, two BaS fractions showed a prominent absorption at 1700 cm^{-1} due to the carbonyl group in addition to the strong absorptions at 3600-2500 cm^{-1} due to O-H stretch, 3000-2800 cm^{-1} due to nonaromatic C-H stretch, 1600 cm^{-1} due to aromatic C-C stretch with -O- substituent, and 1500-1000 cm^{-1} due to C-O stretch and nonaromatic C-H bend, which are common to coal-derived liquids or coals. Other fractions, BaI-AS and BaI-PS, had a less intense absorption at 1700 cm^{-1}. These carbonyl absorptions are due to carboxylic acids, as evidenced by CO_2 evolution and the solubility of the product fractions in basic solutions. Thus, the carbonyl groups exist in the feed coal. The origin of the carbonyl groups appears to be mostly esters and some other carbonyl form according to the additions of hydrogen and oxygen to the product, as well as the solution behavior of the product fractions.

The reaction products were further examined by ^{1}H-NMR. The spectra of the Sub-300 fractions, Fig. 4, show a broad, well-resolved peak with a maximum at 10 ppm. The quantitative determination of this acid proton revealed that the ratios of the proton to oxygen atom in the fractions were close to two, as shown in Table 6; almost all oxygen atoms exist in carboxylic groups. The water-soluble fraction, BaS-HS, contains the largest number of carboxylic groups, while the basic-solution insoluble fraction, BaI-AS, contains the smallest number of carboxylic groups.

The spectroscopic data and the elemental balances examined indicate that the oxygen functional groups in the feed coal underwent a drastic change during the NaOH/ethanol reaction. The result is a reduction of molecular weight and the large increase in the H/C ratio of the products. The determination of the carboxyl group contents in the Sub-300 fractions revealed that most of oxygen linkages were cleaved, while nonoxygen structural features of the feed coal remained intact during the solubilization reaction with NaOH/ethanol/H_2O. A similar conclusion, i.e., the conservation of aromatic clusters, has been drawn in the same reaction with a Utah bituminous coal.[1,2] The following structural analysis of the experimental data is aimed at extracting more information on the stable structures in the coal, as well as in the products themselves.

STRUCTURAL PARAMETERS OF SUB-300 PRODUCT FRACTIONS

Although the solubilization product fractions are complex mixtures of numerous components, they can be characterized in terms of molecular structural parameters to describe their chemical nature and the related chemistry on a molecular level. The preparation of the product fractions including their fractionation is a critical part of the characterization for the desired information.

To derive molecular information, each solubilized coal product fraction was represented by an average molecule. The characteristics of the average molecule were quantified from various analytical data in terms of structural parameters. The commonly used formulae to calculate structural parameters[1,8] were modified to account for the carbonyl groups observed in the products as listed in Table 7. C and H are the numbers of carbon and hydrogen atoms in the empirical formula of an average molecule. C_C represents the number of carbon atoms in carbonyl groups in an average molecule. Hydrogen (H) was divided into five types based on ^{1}H-NMR spectra; H_A, 5-9 ppm; $H_{2\alpha}$, 2.2-5 ppm; $H_{3\alpha}$, 2.0-2.2 ppm; H_β, 1.1-2.0 ppm; and H_γ, 0.0-1.1 ppm. In most cases $H_{3\alpha}$ was included in $H_{2\alpha}$, since the NMR spectra did not show well-defined separation between these two proton groups.

In the product fractions, the aromaticity and the total number of rings can be calculated by adding a term, C_C, to the formulae. However, the positions of the carbonyl groups must be known to calculate the other parameters. For example, whether or not a carboxylic group is attached directly to an aromatic ring makes a large difference in the calculated number for aromatic clusters and aromatic rings in an average molecule.

The structural parameters of the Sub-300 fractions are listed in Table 8. The aromaticities of the four fractions were low, ranging from 0.43 to 0.58. This result indicates that the aromaticity of the feed coal should be lower than 0.4, taking into account the carbonyl carbon (nonaromatic) which was removed as CO_2. There are several aromatic and hydroaromatic rings in average molecules of these fractions. Nevertheless, these rings are separated by nonaromatic bonds, forming individual aromatic clusters as indicated by the number of aromatic clusters, N_{Cl}.

The cluster parameters show large differences among the three Sub-300 fractions. BaS-HS was made of single-aromatic-ring clusters, BaI-AS consisted of two-fused-ring clusters and BaS-HI was a mixture of single-ring clusters and two-fused ring clusters, as indicated by I_{CS}. For example, I_{CS} of benzene, naphthalene and anthracene or phenanthrene are 1.00, 0.80 and 0.71, respectively. BaI-PS consisted of four- or more-fused aromatic-ring clusters. There was little evidence of three-fused ring clusters in these fractions, since their I_{CS}'s are much different from 0.71 of a three-fused ring cluster. The cluster weights of these fractions increase as I_{CS} decreases.

Three important observations may be made from the large differences in the cluster parameters among the fractions. First, the separation method to obtain these fractions was effective in apportioning the condensed product according to aromatic cluster size. Second, since it is unlikely that those clusters were altered during their preparation process, the feed coal itself must have consisted of the

different aromatic clusters characterized by the cluster parameters. Furthermore, these aromatic clusters seemed to be linked to one another in an orderly manner. For example, single-aromatic-ring clusters in BaS-HS were connected to, on the average, 3.6 other similar clusters as revealed by I_{cs} and N_{cl}. In BaI-AS, two-fused-aromatic-ring clusters were connected to, on the average, 1.8 other similar clusters. These structural characteristics of the Sub-300 fractions can be related to the original structures of the feed coal as well as to the potential product distribution resulting from complete liquefaction of the coal.

CHEMICAL STRUCTURE OF THE WYOMING COAL AND ITS LIQUEFACTION POTENTIAL

Since the Sub-300 product fractions were obtained by selective cleavage of oxygen functional groups, as discussed in the first section, the stable structures such as the aromatic clusters and aliphatic linkages remaining in these fractions must have been the same as those in the feed coal. Thus, the characteristics of the stable structures of Sub-300 fractions were equivalent to those of the coal, and provided information on two important aspects of coal composition, polymeric nature and heterogeneity. The molecules of the coal consisted of repeating structural units (such as aromatic clusters) of similar size, although the actual structures of each unit may vary. The coal, however, is a mixture of different polymeric constituents: e.g., the BaS-HS fraction of the coal consisted of small clusters, while the other fractions consist of larger clusters. The sketch of this structural arrangement is shown in Fig. 5, along with other models. In the figure, the size of circles represents the relative size of aromatic clusters, and a line represents a linkage. Although the models by Wender and Wiser are excellent conceptual representations of the components in coal structure, they are not specific to a given coal. The Utah bituminous coal that had been examined by the earlier methodology showed similar structural characteristics to the Wyoming subbituminous coal with respect to similar size clusters being bound to each other. However, the sizes and the distributions of aromatic clusters in two coals were different. The average aromatic cluster size was 1.8 in the Wyoming coal, while it was 2.2 in the Utah coal.

In addition, much information on weak functional groups or linkages of the Wyoming coal is available. The involvement of oxygen functional groups in Sub-215, Sub-260 and Sub-300 revealed that the stable structures like those found in Sub-300 product fractions were held together by oxygen functional groups in the feed coal. Three major functional groups connect the aromatic clusters: ester/ carbonyl, ether, and alkyl groups. Ester linkages have not been considered a major functional group in bituminous or subbituminous coals.[9,10] Our observation of CO_2 evolution and the addition of hydrogen and oxygen showed that as much as 58% of

the oxygen in the coal was in ester and carbonyl groups. However, the production of more H_2O-soluble material at 300°C than at 260°C without CO_2 evolution suggests that the ether group was cleaved. The remaining linkages in Sub-300 fractions must be alkyl groups, since almost all oxygen atoms in the fractions are in carboxylic groups.

The information on the oxygen functional group distribution was combined with that on the stable structures of the coal, Fig. 5, to give an overall chemical structural picture of the coal as shown in Fig. 6. Some of the important features of this particular coal were found to be:

1. The empirical formula of the coal after vacuum drying at 100°C, based on 100 carbon atoms, is: $C_{100}H_{78.0}N_{0.8}O_{28.2}$. The coal is so sensitive to thermal treatment that its composition changes with excessive drying.

2. The aromaticity of the coal is only 0.4. It can vary with drying conditions and experimental methods due to the large amount of facile carboxyl groups.

3. There are 1.8 fused-aromatic rings in the average aromatic cluster.

4. At least four single-aromatic-ring clusters on the average are linked to each other by alkyl C-C bonds, making a group of single-ring clusters. These groups are connected to each other by ester groups. Each cluster has at least one oxygen functional group which can be converted to carboxylic groups at 300°C. At least two two-fused aromatic-ring clusters are joined by alkyl C-C bonds, making a group of two-fused ring clusters. These groups are connected to each other by ester groups and also probably by ether groups. Four or more fused-aromatic-ring clusters are connected to each other in a similar manner. The change in the distribution of the condensed product fractions in Sub-215, Sub-260 and Sub-300 suggests that small cluster groups are connected to each other, and large ones are connected to each other.

5. Ester/carbonyl groups appear to be major linkages joining the aromatic clusters groups, while most of the ether groups are in small aliphatic side chains.

6. 72% of the coal consists of stable structures which will become condensed products from liquefaction reactions carried out under moderate conditions. Among the stable structures, 39% are made of single aromatic ring clusters; 35%, two-fused-aromatic ring clusters; and 26%, three or more fused-aromatic-ring clusters.

All these structural features are important for understanding and controlling the liquefaction chemistry. In the following discussion, the findings on the chemical structure and reactivity of the Wyoming coal will be used to obtain a potential product distribution upon complete liquefaction of the coal.

Since Sub-300 product fractions retained the stable structures of the coal, structural characteristics of these fractions provided valuable information on poten-

tial condensed products which form upon liquefaction of the coal. As shown in Table 8, the average molecules of the three Sub-300 fractions, BaS-HI, BaS-HS and BaI-AS, were made of aromatic clusters and nonaromatic linkages. Although the linkages were not cleaved in the NaOH/ethanol reaction at 300°C, they were expected to be cleaved under hydroliquefaction conditions, e.g., at 400° to 450°C. Thus, upon further liquefaction, the average molecule of BaS-HI, which had 2.8 aromatic clusters, will become 2.8 smaller molecules, each having only one aromatic cluster with the average molecular weight 280.

Similarly, BaS-HS and BaI-AS will become products having average molecular weights of 210 and 340, respectively. Assuming the carboxyl groups in these fractions will be removed or reduced during liquefaction, all the new products should be distillable under vacuum, based on our previous observations on the Utah coal.[1,3] In the previous work, a CDL product fraction with an average molecular weight larger than 390 was not distillable. In a liquefaction process with a hydrogen-donor solvent, the yield of distillable product from the Wyoming coal should be at least 52% of the feed according to the yields of BaS-HI, BaS-HS, BaI-AS and H_2O-soluble. The yield could be even larger if part of the BaI-PS is included in the product and some carbonyl groups are reduced to methylene groups, $-CH_2-$. The material that was lost in the wash water in the NaOH/ethanol reaction will become gaseous product, e.g., CH_4 and C_2H_6, under hydrogenation conditions. It was found earlier that 8.2% of the carbon in the coal evolved as CO_2 (Table 4).

This product distribution is compared to that of a separate liquefaction experiment on the same coal at 450°C with a hydrogenated coal-derived solvent[11] in Table 9. The predicted yields of distillable product and C_1-C_3 gas are very close to those obtained in the hydroliquefaction experiment. The yields of CO_2 and CO, however, show a large difference, 8.2% C vs 3.4% C. This difference is due to the dissimilar nature of the NaOH/ethanol reaction and the hydrogenative liquefaction, but it does not significantly affect the overall excellent agreement.

The agreement in the C_1-C_3 gas yield shows that the gaseous products primarily arise from cleaving the side chains containing oxygen functional groups in the original structure of the coal. This observation indicates that some side chains may be retained in liquid$_0$products by not cleaving them off as gaseous product: e.g., hydrogenation of ϕ-C-CH_2CH_3 to ϕ-CH_2-CH_2CH_3. Recent results from the two-stage catalytic liquefaction of Illinois No. 6 coal revealed such a possibility.[12]

In addition, the structural parameters of Sub-300 product fractions can be used to estimate the number of strong linkages (i.e., nonoxygen or aliphatic linkages) to be cleaved and the amount of hydrogen required for the cleavage to obtain the predicted product distribution. The number of strong linkages in the average

molecule of a product fraction is equal to N_{c1}-1, where N_{c1} is the number of aromatic clusters in Table 8. These linkages are aliphatic, and the cleavage and quenching of each linkage under hydroliquefaction conditions require two hydrogen atoms to result in two smaller molecular species: the hydrogen consumption is directly related to the number of aliphatic linkages. Based on this relationship, the amount of hydrogen required in cleaving strong linkages in order to obtain the product distribution in Table 8 is 0.2 to 1.3% of the coal. This number compares to 6% in the "Wyo" liquefaction. The difference, 4.7 to 5.8%, represents the amount of hydrogen consumed to cleave or remove oxygen functional groups of the coal in the "Wyo" liquefaction.

FORMATION OF THE SOLUBILIZATION PRODUCTS FROM THE TEXAS LIGNITE

The product yields shown in Table 10 revealed that the lignite behaved similarly to the Wyoming subbituminous coal in the solubilization reaction with NaOH/ethanol/H_2O. However, the distribution of the products was different. The formation of BaS from the lignite was completed at 215°C, while that from the subbituminous coal continued even beyond 260°C (see Table 1). The CO_2 evolution was approximately 50% of that from the subbituminous coal. The amounts of H_2O-soluble and lost material increased apparently in a similar manner, but a detailed analysis showed a different trend with the lignite.

Elemental balances indicated that substantial amounts of hydrogen and oxygen were added to the feed, while substantial amounts of carbon and oxygen were removed as CO_2 and H_2O-soluble material. These changes resulted in different yield and composition of the condensed-phase products at the three reaction temperatures, as shown in Table 11. The difference between the lignite and Lig-215 product shows that eight hydrogen atoms were added to the feed based on 100 carbon atoms of the feed, while six carbon atoms and one oxygen atom were removed. Between Lig-215 and Lig-260 products, eight carbon atoms and six oxygen atoms were removed from Lig-215 product without any change in the hydrogen content. Between Lig-260 and Lig-300 products, eight hydrogen atoms were added, while ten oxygen atoms were removed with no change in the carbon content. This large amount of oxygen removed accounts for the difference between "lost and error" in Lig-300 and that in Lig-260 in Table 10.

Taking into account the CO_2 evolution and H_2O-soluble formation in Table 10, the above differences in yield and composition reveal that hydrolysis and decarboxylation were main reactions taking place at 215°C. In Lig-260, decarboxylation and H_2O-soluble formations were major processes. In Lig-300, the substantial amount of deoxygenation without additional CO_2 evolution indicates that dehydration took

place. However, the substantial amount of hydrogen addition suggests that reduction of carbonyl or carboxyl groups might have taken place.

In comparison with the Wyoming coal, the hydrolysis accompanying hydrogen and oxygen addition and decarboxylation took place at the same temperatures, 215 and 260°C, respectively. However, the formation of H_2O-soluble material took place at the lower temperature, 260°C, with the lignite than at 300°C with the Wyoming subbituminous coal. Another major difference is the large amounts of hydrogen addition and oxygen removal without any change in carbon recovery with lignite; this was not observed with the Wyoming coal. These differences in the reactivity indicate that oxygen functional groups of the lignite were dissimilar to those of the Wyoming coal in their distribution or even identities.

Supporting data for the dissimilar distribution of oxygen functional groups are shown in Table 12. The hydroxyl and carboxyl group contents in Lig-300 fractions were determined from ^{1}H-NMR spectra, elemental composition and molecular weight. Two fractions, BaS-HS and BaS-HI, contained carboxyl groups and hydroxyl groups. However, the other two fractions did not contain carboxyl groups, but hydroxyl groups. In contrast, most oxygen of similar product fractions from the Wyoming coal was in carboxyl groups, as listed in Table 6. The larger number of hydroxyl groups in these fractions from the lignite supports our interpretation of the substantial deoxygenation due to dehydration.

Further structural characteristics of Lig-300 fractions were described in terms of average molecular structural parameters, shown in Table 13. Fractions BaS-HS and BaS-HI are almost the same. An average molecule of each fraction consists of 3.7 aromatic clusters. The index for the cluster size, 0.92, revealed that each fraction is a 50:50 mixture of single- and two-fused ring clusters. The average molecule of BaI-AS consisted of 1.7 aromatic clusters, and the average cluster was a two-fused ring cluster, as indicated by the cluster size index, I_{CS}. The average molecule of BaI-AI-PS had 4.9 aromatic clusters, and the average cluster was a three-fused ring cluster. The average cluster weight in each of the four fractions ranges from 210 to 390. These structural parameters of Lig-300 fractions can be combined with the information on the oxygen functional groups to construct a chemical structural model of the Texas lignite as we did with the Wyoming subbituminous coal in Fig. 6.

CHEMICAL STRUCTURE OF THE TEXAS LIGNITE AND ITS LIQUEFACTION POTENTIAL

Extensive chemical information was derived from the foramtion of the solubilization products and from the structural characteristics of the product fractions in

the previous section. This can be used to determine detailed chemical characteristics of the Texas lignite. The structural parameters of Lig-300 fractions showed the distribution and arrangement of stable structures, i.e., aromatic clusters and aliphatic linkages, of the lignite. Combining the data on the stable structures with those on oxygen functional groups, we constructed an overall chemical structural picture of the lignite as shown in Fig. 7. The general arrangement of aromatic clusters, aliphatic linkages and oxygen functional groups is similar to that of the Wyoming coal in Fig. 6. Aromatic clusters of a similar size are joined by aliphatic linkages to make a group of aromatic clusters. The aromatic cluster groups are linked to each other by oxygen functional groups. However, major differences from the Wyoming coal are in the distributions of aromatic clusters and oxygen functional groups.

The difference in the distribution of aromatic clusters between the subbituminous coal and the lignite is shown in Fig. 8. The two coals contained a similar amount of single- and two-fused ring clusters, 50 wt% of each coal. However, the amount of three-fused aromatic ring clusters was 15% in the lignite, while there were few such clusters in the subbituminous coal. The amount of four- or more-fused-aromatic-ring clusters was 9% in the lignite, while it was 19% in the subbituminous coal.

Another major difference between the lignite and the subbituminous coal was the distribution of oxygen functional groups, as shown in Fig. 9. The distribution was estimated from the amount of CO_2 evolved, the yields of H_2O-soluble products, elemental balance, and the molecular weight of the soluble product fractions. Approximately 75% of oxygen in the lignite was in hydroxyl and ether groups, while the rest of the oxygen was ester and carbonyl groups. Most of ester and carbonyl groups seemed to be linkages between aromatic clusters, while most of ether and hydroxyl groups seemed to be on side chains. In the Wyoming subbituminous coal, approximately 60% of oxygen was in ester and carbonyl groups. More than half of these functional groups appeared to be linkages between aromatic clusters. The rest of the oxygen was in ether and hydroxyl groups, and most of them were on side chains.

The product distribution in Table 10 and structural parameters in Table 13 were used to predict the product distribution from the hydroliquefaction of the lignite. The distribution in Table 14 was calculated in the same manner as that of the Wyoming coal. The potential yield of distillable product is 60% of the feed. This yield was larger by 15% than that in the subbituminous coal due to the larger amount of three-fused ring clusters in the lignite. Approximately one-half of the

amount of three fused ring clusters was estimated to be distillable due to a large cluster weight of the clusters.

The estimated hydrogen consumption to be required in cleaving alkyl linkages was 0.3 wt% of the feed. This amount was much less than 5% hydrogen consumption in current hydroliquefaction processes, and indicates that substantial improvements in the liquefaction technology is possible.

5. CONCLUSION

A Wyoming subbituminous coal and a Texas lignite were characterized in terms of the distribution and arrangement of aromatic clusters, linkages and oxygen functional groups. The characterization consisted of solubilization of each coal by reactions with NaOH/ethanol/H_2O, solvent fractionation of the product, and detailed analyses of the product fractions to obtain average molecular structural parameters.

The two coals behaved similarly in the solubilization reactions. Material and elemental balances revealed that the oxygen functional groups of each coal were attacked selectively and the complex coal structure underwent an orderly, definable diminution. The solubilization reaction proceeded in a well-defined manner: hydrolysis of ester and carbonyl groups at 215°C, decarboxylation at 260°C, and another hydrolysis or dehydration/hydrogenation at 300°C. Thus, the reaction resulted in the addition of hydrogen from H_2O to the soluble product and the removal of oxygen as CO_2.

The arrangement of aromatic clusters and oxygen functional groups were similar in both the coals. Two to four aromatic clusters of a similar size were linked to each other by alkyl C-C bonds, making a chain of aromatic clusters. Two or more of these chains were connected to each other by ester and ether groups. The size of aromatic clusters ranged from single ring to five-fused ring clusters.

Major differences between the two coals were in the distributions of aromatic clusters and oxygen functional groups. The lignite contained fewer large aromatic clusters than the subbituminous coal, although the two coals contained similar amounts of single- and two-fused ring aromatic clusters. More than 70% of oxygen in the lignite was in hydroxyl and ether groups, while the rest of the oxygen was in ester and carbonyl groups. In the subbituminous coal, 60% of oxygen was in ester and carbonyl groups, and the rest was in ether and hydroxyl groups. Most of oxygen functional groups were on side chains.

These structural data were related to the liquefaction behavior of each coal. The predicted distribution of liquefaction products from the subbituminous coal agreed closely with experimental values in an independent liquefaction study. According

to the predicted distribution, the lignite has 15% more potential yield of distillable product than the subbituminous coal.

In both coals, the amount of hydrogen required to cleave aliphatic linkages should be 0.3% of feed, compared with 5% in current hydroliquefaction processes. This indicates that more than 90% of the hydrogen consumption is due to deoxygenation and the production of gaseous species. Our observation of the reactions between H_2O and oxygen functional groups indicated that a substantial fraction of oxygen in these coals can be removed without consuming molecular hydrogen. Thus, the chemistry of oxygen functional groups may play a major role in substantial improvements of the liquefaction technology.

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Table 1

COMPARISON OF YIELDS (wt%) AT DIFFERENT TEMPERATURES

	Sub-215	Sub-260	Sub-300
BaS-HI	26.9	42.7 (1190)*	14.2 (780)
BaS-HS	24.6	7.0 (1140)	14.9 (770)
BaI-AS	-	-	17.6 (590)
BaI-PS	14.5	25.4 (1400)	14.7 (2100)
BaI-PI	28.9	6.1	4.6
CO as CO_2	3.0	12.4	12.2
H_2O-Soluble	0.0	1.8	5.6
Lost and Error	2.1	4.6	16.2 (C_1-C_2 Soluble?)

*Average molecular weight by vapor phase osmometry

Table 2

YIELD AND ELEMENTAL COMPOSITION OF Sub-215 PRODUCTS

	Yield %	C %	H %	N%	O %*	Ash %	H/C
Dry Coal	100.0	64.9	4.2	0.6	24.8	5.5	0.78
BaS-HI	26.9	67.5	4.9	(0.6)**	26.1	0.9	0.86
BaS-HS	24.6	66.7	4.9	(0.6)	26.8	1.0	0.89
BaI-HI (4.9% Soluble in Pyridine)	12.8	68.4	5.6	(0.6)	17.3	8.1	0.98
BaI-HS (46.3% Soluble in Pyridine)	30.6	59.4	4.5	(0.6)	31.6	3.9	0.91
CO_2	4.7	27.3	-	-	72.7	-	-
Total Yield	99.6	62.8	4.6		28.9	3.6	0.88
Total Recovery		97%	110%		117%	66%	113%

*By difference
**Assumed value: due to instrument malfunctioning

Table 3

YIELD AND ELEMENTAL COMPOSITION OF Sub-260 PRODUCTS

	Yield %	C %	H %	N%	O %*	Ash %	H/C
Dry Coal	100.0	64.9	4.2	0.6	24.8	5.5	0.78
BaS-HI	42.7	68.8	5.5	0.7	23.1	1.9	0.96
BaS-HS	7.0	51.6	4.0	0.5	14.8	2.1	0.93
BaI-PS	25.4	73.6	6.9	(0.6)**	16.5	2.4	1.13
BaI-PI	6.1	73.7	5.2	(0.6)**	18.1	2.4	0.85
CO_2	19.4	27.3	-	-	72.7	-	-
H_2O-Soluble	1.8	ND	ND	ND	ND	ND	ND
Total Yield	102.4	61.5	4.7		32.2	1.7	0.92
Total Recovery		95%	112%		130%	31%	118%

*By difference
**Assumed value: due to instrument malfunctioning
ND: Not determined

Table 4

YIELD AND ELEMENTAL COMPOSITION OF Sub-300 PRODUCTS

	Yield %	C %	H %	N%	O %*	Ash %	H/C
Dry Coal	100.0	64.9	4.2	0.6	24.8	5.5	0.78
BaS-HI	14.2	73.7	7.0	(0.6)**	18.1	0.6	1.15
BaS-HS	14.9	71.2	6.7	(0.6)	19.7	1.8	1.13
BaI-HI							
AS	17.6	80.5	8.5	(0.6)	9.4	1.0	1.27
AI-PS	14.7	75.5	6.6	(0.6)	16.3	1.0	1.04
AI-PI	3.4	80.1	5.0	(0.6)	13.3	1.0	0.75
BaI-HS	1.2	73.1	6.8	(0.6)	18.0	(1.5)**	1.12
CO_2	19.1	27.3	0	0	72.7	0	0
H_2-Soluble	5.6	33.2	4.1	-	-	ND	1.46
Total Yield	90.7	57.0	4.7		24.2	0.7	0.99
Total Recovery		88%	112%		97%	13%	127%

*By difference
**Assumed value: due to instrument malfunctioning
ND: Not determined

Table 5

YIELD AND COMPOSITION OF CONDENSED-PHASE PRODUCT FRACTIONS

		Difference		
		C	H	O
Coal	$C_{100}H_{78.0}N_{0.8}O_{28.2}$	- 5.3	+ 7.8	+ 0.8
Sub-[illegible]	[illegible]	- 8.1	+ 1.6	- 8.4
Sub-260	$C_{86.6}H_{87.4}N_{0.7}O_{20.6}$	- 6.8	- 0	- 8.9
Sub-300	$C_{79.8}H_{87.4}N_{0.5}O_{11.7}$			
	TOTAL	-20.2	+ 9.4	-16.5

Table 6

OXYGEN AND CARBOXYL GROUP CONTENTS IN Sub-300 FRACTIONS

	Empirical Formula	M.W.	Number of Carboxyl Groups*	Number Other Oxygens
BaS-HI	$C_{48}H_{55}O_{8.6}N_{0.3}$	780	3.5	1.6
BaS-HS	$C_{45.6}H_{51.4}O_{9.9}N_{0.3}$	770	5.0	0.0
BaI-HI-AS	$C_{39.6}H_{50.1}O_{3.7}N_{0.3}$	590	1.7	0.3

*From acid protons determined by NMR

Table 7

FORMULAE FOR STRUCTURAL PARAMETERS WITH SAMPLES CONTAINING C = O GROUPS

Number of Aromatic Carbon Atoms:

$$C_A = C - \frac{1}{2}(H_{2\alpha} + H_{2\beta}) - \frac{1}{3}(H_{3\alpha} + H_{\gamma}) - C_C \quad (1)$$

Fraction of Carbon Atoms which are Aromatic (= Aromaticity):

$$f_A = \frac{C_A}{C} \quad (2)$$

Total Number of Rings:

$$R_T = \frac{2C - H + 2}{2} - \frac{1}{2} C_A - C_C \quad (3)$$

Number of Aromatic Clusters:

$$Ncl = \frac{1}{3}(C_{AP} - \frac{1}{2} C_A) \quad (4)$$

$$C_{AP} = H_A + \frac{1}{2} H_{2\alpha} + \frac{1}{3} H_{3\alpha} + C_C(?) \quad (5)$$

Number of Aromatic Rings:

$$R_A = \frac{C_A - 2Ncl}{4} \quad (6)$$

Number of Naphthenic Rings:

$$R_N = R_T - R_A \quad (7)$$

Index for Cluster Size:

$$I_{CS} = C_{AP}/C_A \ (= H_{ARU}/C_{AR}) \quad (8)$$

Cluster Weight:

$$CW = M.W./Ncl \quad (9)$$

Table 8

STRUCTURAL PARAMETERS OF SUB-300 FRACTIONS

	Yield, Wt%	M.W.	f_A	R_T	N_{Cl}	I_{CS}	CW
BaS-HI	14.2	780	0.46	7.1	2.8	0.88	280
BaS-HS	14.9	770	0.47	5.3	3.6	1.01	210
BaI-AS	17.6	590	0.43	5.3	1.8	0.81	340
BaI-PS	14.7	2100	0.58	26.1	3.7	0.64	580

Table 9

COMPARISON OF THE PRODUCT DISTRIBUTION FROM NaOH-ETHANOL REACTION AND "WYO" LIQUEFACTION

	NaOH/EtOH Reaction	U. of Wyoming*
Distillable Product	52% Wt	55% Wt
C_1-C_3 Gas	12% C	13.1% C
CO_2 and CO	8.2% C	3.4% C

*Ref. 11

Table 10
SUCCESSION OF PRODUCT FORMATION (WT% YIELD)

	Lig-215	Lig-260	Lig-300
BaS-HS	55.3	22.6	23.1
BaS-HI	20.1	38.9	4.4
BaI-AS	--	--	19.7
BaI-AI-PS	21.1	11.1	15.4
BaI-AI-PI		11.5	8.6
CO as CO_2	3.5	6.6	6.9
H_2O-Sol	0	0.1	4.0
Lost and Error	0.1	9.2	17.9

Table 11
YIELD AND COMPOSITION OF CONDENSED-PHASE PRODUCTS

		Difference		
		C	H	O
Lignite	$C_{100}H_{84.6}O_{28.4}$	- 5.9	+ 8	- 1.1
Lig-215	$C_{94.1}H_{92.6}O_{27.3}$	- 8.3	0	- 6.0
Lig-260	$C_{85.8}H_{92.6}O_{21.3}$	0	+ 8.3	-10.1
Lig-300	$C_{85.9}H_{101}O_{11.2}$			
	TOTAL	-14.2	+16.3	-17.2

Table 12

HYDROXYL AND CARBOXYL GROUPS IN LIG-300 FRACTIONS*

	Empirical Formula	M.W.	Number of Carboxyl Groups	Number of Hydroxyl Groups
BaS-HS	$C_{48.6}H_{55.3}O_{8.2}$	770	1.4**	5.5**
BaS-HI	$C_{48.9}H_{54.2}O_{9.3}$	790	2.5**	4.2**
BaI-AS	$C_{37.1}H_{48.0}O_{2.9}$	540	0	2.9
BaI-AI-PS	$C_{126}H_{144}O_{18}$	1940	0	15.7

* Based on ^{1}H-NMR data.

** All oxygen atoms were assumed to be in carboxyl and hydroxyl groups.

Table 13

STRUCTURAL PARAMETERS OF LIG-300 FRACTIONS

	Yield, %	M.W.	f_A	R_T	Ncl	I_{cs}	CW
BaS-HS	23.1	770	0.55	6.7	3.7	0.92	210
BaS-HI	4.4	790	0.54	6.5	3.7	0.92	210
BaI-AS	19.7	540	0.46	5.0	1.7	0.79	320
BaI-AI-PS	15.4	1940	0.55	20.7	4.9	0.72	390

Table 14

POTENTIAL PRODUCT DISTRIBUTION IN THE LIQUEFACTION OF THE LIGNITE

Distillable Product	60% wt
C_1-C_2 Gas	10% C
CO_2 and CO	4% C
Residue	9% wt
H_2 consumption	(0.3% wt)*

* Amount to be required in cleaving alkyl linkages.

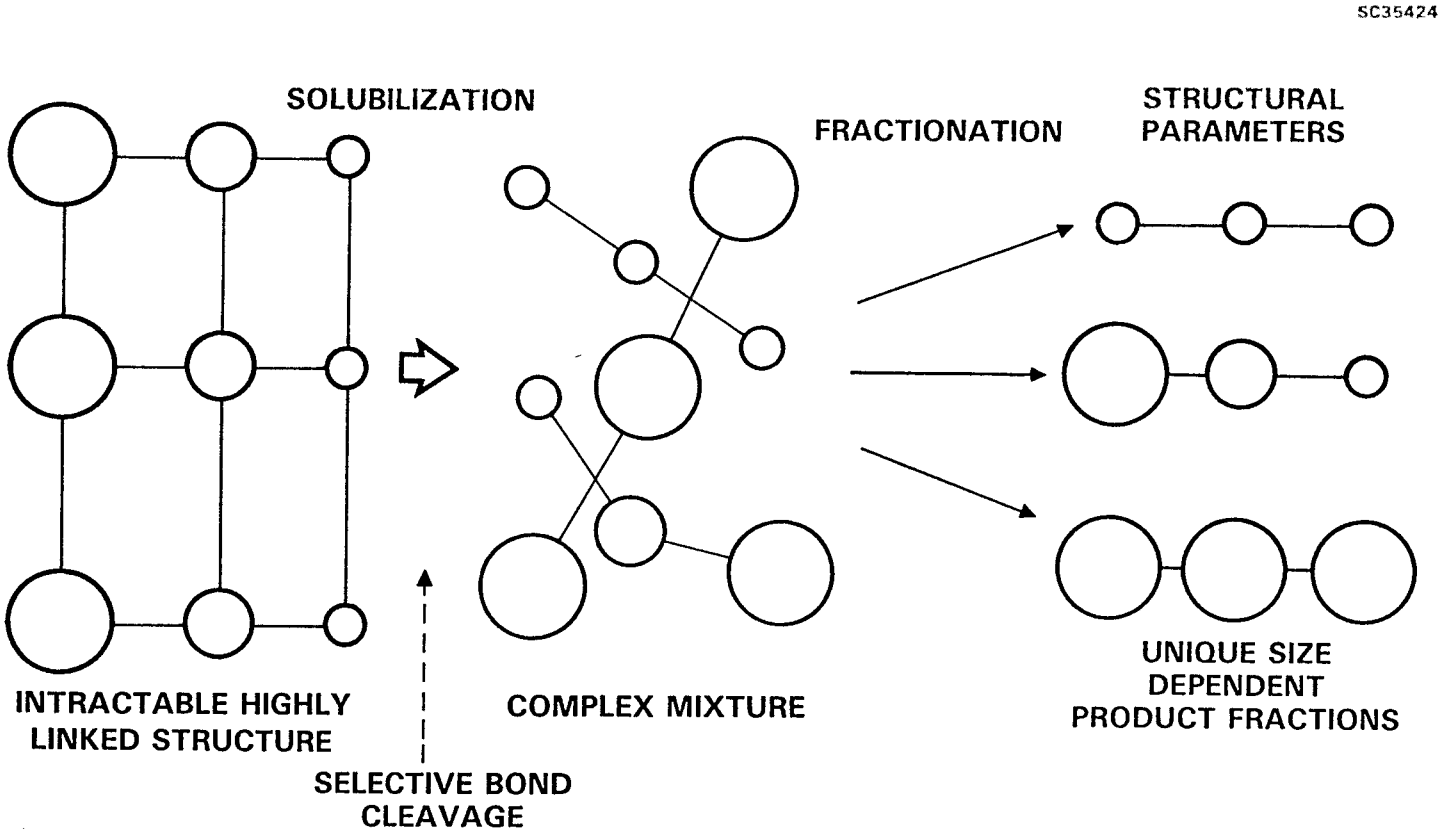

Figure 1. Characterization methodology.

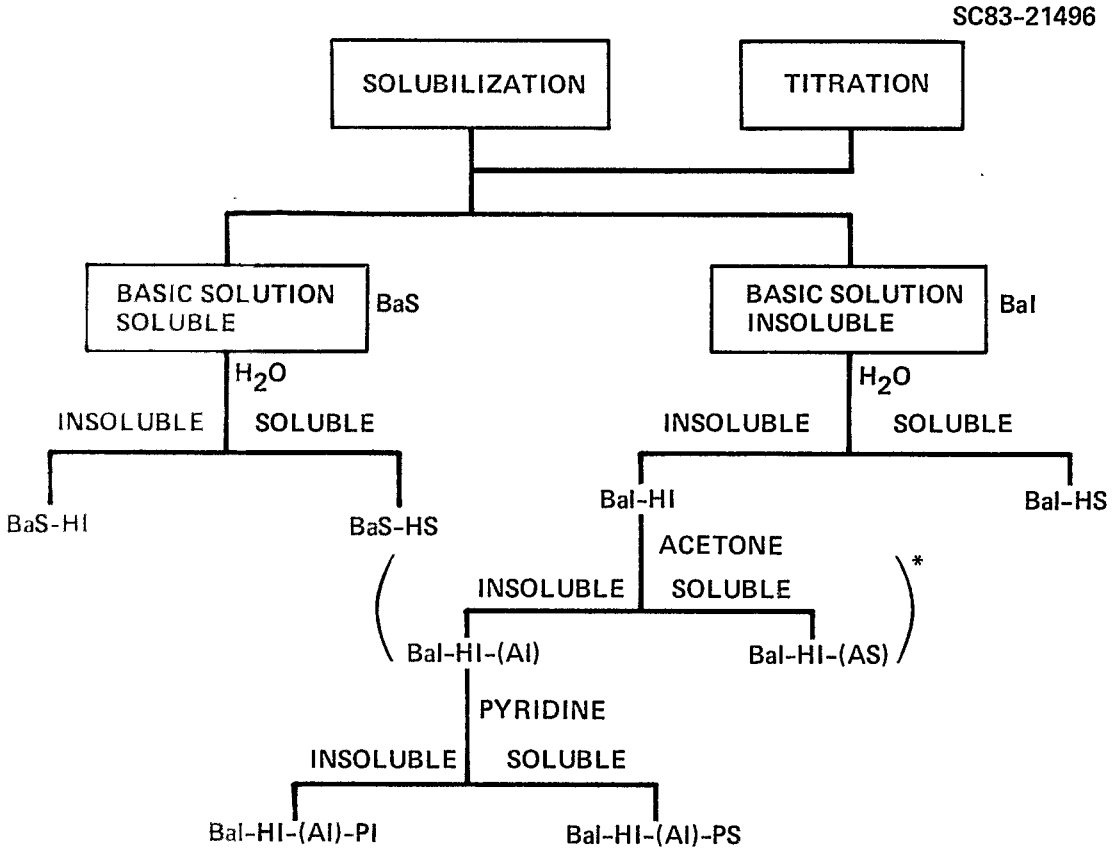

Figure 2. Fractionation of solubilization products.

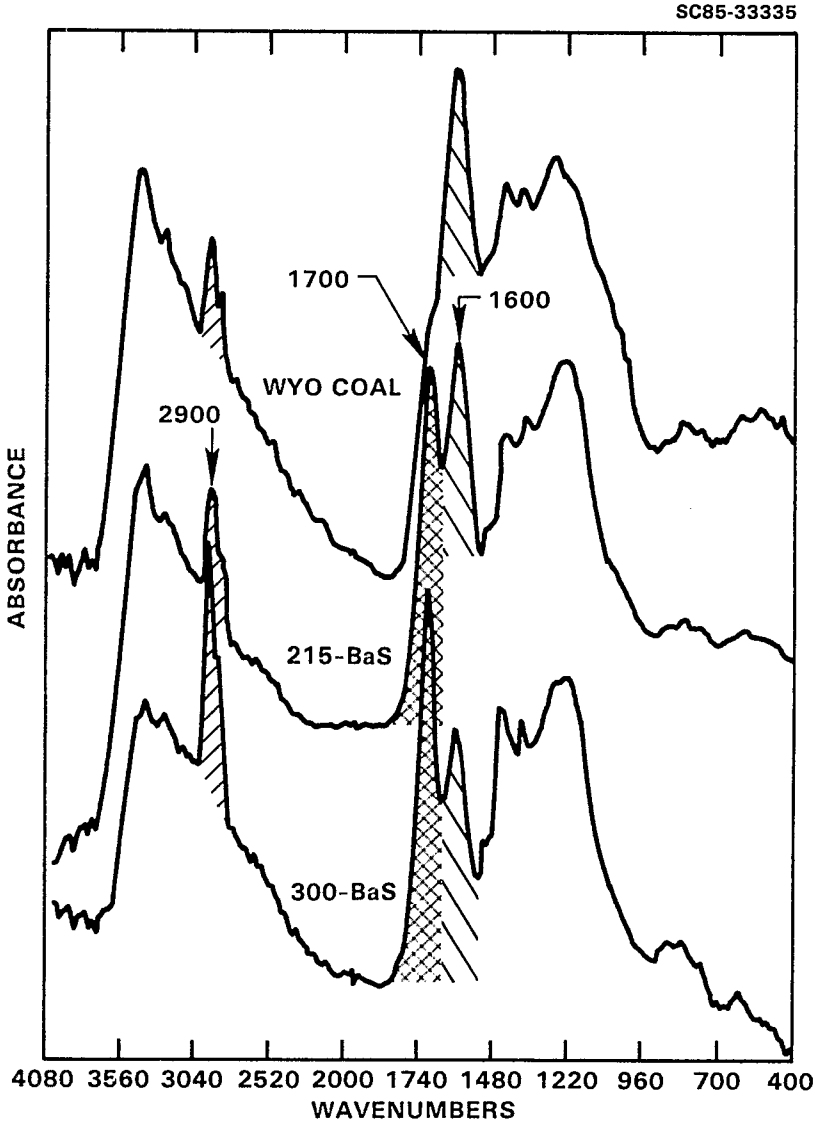

Figure 3. IR spectrum of Wyo coal and products.

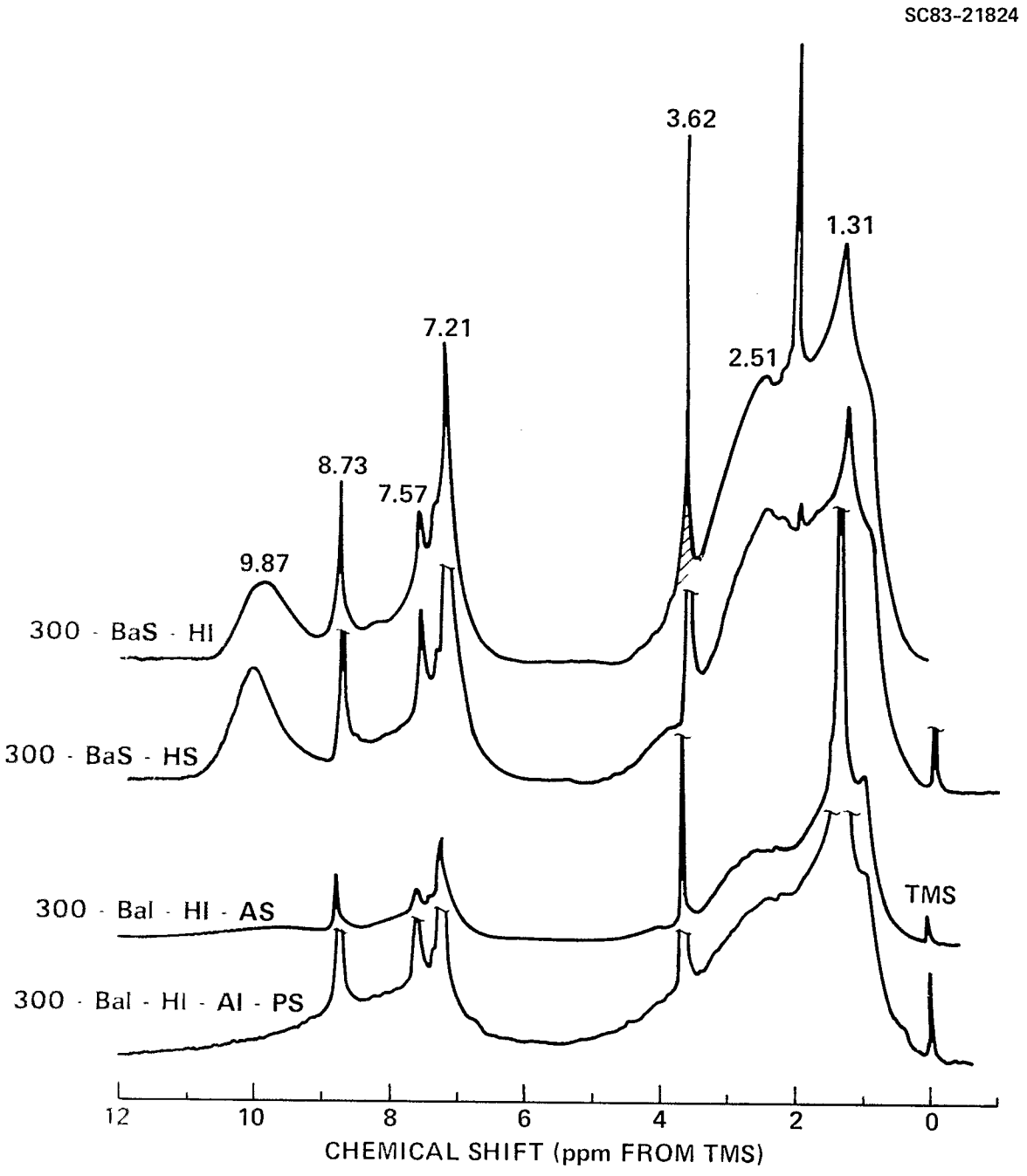

Figure 4. Acid protons in Sub-300 fractions.

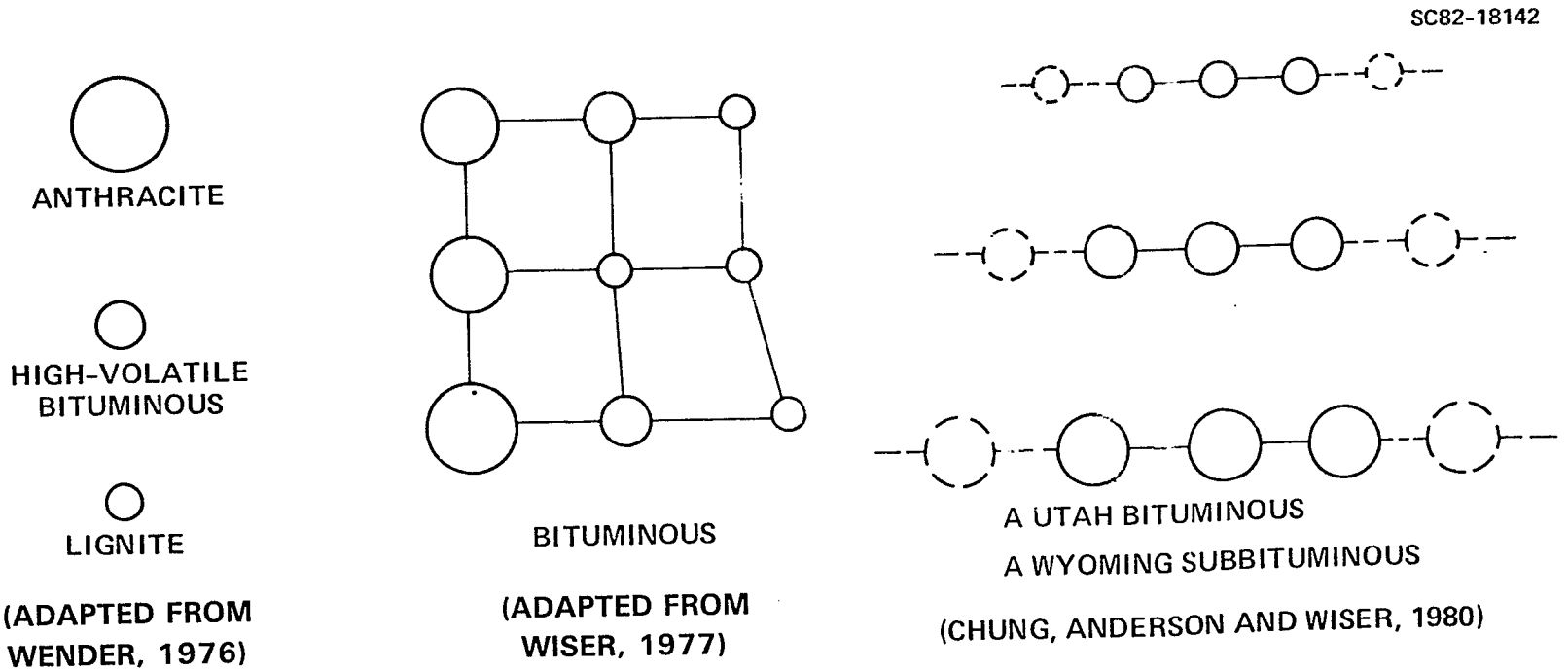

Figure 5. Sketch of structural models of the Wyoming coal.

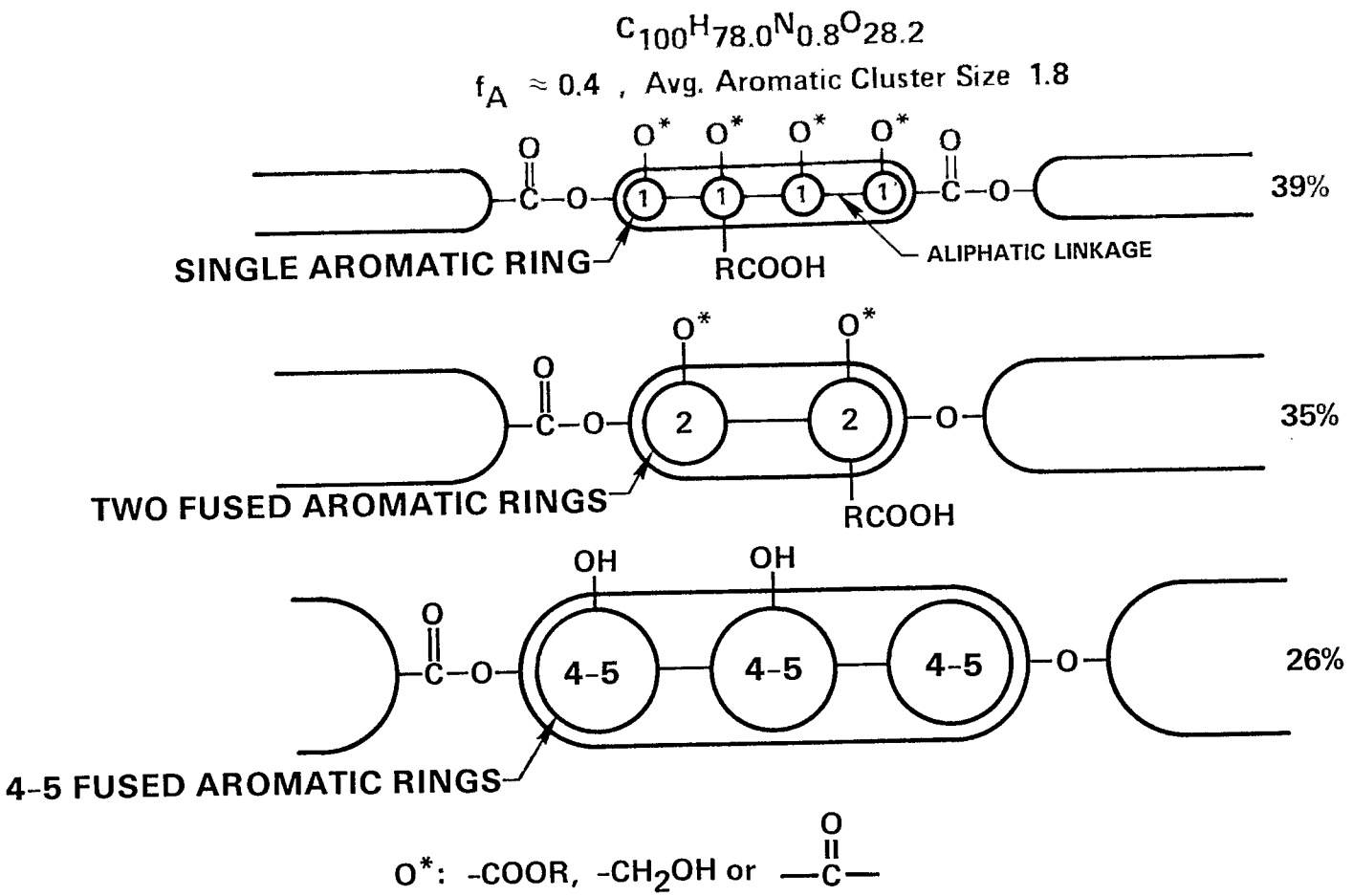

Figure 6. Chemical structure of Wyoming No. 1 coal.

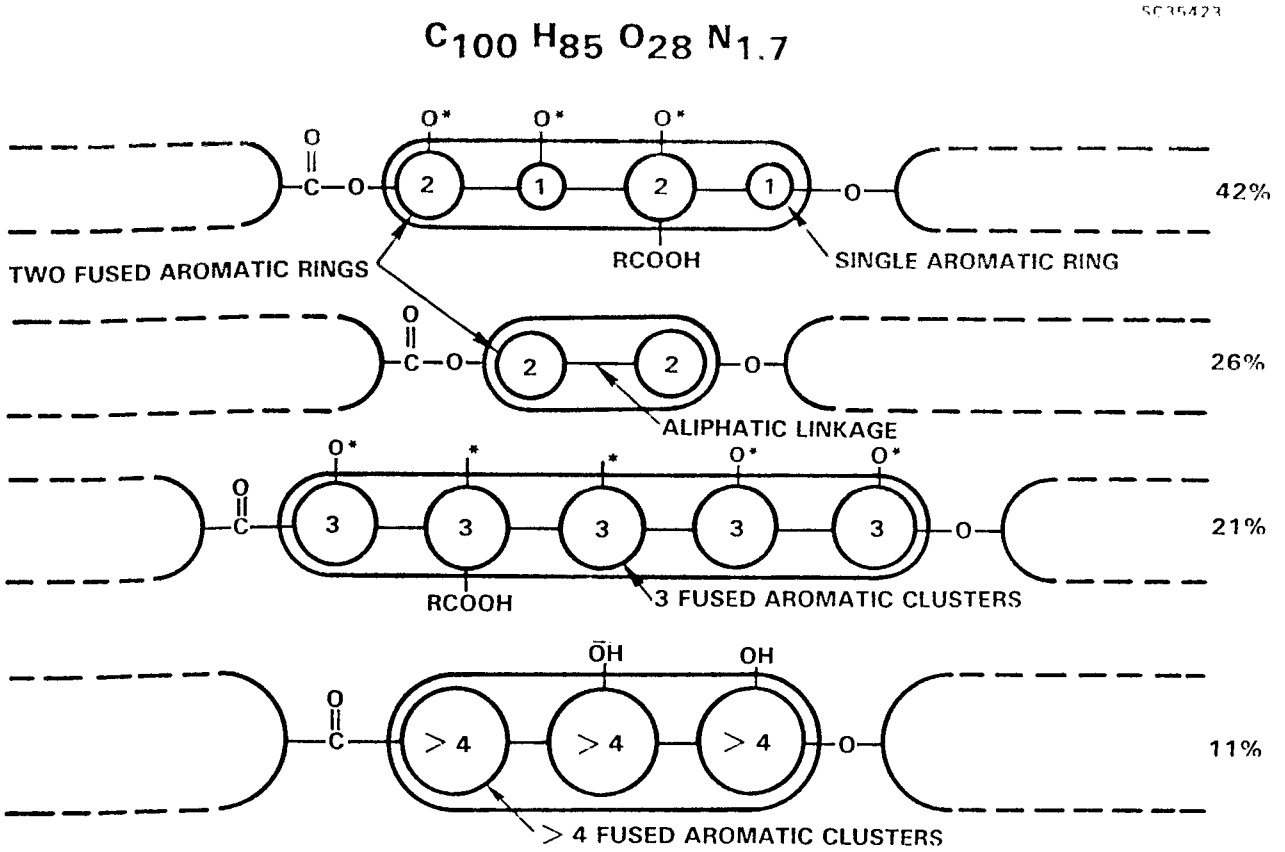

Figure 7. Chemical structure of a Texas lignite.

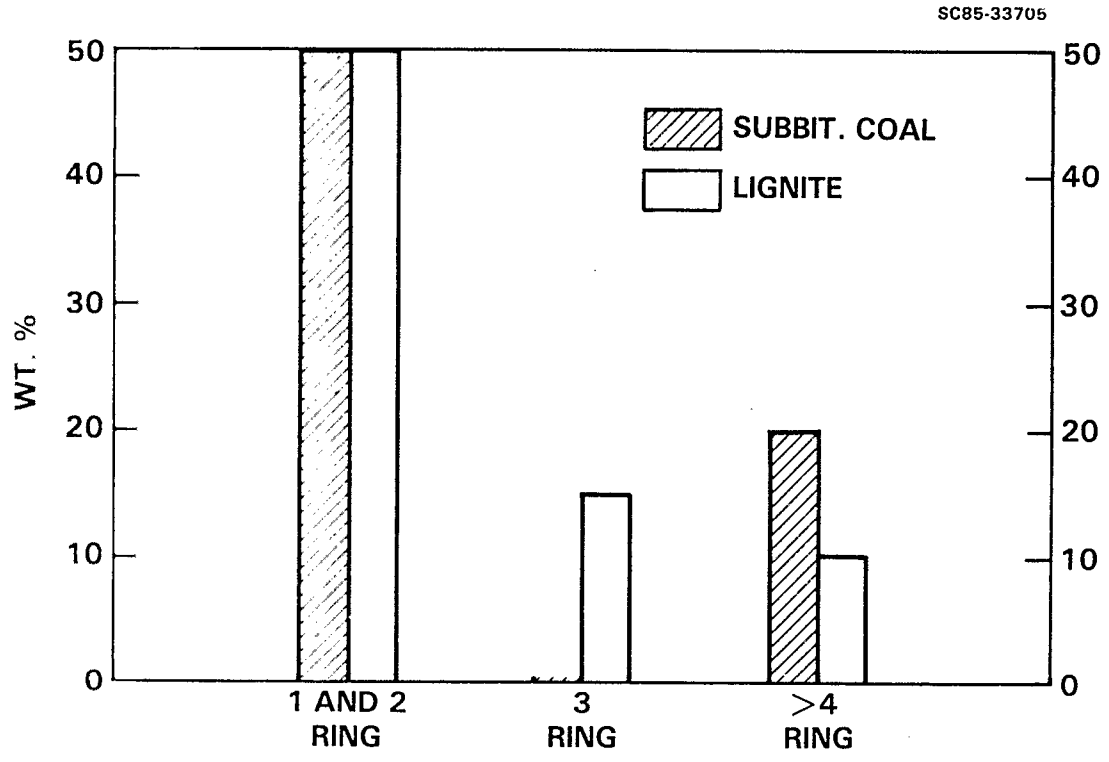

Figure 8. Comparison of the two coals (aromatic ring composition).

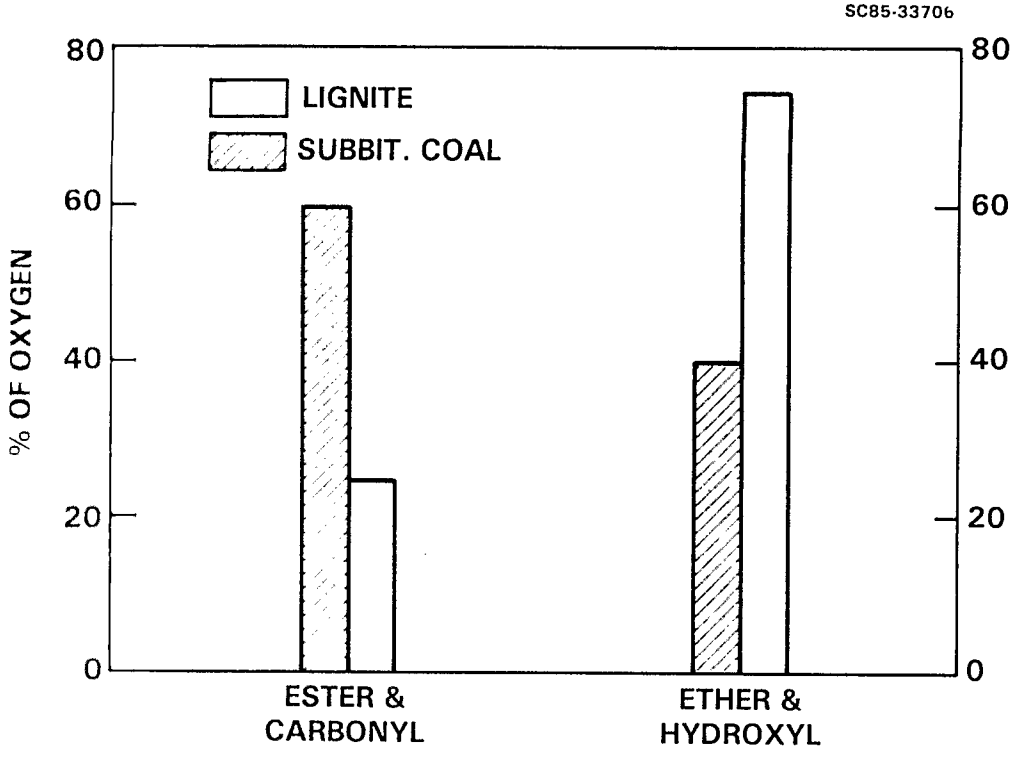

Figure 9. Comparison of the two coals (oxygen functional group distribution).